PHASE EQUILIBRIA AND PRECIPITATION PHENOMENA OF
SODIUM CHLORIDE AND SODIUM SULFATE IN
SUB- AND SUPERCritical WATER

by

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ABSTRACT

Topics relating to solid salt formation and separation during the supercritical water oxidation (SCWO) waste treatment process were examined. In general, inorganic salts have a very low solubility in water at the SCWO bulk reactor conditions of temperatures between 500 and 650°C at a pressure of about 230 to 250 bar, which leads to rapid or "shock-like" crystallization. An experimental apparatus was constructed for high temperature (<600°C) and pressure (<340 bar) studies of phase equilibria and salt nucleation and growth in aqueous solutions. The main component of the apparatus was an optically accessible cell with sapphire windows.

An experimental technique for determining phase boundaries at constant pressure was developed. The method was verified by static isobaric experiments performed on the NaCl-H₂O and Na₂SO₄-H₂O systems at 250 bar. Aqueous solutions of known salt concentration were slowly heated at constant pressure until a phase transformation was visually detected. In the NaCl-H₂O system, a low-density, vapor-phase was nucleated, while in the Na₂SO₄-H₂O system a solid-phase with a dendrite morphology was nucleated.

The solubility of sodium chloride in water vapor was determined in a continuous flow system at supercritical temperatures ranging from 450 to 550 °C and sub- and supercritical pressures varying from 100 to 250 bar. Measured sodium chloride concentrations ranged from 0.9 to 101 ppm (by weight). Hydrolysis of the solid NaCl to form NaOH and HCl was found as a possible explanation for some of the reported discrepancies in the literature. Experiments with sodium sulfate at 500°C and 250 bar were also performed. Measured sodium sulfate concentrations were 0.9 ppm ± 0.2 ppm, and exhibited unsteady behavior. Though only an estimate of Na₂SO₄ solubility could be obtained, this value was over two orders of magnitude lower than that for sodium chloride at identical conditions.

Flow experiments simulating the rapid precipitation of salts during the SCWO process were also performed. In the experiments, aqueous salt solutions were injected into a coaxially flowing supercritical water stream at a constant pressure of 250 bar. Jet concentrations ranged from 0.1 to 10.0 wt% with a typical flow rate of 0.5 g/min and temperature of 150°C. The flow rate of the pure supercritical water stream was typically 10.2 g/min with an initial temperature of 550°C. Results from SEM analysis of collected solids, in-situ laser transmission measurements, and low-magnification microscopic or
visual observation of the jets indicated that at 250 bar sodium chloride solutions first pass through a two-phase, vapor-liquid state before solid salt is formed, while sodium sulfate solutions nucleate solids directly from a homogeneous fluid phase. Sodium sulfate solids appeared much finer and also more aggregated than sodium chloride solids. Primary sodium sulfate particle diameters were typically between 1 and 3 microns, while some aggregates reached diameters up to about 20 microns. In contrast, sodium chloride solids had many hollow inner regions with a size range of 5 to 25 μm for a 0.5 wt% jet and 20 to 100 μm for a 10.0 wt% jet. At a subcritical pressure of 200 bar, the average particle size increased dramatically for both salts. In mixed NaCl/Na₂SO₄ solutions at 250 bar, the extent of small particle nucleation of sodium sulfate decreased with increasing sodium chloride concentration in the jet feed. Both the pressure and mixture effects were explained using isobaric phase relationships in the salt-water systems.

Preliminary modeling of certain individual steps of the shock crystallization process were performed. Diffusion limited growth was shown to be a possible explanation for the micron-sized sodium sulfate precipitates. Agglomeration calculations indicated that primary particle collisions in the bulk supercritical water medium could not account for the large Na₂SO₄ aggregates, which most likely formed near the jet exit where enhanced particle concentrations existed.

Thesis Supervisor: Jefferson W. Tester
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Chapter 1.

Summary / Digest

1.1 Introduction

Phase equilibrium and precipitation kinetics in salt-water systems at extreme conditions of temperature and pressure (T > 250°C, P > 100 bar) are of fundamental importance to many fields, such as, geochemistry, steam power generation, and geothermal heat extraction. These topics are also relevant to the emerging waste treatment technology called supercritical water oxidation, where long-term reliable operation of the process depends on efficient separation of precipitated inorganic solids.

Oxidation in a supercritical water medium is an efficient and clean way of treating many aqueous organic wastes (Modell, 1989; Thomason et al., 1990; Barner et al., 1991; Tester et al., 1992), and it is also currently being considered as a means of waste disposal and water recycle on future long term space missions (Timberlake et al., 1982, Hong et al., 1987 & 1988). Supercritical water oxidation (SCWO) is defined as oxidation that takes place above the critical temperature and pressure of pure water, 374°C and 221 bar (3205 psia), respectively. At typical process operating conditions of 500 to 600 °C and 250 bar, supercritical water has a low dielectric constant (<2) and dissociation constant (<10^-22) and as such exhibits non-polar solvation properties which lead to total miscibility of oxygen and organics in a single supercritical water-rich phase. Also, under these conditions salts, in general, have very low solubility. Thus, in addition to the near complete destruction of the organic components in relatively short reaction times of order 1 minute, the SCWO process also provides a means for the separation of salts from the aqueous waste stream.

Typically, salts enter the SCWO reactor dissolved in the cold pressurized liquid waste feed stream, and undergo rapid crystallization when this feed stream mixes with and
is heated by a supercritical water recycle stream. This rapid or "shock-like" precipitation is a result of the extreme drop in salt solubility that occurs as the feed stream becomes supercritical. Salts are contained as dissolved species in metabolic wastes and frequently in industrial aqueous wastes, and are also formed during the oxidation and subsequent in-situ neutralization of organic compounds containing chloride, fluoride, sulfur, and other heteroatoms. Examples of the latter include, methylene chloride, dimethyl sulfoxide, and any chlorofluorocarbon (CFC).

Solid salt separation is a important engineering design issue in the SCWO process. Although much of the research and process development in this area remain proprietary, general salt separator requirements and design concepts can be found in patents and published process descriptions (eg. Modell, 1985; Hong et al., 1989). In one proposed separator design (Barner et al., 1991), precipitated salts are redisolved in an aqueous solution at the bottom of the reactor, which is kept at a subcritical temperature. The brine solution is then removed using a pressure letdown valve. A filter is also placed on the effluent line to remove some of the entrained solids. Several problems still persist during salt separation, such as, corrosion by the brine solutions, accumulation of sticky salts on reactor walls, and potential clogging of down stream process lines by fine salt particulates. Although considerable progress in SCWO salt separation techniques has been made in industry, a fundamental understanding of phase equilibria and solid salt formation in subcritical and supercritical water is needed to optimize performance of current designs and to facilitate the development of the next generation of salt separators.

1.2 Objectives

The primary objective of this research project has been to explore the relationship between phase behavior and precipitation mechanisms in salt-water systems at temperatures (up to 550°C), pressures (100 to 300 bar), and waste stream salt concentrations (up to 10.0 wt%) encountered in the SCWO process. In particular, to:

1) Correlate and evaluate existing thermodynamic models for the NaCl-H₂O system and test the applicability of other conventional approaches for modeling this system under extreme temperatures and pressures.
2) Perform isobaric phase equilibrium experiments on the model salt-water systems of NaCl-H₂O and Na₂SO₄-H₂O to observe phase transitions and verify the phase diagrams.

3) Measure vapor-phase solubilities of the model salts in supercritical water at temperatures and pressures of interest to the SCWO process.

4) Perform experiments to simulate the rapid precipitation of the model salts from supercritical water, thus determining formation mechanisms and providing particle size estimates.

5) Predict homogeneous nucleation rates and particle growth rates by diffusion limited kinetics and agglomeration by applying the classical theories to salt-water systems at supercritical conditions.

These objectives represent fundamental steps needed to characterize and understand salt formation occurring during the SCWO process. Sodium chloride and sodium sulfate were chosen as the model salts because they are both contained in metabolic waste and many industrial waste streams. An extensive thermodynamic database also exists for the sodium chloride-water system. The approach taken focuses on developing experimental techniques, since little information is available on the precipitation of salts from supercritical water. The theoretical objectives evolved mainly to aid in the interpretation of the experimental results.

1.3 Thermodynamic Modeling

Theoretical modeling of the shock crystallization of salts in supercritical water requires thermodynamic relationships in salt-water systems at both subcritical and supercritical conditions. This includes the prediction of phase boundaries, stability limits, and densities of the stable phases. Thermodynamic relationships valid for this wide range of conditions exist only for the NaCl-H₂O system. Characteristic of most of the models is an extreme temperature and density dependence of the fitted parameters. This is unavoidable, due to the highly non-ideal nature of the system. All the available models for the NaCl-H₂O system do a respectable job in describing the phase behavior of the system in their valid ranges. However, these models also tend to be complicated to use, and would require modifications and fitting of additional parameters to be applied to the
mixed salt systems which prevail during the SCWO of metabolic wastes. It would be advantageous then, to be able to extend existing room temperature liquid-phase activity coefficient models or apply a fluid-phase equation of state model to salt-water systems at extreme conditions. Both of these ideas have been tested for the sodium chloride-water system, and are discussed below.

1.3.1 Extension of Low Temperature Activity Coefficient Models

A number of successful models exist for estimating activity coefficients of aqueous electrolytes. Typically, aqueous systems of both single salts and mixed salts are modeled at temperatures below 100°C and moderate pressures. Three of these models were used in predicting the solubility of sodium chloride in liquid water as one approaches supercritical conditions, where a three-phase system exists comprised of a concentrated liquid-phase, a dilute vapor-phase, and a pure salt solid-phase. All three models were tested beyond their recommended temperatures and concentration limits.

The first electrolyte model tested was developed by Pitzer. Pitzer’s activity coefficient model is an extended Debye-Hückel equation with added terms to account for the effect of ionic strength on long range forces (Pitzer, 1979). The second electrolyte model tested was that of Chen and Evans (1986). In their model, the excess Gibbs free energy is expressed by applying local composition concepts and the nonrandom two-liquid (NRTL) theory for short-range effects and an extended Debye-Hückel theory for long-range effects. The final model tested was an empirical model of Meissner and associates (Meissner and Tester, 1972; Kusik and Meissner, 1978), which has been successfully applied to many electrolyte systems at high concentrations.

Figure 1.1 shows the prediction of NaCl solubility in saturated aqueous solutions using the three models as compared to experimental solubility values (in molality units) taken from Linke (1958). Both Meissner’s and Chen’s models show significant deviations from the experimental values above temperatures of 150°C. This is most likely due to the small temperature correction incorporated in their models, which were originally developed to be used at only moderate temperatures to about 120°C. Pitzer’s model adequately predicts the solubility up to a temperature of 250°C; primarily as a result of the elaborate temperature dependence of the model’s fitted parameters. All three models
Figure 1.1  Predictions of tested activity coefficient models for the saturated liquid composition in the NaCl-H₂O system.
would require significant modifications and/or additional parameter dependencies to allow prediction of mixed electrolyte solubilities in aqueous solutions at extreme temperatures and pressures.

1.3.2 Modeling Solubilities with a Cubic Equation of State

Cubic equations of state are frequently used to predict the phase behavior of supercritical fluid and solute systems (McHugh and Krukronis, 1986). In low density, aqueous supercritical fluids, salts do not dissociate into ions, they remain in their molecular state due to the non-polar nature of supercritical water; consequently, salts are usually only slightly soluble under these conditions. For these vapor-like supercritical phases, an equation of state approach for phase equilibrium modeling is advantageous over an liquid-phase activity coefficient approach. The Peng-Robinson equation of state (PREOS, Peng and Robinson, 1976) was used to model the sub- to supercritical (vapor-like) fluid phase of saturated solutions of sodium chloride over a temperature range from 300 to 500°C, and a corresponding pressure range from 58 to 345 bars. This two-component (NaCl-H₂O), three-phase (vapor, liquid, and solid salt) system at equilibrium is monovariant. Therefore, specifying the temperature of the system fixes the total vapor pressure and the compositions of both the vapor and liquid phases.

If the critical properties of each component are known, then the PREOS has one adjustable binary interaction parameter, k₁₂, that is fit to data. For the NaCl-H₂O system, k₁₂ was found to be a strong function of temperature, as shown in Figure 1.2(a). A fourth-order polynomial was used to empirically represent the variation of k₁₂ with temperature. Figure 1.2(b) shows the solubility prediction of the PREOS using the fourth-order temperature correlation for k₁₂. The calculated weight percent of NaCl in the vapor was very sensitive to the value chosen for k₁₂ at any given temperature. Figure 1.2(c) shows this relationship. For a 1% change in k₁₂, there was more than a 10% change in the calculated weight percent. This high sensitivity to k₁₂ severely limits the extrapolation of the results to temperatures out of the range of the fitted constant, since large errors will most likely occur. These procedures suggest that the PREOS is not be adequately representing the degree of non-ideality that exists in the saturated vapor phase in the NaCl-H₂O system at the conditions tested.
Figure 1.2 Results of Peng-Robinson equation of state (PREOS) based prediction of saturated vapor composition in the NaCl-H₂O system.
1.4 Isobaric Phase Equilibria Experiments

An experimental technique was developed for observing phase transformations and estimating phase boundaries in salt-water systems at constant pressure and extreme temperatures. Testing in an isobaric mode is desirable, since the oxidation and salt separation steps in the SCWO process occur at constant pressure. Furthermore, salt formation mechanisms may depend on phase behavior. To evaluate this technique, static isobaric experiments were performed on the NaCl-H₂O, Na₂SO₄-H₂O, and NaCl-Na₂SO₄-H₂O systems at the typical process pressure of 250 bar.

1.4.1 Apparatus and Procedures

A cell was designed and constructed in cooperation with Harwood Engineering (Walpole, Ma.) for optically accessible in-situ measurements of phase equilibria and solid salt formation in supercritical water. The cell was designed for service to 340 bar (5000 psig) at temperatures up to 700°C. The cell was constructed from a corrosion resistant, high strength nickel alloy, Inconel 625, and the windows were optically clear, synthetic sapphire (α-Al₂O₃). A cross-sectional diagram of the optical cell is show in Figure 1.3. The cell was cubic in shape with an outer length of 12.7 cm (5 in.), and an inner volume of approximately 25 cm³. All six faces of the cell contained threaded ports, in which either Inconel 625 window holders, plugs or flow tubes were inserted. All the ports were interchangeable, which allowed for many different cell configurations. The cell was designed for both side and forward light scattering measurements up to angles of 10° from the centerline.

A schematic of the experimental setup incorporating the optical cell for examining phase behavior in salt-water systems at extreme temperatures and pressures is shown in Figure 1.4. For the static experiments, only one flow tube was inserted in the top port of the cell, and it was used for internal temperature measurement and solution bleed-off during heating. Inconel 625 plugs were placed in the bottom and two side ports of the cell, while window holders were inserted in the remaining two side ports (front and back).

In a typical static isobaric experiment, the cell was first filled with a homogeneous solution of known salt concentration at room temperature. The cell was then slowly heated at constant pressure. A phase transformation was identified visually or by light
Figure 1.3 Cross-sectional view of high temperature and pressure optically accessible cell.

Figure 1.4 Schematic of apparatus for static isobaric phase equilibrium experiments.
extinction. The temperature of the inner solution and of the cell block was recorded when the nucleation of the new phase was first identified. The inner solution temperature was measured using a thermocouple inserted through the flow tube, while the cell block temperature was measured with thermocouples placed in the top and bottom thermowells in the cell body.

A simple technique was developed for conducting the isobaric experiments. During an experiment, the high pressure pump was used to flow pure water through a straight length of tubing, while the pressure was held constant using a back pressure regulator. The optical cell was connected to the system using a high-pressure cross (as shown in Figure 1.4), and as the cell was heated the bleed-off combined with the pumped pure water. Since the flow rate of the pump was kept appreciably above the required bleed-off rate for isobaric heating, the total pressure in the system remained nearly constant. For a typical isobaric run with a heating rate between 1.0 and 2.0 °C/min, the pressure varied by only 1 to 2 bar if the flow rate of the pure water was kept at 2.0 g/min.

1.4.2 NaCl Experiments at 250 bar

Solutions of known sodium chloride concentration were heated at a rate of approximately 1.5 °C/min while maintaining a constant pressure of 250 bar. The initial concentration of the solutions ranged from 0.1 to 20.0 wt% NaCl. As each solution was heated from room temperature, it passed from the one-phase fluid region into the vapor-liquid region of the phase diagram. Video taping was routinely carried out to document observations. For solutions of concentration of 1.0 wt% or greater, a well-defined phase transformation was identified visually, appearing as a burst of very small vapor bubbles nucleated from the homogeneous fluid. The vapor bubbles seemed to emerge from the inner walls of the cell, which were hotter than the bulk solution because the cell was heated externally. Neglecting any significant penetration into the metastable region, the temperature at which the bubbles first appeared locates the vapor-liquid boundary in the phase diagram at the concentration of the initial solution.
Figure 1.5 compares the results of the NaCl isobaric runs at a pressure of 250 bar, which are plotted as solid triangles with error bars, with interpolated data from isothermal experiments reported by other investigators. The bottom error limit corresponds to the measured bulk solution temperature as the initial vapor bubbles nucleated, and the top error limit corresponds to the cell block temperature at the onset of nucleation. Averages of the upper and lower experimental temperatures are plotted as the solid triangular points. Since nucleation occurred consistently on the inner walls of the cell, it is believed that the bulk solution temperature and the block temperature provide an upper and lower bound for the actual phase nucleation temperature. The excellent agreement of our data with others along the vapor-liquid binodal line for the NaCl-H₂O system confirms that the isobaric experimental technique can accurately estimate phase boundaries. Also, since the isobaric method can be performed directly at the pressure of interest, measurement and interpolation of isothermal data is not required.

1.4.3 Na₂SO₄ Experiments at 250 bar

In the sodium sulfate-water system at a pressure of 250 bar and temperatures encountered in the supercritical water oxidation process, only a single-phase, saturated fluid solution can exist in equilibrium with solid Na₂SO₄. This conclusion was based on the Russian study of Ravich and Borovaya (1964). Thus, if a sodium sulfate solution is heated isobarically at this pressure, pure Na₂SO₄ should be nucleated once the solid-fluid phase boundary is crossed.

Three isobaric experiments with varying initial sodium sulfate concentrations were performed to verify the 250 bar phase behavior for this salt. For two of the runs with initial concentrations of 3.0 and 10.0 wt% Na₂SO₄, solid nucleation was observed during the heating, and the solids appeared as fine particles settling inside the optical cell and salt crystals with needle/dendrite morphology growing on the inner window surface. These results are plotted on the sodium sulfate-water phase diagram in Figure 1.6(a). The error limits on the points represent the temperature of the inner solution (lower limit) and the cell block (upper limit) at the first observation of solid phase nucleation, and the solid triangle is the arithmetic average of the two temperatures. Both points fall above the Russian data. This could be a result of difficulties in detecting the first nucleated solids,
Figure 1.5  Results of sodium chloride static isobaric experiments shown on the temperature-composition NaCl-H$_2$O phase diagram at 250 bar.
Figure 1.6  Results of sodium sulfate isobaric experiments at 250 bar, (a) temperature-composition Na$_2$SO$_4$-H$_2$O phase diagram, (b) light microscope photo of sodium sulfate dendrite morphology.
which most likely occurred on the hot inner walls of the vessel. Alternatively, a significant metastable zone may exist. For the most dilute run with an initial loading of a 1.0 wt% Na$_2$SO$_4$ solution, not enough particles were formed to allow visual detection, but dendrite needles were observed attached to the inner walls of the vessel after the cell was cooled and opened. Figure 1.6(b) shows an optical photomicrograph of dendrite needles which grew on the inner surface of sapphire window during the 3.0 wt% Na$_2$SO$_4$ run. The dendrites are arranged in a branch or fern-like structures with primary and secondary branches aligned perpendicular to the main stems.

1.4.4 Mixed NaCl/Na$_2$SO$_4$ Solution Experiment at 250 bar

A single static experiment with the ternary system, NaCl-Na$_2$SO$_4$-H$_2$O, was performed at a pressure of 250 bar. The initial composition of the homogeneous solution loaded into the cell was 3.0 wt% NaCl and 3.0 wt% Na$_2$SO$_4$. As the solution was slowly heated, both types of nucleated phases (solids and vapor bubbles) were observed with no appreciable differences in nucleation temperatures from the experiments with the binary salt-water systems at similar concentrations. The first nucleated phase occurred at an average temperature of 368°C, and appeared as solids settling to the bottom of the cell and dendrite crystals growing on the inner surface of one of the sapphire windows, similar to the pure Na$_2$SO$_4$ experiments. The second nucleated phase appeared as small vapor bubbles rising to the top of the cell, and at higher temperatures a vapor-liquid interface emerged (at an average temperature of approximately 396°C), similar to the pure 3.0 wt% NaCl run.

Some additional information from the mixed salt experiment can be inferred. During solid nucleation, the total amount of solids settling in the cell did not appear as intense as in the pure 3.0 wt% Na$_2$SO$_4$ experiment. Also, the dendrites which grew on the window surface began to redisolve as the vapor-liquid interface came into view. Finally, the collected solids were caked on the bottom surface of the cell, and did not have a dendritic appearance. These results suggest that the sodium sulfate dendrites, which initially formed, were redisolved in the concentrated NaCl liquid brine.
1.5 Dense Vapor Phase Solubility Measurements

Experiments were performed to obtain solubilities of two common salts, sodium chloride and sodium sulfate, at conditions prevalent in the supercritical water oxidation process. Subcritical pressures were examined for sodium chloride to help resolve some of the discrepancies in the data reported in the literature. Salt solubility at lower pressures is also important to a recently proposed modification of the SCWO process (Hong, 1992). The solubility predictions of two thermodynamic models for NaCl were also compared to experimental results.

1.5.1 Apparatus and Procedures

In the experiments, pure deionized water was flowed continuously through a salt bed using a high-pressure liquid chromatography pump. The feed was heated using two electrical resistance heating units. The solid salt was packed loosely in an Inconel 625 tube, which was placed in a furnace. The length and diameter of the salt bed were approximately 22 cm and 0.91 cm, respectively. A three-zone temperature control scheme was used to ensure that the water temperature at the bottom of the salt bed and the exit temperature at the top of the salt bed were kept within ±1 °C of the desired temperature. The collected samples were analyzed for all expected dissolved ions. H⁺ was measured with a pH electrode, Na⁺ with an Inductively Coupled Plasma (ICP) atomic emission spectroscopy instrument, and Cl⁻ and SO₄²⁻ with a visible spectrophotometer using colorimetric and turbidimetric techniques, respectively.

1.5.2 NaCl Solubility Experiments and Solvation Model Regression

Sodium chloride solubility experiments were conducted at temperatures of 450, 500 and 550 °C and pressures ranging from 100 to 250 bar. In the experiments, no uniform dependence of concentration on flow rate was observed. Figure 1.7 shows the results at 500°C. At pressures of 150 bar and above, our results fall close to those of Styrikovich et al. (1955) and Martynova (1964). At a pressure of 100 bar, our results are closer to those of Galobardes et al. (1981). For all of our experiments, solubilities were about one to two orders of magnitude below those reported by Sourirajan and Kennedy (1962) or Alekhin and Vakulenko (1988). A solvation model was used to regress our
Figure 1.7  Comparison of sodium chloride solubility measurements and model prediction at 500°C.
data. In the fit, we included a subset of Galobardes's data (three points at each temperature) and also the data of Bischoff et al (1986). The resulting correlation was,

$$\log C_{NaCl} = 3.866 \log \rho_w - \frac{1233.4}{T} + 7.772$$  \hspace{1cm} (1.1)

where log is the logarithm in base 10, $C_{NaCl}$ is the saturated NaCl concentration in ppm, $\rho_w$ is the pure water density in g/cm$^3$, and T is the temperature in Kelvins. As shown in Figure 1.7, the simple solvation model represents our solubility data reasonably well over the full temperature and pressure range examined. The Pitzer and Pabalan (1986) model also provides a reasonable representation of our data.

In our experiments, hydrolysis of solid NaCl was detected at all temperatures and at several of the experimental pressures:

$$NaCl_{(s)} + H_2O_{(v)} = NaOH_{(s)} + HCl_{(v)}$$  \hspace{1cm} (1.2)

In this reaction, a solid phase solution of NaCl and NaOH is proposed to be formed resulting in HCl. Thus, HCl may be another source of chlorine in the vapor phase, in addition to dissolved NaCl. Hydrolysis was most significant at a pressure of 100 bar. Figure 1.8 shows the results of our experiments at 100 bar and those of Galobardes et al. (1981) and Martynova (Martynova and Samoilov, 1962; Martynova, 1964). One possible explanation for the discrepancies in the data can be developed. If the measured chlorine concentration is used to calculate the solubility of NaCl (as done by Martynova and Samoilov), the estimated solubility will be too high due to the hydrolysis reaction. This is verified by our results showing the calculated NaCl solubility from Cl$^-\hspace{1cm}$ measurements versus Na$^+\hspace{1cm}$ measurements. A predicted NaCl solubility curve is also plotted showing the effect of using total chlorine concentration to determine NaCl solubility. The contribution of the hydrolysis reaction was predicted assuming phase equilibria in equation (1.2), while the contribution of chlorine from the actual dissolved NaCl was obtained using the solvation model parameters of Galobardes et al. (1981).
Figure 1.8  Extent of measured sodium chloride hydrolysis at 100 bar, --- solvation model of Galobardes et al. (1981), --- model of Pitzer and Pabalan (1986), --- calculated NaCl concentration based on total Cl\(^-\) from solvation and hydrolysis.
1.5.3 $\text{Na}_2\text{SO}_4$ Solubility Experiments

Sodium sulfate solubility experiments were conducted at temperatures of 450 and 500 °C and pressures of 250 and 300 bar. Water flow rates were varied from 0.5 to 1.5 g/min. The measured sodium concentrations in the effluent samples showed an unsteady nature, which hindered the determination of sodium sulfate solubility. By smoothing these fluctuations, the solubility of $\text{Na}_2\text{SO}_4$ was estimated as 0.9 ppm ± 0.2 ppm at 500 °C and 250 bar. However, because of these seemingly inherent unsteady characteristics of operating the open, flowing system, a closed or batch autoclave experimental system to determine solubilities is recommended for this salt.

1.6 Shock Crystallization Experiments

Flow experiments were performed to characterize salt formation at temperatures, pressures, and supersaturation values similar to those found in the actual SCWO process. In the experiments, high levels of supersaturation were achieved by injecting a cool aqueous salt solution into a coaxially flowing supercritical water stream. This resulted in a rapid or "shock-like" precipitation of solid salts. These experiments were used to identify important mechanisms of salt growth and estimate particle sizes of the solids formed in the process.

1.6.1 Apparatus and Procedures

The dynamic experiments were designed to simulate the rapid mixing of a waste stream containing dissolved salts with supercritical water in the SCWO process. The two feeds in the experiments were a pure supercritical water (SCW) stream (typically at 550°C, 250 bar, and flowing at 10.2 g/min) and a cool salt solution (0.5 to 10.0 wt%, typically at 150°C, 250 bar, and flowing at 0.5 g/min). The Inconel 625 optical cell was configured with two large flow tubes (0.912 cm ID) in the top and bottom ports, two window holders in the front and back ports for photographic documentation and light scattering measurements, and two Inconel 625 plugs in the other side ports.

Figure 1.9 shows the apparatus for the shock crystallization experiments. The supercritical water feed stream is shown in the upper right corner of the figure. Cold distilled water was fed using a high pressure liquid chromatography pump (HPLC), and
Figure 1.9  Schematic of apparatus for flow/shock crystallization experiments.
an electrical resistance heater was used to raise the temperature of the water to supercritical. A low-pulse HPLC pump was used to deliver the jet feed to the cell (upper left of Figure 1.9). This feed was either pure deionized, distilled water or a salt solution. For the pure water feed, salt solution samples were introduced into the jet feed stream with a six-port injection valve. The salt solution was injected co-axially into the SCW stream as a jet using a cooled nozzle, which passed down the center of the top flow tube. The nozzle diameter was approximately 0.8 mm, and the internal coolant flow (distilled H₂O) was finely controlled to provide ample insulation of the salt solution jet, while not removing a significant amount of heat from the SCW feed stream.

Particle collection runs and laser transmission measurements were performed with the nozzle exit located in the upper flow tube to assure complete mixing of the jet and the SCW stream. After the experiments, the system was flushed with nitrogen to remove water vapor, which when condensed would dissolve any formed solids. Once ambient temperature was reached, the cell was opened, and the solid salt was collected for scanning electron microscopy (SEM) and X-ray analysis.

1.6.2 General Jet Characteristics

Figure 1.10 shows photos of various salt jets mixing with a coaxially flowing SCW stream at 250 bar. A pure water jet is also shown for comparison. The photos were taken using 35 mm film, a camera shutter speed of 1/500 sec, and white light entering through the rear window of the cell for illumination. The SCW to jet feed ratio was 20:1, which resulted in a mixed stream temperature of approximately 530°C. Additional heating was also provided by the cell body, which was held at approximately 600°C. The pure water jet shown in Figure 1.10(a) appears fairly unstable due to the density differences in the two feeds. The 3.0 wt% NaCl jet shown in Figure 1.10(b) appears somewhat more stable than the pure water jet. The third jet shown in Figure 1.10(c) had an initial concentration of 10.0 wt% NaCl. This jet appears much narrower and more focussed than the pure water jet, and can be seen breaking up into droplets with diameters of approximately 0.7 mm. The large vapor-liquid equilibrium region in NaCl-H₂O phase diagram at 250 bar (see Figure 1.5), most likely caused the apparent two-phase flow seen in Figure 1.10(c). In the more dilute 3.0 wt% NaCl jet, the volume of the
Figure 1.10  View of jets mixing with a coaxially flowing SCW stream at 250 bar.
nucleated liquid phase may have been too small to coalescence into droplets large enough to be visible. The 3.0 wt% Na₂SO₄ jet shown in Figure 1.10(d) appears much darker than the previous ones. Possibly, this was caused by small particles which nucleated homogeneously from the solution, scattering the light. In the Na₂SO₄-H₂O system at 250 bar, there is a continuous falloff in solubility as the critical temperature of water is approached, and no vapor-liquid region in the temperature range of interest (see Figure 1.6(a)). The final jet shown in Figure 1.10(e), is a mixed solution containing 3.0 wt% NaCl and 3.0 wt% Na₂SO₄. The appearance of the jet is closer to that of the 3.0 wt% NaCl jet, and no noticeable scattering from fine particles is evident, as was the case for the 3.0 wt% Na₂SO₄ jet. Na₂SO₄ solubility is high in NaCl brines, which could explain the mixed jet appearance, since no Na₂SO₄ precipitation was observed in the initial mixed region of the jet.

A number of jets were examined at a pressure of 200 bar, which is below the critical point of pure water (221 bar). Significant changes in the appearance of the jets were observed. The pure water jet shown in Figure 1.11(a) appears much different than the 250 bar pure water jet shown in Figure 1.10(a). As the 200 bar water jet was heated, it passed through the two-phase, vapor-liquid region the phase diagram for pure water. This resulted in a narrow liquid jet which appears to become narrower as it flows downward, possibly due to water vaporization during heating. The exit Reynolds number of the jet was approximately 62, and it does indeed appear laminar, unlike the 250 bar water jet, whose Reynolds number was 60 (Figure 1.10(a)).

A 200 bar, 10.0 wt% NaCl jet is shown in Figure 1.11(b). Like the 250 bar NaCl jet shown in Figure 1.10(c), the 200 bar jet also appears to breakup into liquid droplets, but the droplets form closer to the nozzle exit. This could be due to a shift to lower temperature of the vapor-liquid region in the NaCl-H₂O system as the pressure decreases from 250 to 200 bar. The initial droplet sizes measured from the photo are approximately 0.8 mm. The final jet shown in Figure 1.11(c) is a 5.0 wt% Na₂SO₄ jet, which appears much different than the 250 bar Na₂SO₄ jet (see Figure 1.10(d)). There seems to be no rapid precipitation of fine solids in the 200 bar jet. Also, two-phase, vapor-liquid flow is evident. This later observation is consistent with the Na₂SO₄-H₂O phase diagram, which contains both a three- (V-L-S) and two-phase (V-L) region at pressures below 221
Figure 1.11  View of jets mixing with a coaxially flowing subcritical water stream at 200 bar.
bar (discussed in Section 1.6.4).

*In-situ* laser transmission measurements were performed to quantify the extent of solid formation during the shock crystallization experiments. Transmission is defined as the attenuation of light intensity by scattering, which was calculated as the measured laser power with a pure water jet (I₀) divided by the laser power measured during salt injection (I). Figure 1.12 compares the transmission values for various NaCl and Na₂SO₄ jets. At 250 bar, the transmission measured during shock crystallization experiments with sodium chloride jets was always much greater than that for sodium sulfate jets under identical run conditions. Although only rough estimates, the average Na₂SO₄ particle sizes calculated from the data were all between 0.3 and 1.6 μm, while the calculated NaCl particle sizes ranged from 5 μm for the 0.5 wt% jet to 90 μm for the 10 wt% jet. Transmissions for the 200 bar jets were all approximately 100%, which suggests a shift to higher average particle sizes due to the subcritical pressure.

### 1.6.3 NaCl Precipitation

Figure 1.13(a) shows the particles formed from a 3.0 wt% NaCl jet mixed with a coaxially flowing SCW stream at 250 bar. The particles were grouped in clusters of amorphous kernel-shaped particles with lengths between 10 and 100 μm, and appeared to have many hollow inner regions. The size range of the collected sodium chloride particles was affected by the jet concentration. Figure 1.13(b) shows a SEM photomicrograph of particles formed from a 0.5 wt% NaCl jet. Many of the solids formed from the dilute, 0.5 wt% jet appear shell-like, and are much smaller than the solids collected from the more concentrated jet.

The particles shown in Figure 1.14 were formed from a 3.0 wt% NaCl jet mixed with a coaxially flowing SCW stream at 200 bar. The top SEM photomicrograph shows the overall morphology of the particles, whose lengths ranged from 0.5 to 1.0 mm. The lower SEM in Figure 1.14 is a magnification of the surface of one of the particles, which appears very porous. The particles formed at 200 bar were over an order-of-magnitude larger than the particles formed from the 3.0 wt% jet at 250 bar (Figure 1.13(a)).

A schematic of the path taken by a 3.0 wt% NaCl jet, as it is simultaneously heated and diluted by rapid mixing with a hot supercritical water stream, is shown in
Figure 1.12  Laser transmission measurements as a function of jet concentration.
Figure 1.13  SEM photos of NaCl particles precipitated from a jet mixed with supercritical water at 250 bar. (a) 3.0 wt% jet, (b) 0.5 wt% jet (Jet feed: 1.0 g/min, 110-140°C; SCW feed: 10.2 g/min, 540°C).
Figure 1.14  SEM photos of NaCl particles precipitated from a 3.0 wt% jet mixed with subcritical water at 200 bar, (a) overall morphology, (b) surface of particle. (Jet feed: 0.5 g/min, 115-130°C; Pure water feed: 10.3 g/min, 550°C).
Figure 1.15 on the NaCl-H₂O isobaric phase diagrams at 200 and 250 bar. A final dilution factor of twenty was assumed. A possible mechanism for shock crystallization in this system is that a highly concentrated aqueous brine serves as a precursor to solid NaCl precipitation. At both pressures, the vapor-liquid region extends over a wide concentration range. During heating the jet enters the vapor-liquid region, and a disperse concentrated liquid phase should form. The liquid droplets will become more concentrated in salt as the solution gets hotter, while the volume of the liquid phase will diminish due to its increasing salt composition. Once the three-phase temperature is reached (420°C for 200 bar and 450°C for 250 bar), the liquid brine will become unstable, and a phase transformation from vapor-liquid to vapor-solid will occur.

The mechanism derived from the phase behavior of the NaCl-H₂O system provides a possible explanation for experimental findings. At both pressures, two-phase flow containing liquid droplets was observed. Unstable solid growth from disperse liquid droplets is a possible cause of the amorphous morphology and relative large size of the NaCl solids. The particles also appeared quite porous with many hollow inner regions, which would be expected if the concentrated brine droplets (up to 50 wt% salt at 250 bar) underwent rapid transformation by water evaporation, leaving behind a solid salt skeleton.

Both the size of the photographed liquid droplets and the dimensions of the collected particles increased significantly as operating pressure was lowered from 250 to 200 bar in separate runs. This change was possibly caused by the distinct difference in the shapes of the vapor-liquid regions at 200 and 250 bar (see Figure 1.15). At the subcritical pressure of 200 bar, the vapor and liquid region starts at a point on the boiling curve of pure water (0 wt% NaCl), while at the supercritical pressure of 250 bar the region begins at a point on the binary critical locus (approximately 0.9 wt% NaCl). Therefore, the 200 bar vapor-liquid region is much flatter than the 250 bar region, which may have caused more rapid formation and coalescence of the liquid-phase in the jet. Also, since the vapor-liquid region occurs at lower temperatures, there was less time for the liquid-phase to disperse.
Figure 1.15  Schematic of heated jet path shown on the temperature-composition NaCl-H₂O phase diagram (logarithmic concentration scale).
1.6.4 Na$_2$SO$_4$ Precipitation

The dark appearance of the sodium sulfate jet shown in Figure 1.10(d) was attributed to light scattering by fine particles. Many of the particle collection runs verified that small micron particles were precipitated, though with some particle collection methods only the largest particles were gathered. The large particles appeared as partially coalesced agglomerates of micron sized primary particles.

Similar runs to those described above, with a jet feed of 3.0 wt% Na$_2$SO$_4$, were conducted using either a Hastelloy disk or frit secured in the cell to collect the precipitated solids. Only the larger particles were trapped by the disk, while over 90% of the salt in the jet feed was collected as solids on the frit surface. Figures 1.16(a) and 1.16(b) show the particles collected on the Hastelloy disk and the Hastelloy frit, respectively. The large particles collected on the disk appear fairly spherical with long tails, and widths between 5 and 25 μm. It is possible that the particles were formed by agglomeration and partial coalescence of smaller primary particles with diameters of approximately 1 to 3 μm. The agglomerates most likely formed near the jet exit where high salt concentrations existed, while the tails of the particles may have been caused by shear forces from velocity gradients in the jet, which deformed the soft, sticky solids. A primary particle size of 1 to 3 μm is consistent with calculated average particle sizes from laser extinction measurements and measured sizes of the particles collected on the frit (Figure 1.16(b)).

A similar particle collection run was conducted at a subcritical pressure of 200 bar. The jet feed was a 1.0 wt% Na$_2$SO$_4$ solution flowing at 0.5 g/min, and the pure water feed was 10.3 g/min. Over 90% of the particles were collected on the Hastelloy disk secured in the cell, unlike similar runs at 250 bar, where disk collection efficiencies were less than 5%. Figure 1.17 shows the particles collected during the 200 bar run. The size distribution is wide, however, there are a significant number of large particles over 25 μm in length. As discussed above, there was no measurable turbidity during the 200 bar sodium sulfate run. These results suggest a change in precipitation mechanism for this salt at subcritical pressures.

The 200 and 250 bar Na$_2$SO$_4$-H$_2$O phase diagrams are shown in Figure 1.18, in addition to the lower region of the saturation curve and a schematic of the path taken by
Figure 1.16  SEM photos of Na$_2$SO$_4$ particles precipitated from a 3.0 wt% jet mixed with supercritical water at 250 bar, (a) aggregates collected on a Hastelloy disk, (b) primary particles collected on a Hastelloy frit (Jet feed: 0.5 g/min, 110-140°C; SCW feed: 10.5 g/min, 550°C).
Figure 1.17  SEM photos of Na₂SO₄ particles precipitated from a 1.0 wt% jet mixed with subcritical water at 200 bar (Jet feed: 0.5 g/min, 110-130°C; Pure water feed: 10.3 g/min, 540°C).
Figure 1.18  Schematic of heated jet path shown on the temperature-composition $\text{Na}_2\text{SO}_4$-$\text{H}_2\text{O}$ phase diagram.
a heated 3.0 wt% jet. The 250 bar salt solubility curve decreases continuously with increased temperature, and does not intersect the saturation or three-phase line. Therefore, solid precipitation can occur directly from the homogeneous fluid without first forming a concentrated liquid brine. This absence of a vapor-liquid region in the Na₂SO₄-H₂O system at 250 bar most likely caused direct homogeneous nucleation and rapid growth of many small particles. The precipitation commenced once the solubility curve was crossed and continued as the jet was heated to the final mixed temperature. Below 221 bar, a two- (V-L), and three-phase (V-L-S) region exists in the Na₂SO₄-H₂O system. The 200 bar solubility curve shown in Figure 1.18 intersects the saturation line at approximately, 365°C and 1.0 wt% Na₂SO₄. Although some precipitation of fines could occur as the jet approaches the three-phase temperature, most of the solid will form during the phase transformation from the 1.0 wt% liquid brine to pure solid and a dilute vapor solution. This hypothesis is supported by the large sizes of the collected solids and the zero turbidity of the mixed stream.

1.6.5 Mixed NaCl/Na₂SO₄ Solution Precipitation

Laser transmission measurements were performed on 1.0 wt% Na₂SO₄ jets with varying NaCl concentration. Figure 1.19 shows the measured transmission from the mixed solutions as a function of NaCl concentration. The transmitted laser power increased with NaCl concentration in the jet. Sodium sulfate solubility in high temperature aqueous sodium chloride solutions increases with sodium chloride concentration, which would lead to a decreased rate of Na₂SO₄ precipitation and greater light transmission. Thus, as the concentration of NaCl increased in the jet, the amount of Na₂SO₄ dissolved in the liquid phase also increased, which resulted in less homogeneous nucleation of fine particles, and more solids formed by the typical mechanism observed with pure NaCl jets (crystallization of solids from concentrated brine droplets).

Schematics of the paths of three different heated jets are shown in Figure 1.20 in the upper-portion of the 250 bar phase diagram for the NaCl-Na₂SO₄-H₂O system. Four levels of mixing of the jet and the SCW feed are shown. The initial locations of the jets are all in the homogeneous, liquid phase region (150°C diagram). With the addition of
Figure 1.19  Effect of NaCl concentration on laser transmission from 1.0 wt% Na$_2$SO$_4$ jets.
Pressure = 250 bar
Jet Feed: 0.5 g/min 150 °C
\( a \): 1.0 wt% Na\(_2\)SO\(_4\) & 3.0 wt% NaCl
\( b \): 3.0 wt% Na\(_2\)SO\(_4\) & 3.0 wt% NaCl
\( c \): 3.0 wt% Na\(_2\)SO\(_4\) & 1.0 wt% NaCl
SCW Feed: 10.0 g/min 550 °C

Figure 1.20 Composition of three mixed solution jets at various levels of SCW entrainment (shown on the upper corner of the ternary system phase diagram at 250 bar).
3.7% of the SCW feed, the jets are partially diluted and heated to approximately 370°C. At this temperature, Na₂SO₄ precipitation should occur from jet c, and perhaps from jet b, which is very close to the qualitatively drawn phase boundary. The amount of precipitation from jet c would also be greater than that from jet b, given the positions of the jets in the Sₚ-L region. No Na₂SO₄ precipitation would be expected from jet a, even at temperatures up to the fully mixed value of 515°C, since the only solid phase is NaCl, however, a liquid brine phase concentrated in Na₂SO₄ would be formed. This complicated effect of NaCl concentration on Na₂SO₄ precipitation was observed during the laser transmission measurements.

1.7 Modeling of Shock Crystallization

The rapid or shock-like precipitation of salts from supercritical water is complex, since it involves multi-component, multi-phase thermodynamics; extreme temperature, density, viscosity, and composition gradients; non-linear nucleation and growth kinetics; and heat, mass, and momentum transfer. At this time, the development of a rigorous model for shock crystallization is not possible, since many (or most) of the required rate parameters are unknown. As a start, the total problem was dissected and only certain individual steps were examined.

1.7.1 Nucleation and Growth at High Supersaturation

In the sodium sulfate shock crystallization experiments, high supersaturation values and rapid nucleation and growth of solid salt particles were observed. Even without direct experimental data on the high-temperature and high-supersaturation rates of nucleation and growth of salt particles in supercritical water, we believe the shock crystallization rates are controlled by homogeneous nucleation and mass transfer limited growth based on order of magnitude comparisons to typical intrinsic growth kinetic rates.

In the classical theory of homogeneous nucleation, the free energy required to form a cluster of molecules from a fluid phase is used to estimate nucleation rates and critical nuclei sizes. The effect of supersaturation on the nucleation rate is highly dependent on the value of interfacial surface energy or tension between the molecular cluster and the fluid. The difficulty of obtaining a value of this interfacial tension at our
conditions by direct measurement is a major problem, which hinders the application of the homogeneous nucleation theory.

For bulk diffusion-limited growth, the linear growth rate of an approximately spherical crystal can be written as (Nielsen, 1964),

\[ \frac{dr}{dt} = \frac{v_s D_s (C - C_{eq})}{r} \]  

(1.3)

where \( t \) is the time, \( v_s \) is the solute molecular volume, \( D_s \) is the diffusion coefficient of the solute, and \( C \) and \( C_{eq} \) are the solute concentration and equilibrium solubility, respectively, in units of molecules/cm\(^3\). The diffusion coefficient of a Na\(_2\)SO\(_4\) in supercritical water was estimated from the pure water self-diffusion coefficient (Lamb \textit{et al.}, 1981), while the equilibrium concentration was estimated as 1 ppm, which corresponds to \( 1.3 \times 10^{15} \) molecules/cm\(^3\) at a temperature of 385°C (water density of 0.315 g/cm\(^3\)). The predicted particle-time growth curve is shown in Figure 1.21. Although this is a rough estimate, the plot does show that diffusion-limited growth is consistent with the final primary particle sizes collected during the sodium sulfate shock crystallization experiments. Rapid growth could explain the relatively large size of the collected sodium sulfate particles, since homogeneous nucleation would produce initial clusters of size much less than 1 μm.

1.7.2 Growth by Agglomeration

Agglomeration following inter-particle collisions may also be an important mechanism effecting the final size and morphology of solids formed in the supercritical water oxidation process. Some of the sodium sulfate particles collected during the shock crystallization experiments appeared to be partially coalesced aggregates (see Figure 1.16(a)). Also, clusters of sodium chloride particles were frequently gathered, but the aggregates may have formed on the collection device and not in the supercritical water medium (see Figure 1.13(a)). A numerical model was developed to estimate collision rates and final aggregate sizes of salt particles formed during the shock crystallization experiments.

The collision frequency depends on particle size, fluid properties, and collision
Figure 1.21  Predicted time required to reach a final particle diameter of 1 μm assuming diffusion limited growth.
mechanism. Mechanisms considered were Brownian motion, laminar shear, and
differential sedimentation. A particle balance was used to keep track of the size
distribution of a system of particles as a function of time. This required the solution of
many differential equations, one for each cluster size. For a cluster of \( k \) primary particles, the differential equation is,

\[
\frac{d n_k}{d t} = \frac{1}{2} \sum_{j=1}^{k-1} \beta_{j,k-j} n_j n_{k-j} - \sum_{j=1}^{k} \beta_{j,k} n_j n_k
\]  \hspace{1cm} (1.4)

where \( n_i \) is the concentration of clusters with \( i \) primary particles. The first term accounts
for the creation of \( k \) clusters by collisions between clusters of size \( j \) and \( k-j \), while the
second term accounts for the loss of \( k \) clusters by collision with clusters of any size. \( k_{\text{max}} \)
is the maximum cluster size considered in the numerical solution, and it must be chosen
high enough to assure negligible loss of particle mass by cluster size cut-off.

The agglomeration calculations were performed for a monodisperse system of
spheres with diameters of 1 \( \mu \text{m} \). The initial particle concentration, \( N_0 \), was calculated by
assuming all the salt in the jet feed crystallized. The calculations were performed at the
typical mixed stream conditions of 550°C and 250 bar. Since many salt particles, such
as sodium sulfate, tend to be "sticky" at the bulk SCWO reactor conditions, the collision
efficiency was assumed to be one. Because of the uncertainty of the velocity profiles in
the optical cell, it is difficult to estimate an average velocity gradient required to calculate
the collision frequency for laminar shear. For the calculation which follows, a mean
centerline velocity of 5.0 cm/s and a jet radius of 1 cm were assumed, which resulted in
an average velocity gradient of 5.0 \( s^{-1} \).

The predicted aggregate cluster size distributions at two times are shown in Figure
1.22. The times of 5 s and 10 s correspond to typical fluid residence times for
experiments with the nozzle tip near the center of the cell and in the upper flow tube,
respectively. In both cases, the predicted contributions of laminar shear and differential
sedimentation are small. The maximum cluster sizes are fairly small, and could not
account for the large aggregates collected in the sodium sulfate experiments. Hence, the
Figure 1.22  Prediction of final size distribution of aggregates formed during the shock crystallization of a 3.0 wt% Na$_2$SO$_4$ jet.
simulation results support the hypothesis that the large aggregates formed near the jet exit where enhanced particle concentrations and shear rates existed. It is difficult to account for these factors in the agglomeration calculations, since the actual mixing rates in the jet are unknown.

1.8 Conclusions

1. **Experimental Apparatus.** An apparatus for gathering high temperature and pressure equilibria and precipitation data in salt-water systems was designed, constructed, and tested.

2. **NaCl thermodynamic modeling.** Conventional thermodynamic approaches have been applied to the NaCl-H₂O at extreme conditions. In their present form, these approaches do not satisfactorily describe the very non-ideal nature of the system in the temperature, pressure, and composition ranges tested.

3. **Isobaric phase equilibria experiments.** A method for observing phase transformations and locating phase boundaries under isobaric conditions was developed and tested on the NaCl-H₂O and Na₂SO₄-H₂O systems at 250 bar. The method not only provides direct observation of phase changes and location of phase boundaries by visual means, it can also be used to verify interpolated data from traditional isothermal experiments which use sampling techniques.

4. **NaCl solubility in sub- and supercritical Water.** The solubility of sodium chloride in water vapor was determined in a continuous flow apparatus at supercritical temperatures ranging from 450 to 550 °C and sub- and supercritical pressures varying from 100 to 250 bar. Measured sodium chloride concentrations ranged from 0.9 to 101 ppm (by weight). Hydrolysis of the solid NaCl was found as a possible explanation for some of the reported discrepancies in the literature. The hydrolysis of sodium chloride to form sodium hydroxide and hydrochloric acid becomes significant at temperatures above 500°C.

5. **Na₂SO₄ solubility in SCW.** Experiments 500°C and 250 bar were performed. Measured sodium sulfate concentrations were about 0.9 ppm ± 0.2 ppm, and exhibited unsteady behavior. Although only an estimate of Na₂SO₄ solubility could be obtained, this value was over two orders of magnitude lower than that for sodium chloride at identical conditions.

6. **NaCl and Na₂SO₄ precipitation at 250 bar.** The phase behavior in the sodium chloride-water and sodium sulfate-water systems has a profound effect on the morphology and size of the precipitated solids. Results indicate that sodium chloride solutions first pass through a vapor-liquid equilibrium state before solid salt is formed, and that sodium sulfate solutions nucleate solids directly from a homogeneous fluid phase. The sodium sulfate solids appeared much finer and also more aggregated than
the sodium chloride solids. The diameter of the primary sodium sulfate particles were typically between 1 and 3 microns, while some aggregates reached diameters up to about 20 microns. Sodium chloride solids had many hollow inner regions with a size range of 5 to 25 μm for a 0.5 wt% jet and 20 to 100 μm for a 10.0 wt% jet.

7. **NaCl and Na₂SO₄ precipitation at 200 bar.** For NaCl, the subcritical pressure caused a dramatic increase in particle size, most likely due to a phase boundary shift in the NaCl-H₂O system. For Na₂SO₄, the precipitation mechanism changed with pressure, and particle size range increased to between 2 and 50 μm.

8. **Mixed NaCl/Na₂SO₄ solution precipitation at 250 bar.** The increased solubility of Na₂SO₄ in NaCl brines causes less fine particle nucleation, and favors liquid brine formation.

9. **Shock crystallization modeling.** Diffusion limited growth was shown to be a possible explanation for the micron size of the sodium sulfate precipitates. Agglomeration calculations showed that primary particle collisions in the bulk SCW medium could not account for the large Na₂SO₄ aggregates, which most likely formed near the jet exit.

1.9 **Recommendations**

1. The isobaric technique for locating phase boundaries and characterizing phase equilibria should be used to study other common salts, such as, KCl, K₂SO₄, and Na₂CO₃ in supercritical water. This information is required to develop precipitation mechanisms for these salts in the SCWO process.

2. Additional solubility data for Na₂SO₄ should be obtained using an autoclave operated in a batch mode. The data should then be regressed with a solvation model, for use in predicting supersaturation values required to model shock crystallization.

3. The effect of other components, such as organics or gases, on the phase behavior and precipitation mechanisms in the model salt-water system should be explored, since these components make up a significant percentage of the actual SCWO reactor contents.

4. The creation of salts by *in-situ* neutralization of acidic oxidation products is another important source of solids in the SCWO process. Oxidation/neutralization experiments should be performed to determine the sizes of solids formed by this mechanism. Model waste compounds with chlorine and sulfur heteroatoms should be selected, preferably ones with known oxidation kinetics. The jet feed could be an aqueous solution of an organic compound and NaOH, while either O₂ or H₂O₂ could be added to the SCW feed. The precipitated solids could be collected on a Hastelloy frit, while laser transmission or other light scattering measurements are performed.
5. Additional shock crystallization experiments should be performed to determine the effect of nozzle diameter on NaCl and Na₂SO₄ particle sizes and morphologies. Laser drilling can be used to obtain very small diameters (<100 μm). This information is required for proper extension of the results to systems of larger scale.

6. Experiments using a low-angle light scattering instrument to measure in-situ particle size distribution were hindered by laser power fluctuations. Before additional tests are conducted, modifications to the experimental apparatus are necessary to decrease the temperature gradients in the optical cell, especially from the window ports. Small heaters could be attached to the window retainers and controlled with a thermocouple in contact with the window surface.

7. The nucleation and growth calculations should be extended to estimate the effects of concentration and temperature gradients at the jet exit. These gradients can be approximated from transport modeling. Numerical simulations of a laminar jet exhibited very slow mixing rates, thus some degree of buoyancy driven turbulence must be considered.
Chapter 2.
Introduction and Background

Phase equilibrium and precipitation kinetics in salt-water systems at extreme conditions of temperature and pressure ($T > 250\,^\circ\mathrm{C}$, $P > 100$ bar) are of fundamental importance to many fields, such as, geochemistry, steam power generation, and geothermal heat extraction. These topics are also relevant to the emerging waste treatment technology called supercritical water oxidation, where long-term reliable operation of the process depends on efficient separation of precipitated inorganic solids. The following sections describe the SCWO process, the unique properties of supercritical water, and salt formation and separation during the process.

2.1 SCWO Process Description

The oxidation of organic waste in supercritical water has been proposed as a method of hazardous waste treatment (Modell, 1982 and 1985), and is currently being developed for commercialization by Modar Inc. (Natick, MA), Modell Development Corp. (Framingham, MA), Eco Waste Technologies (Austin, TX), and possibly other companies. Supercritical water oxidation (SCWO) is defined as oxidation that takes place in a water medium above the critical point of pure water, $374\,^\circ\mathrm{C}$ and 221 bars.

For aqueous waste containing 1 to 20 wt.% organics, supercritical water oxidation is more efficient than wet oxidation, and projected to be less costly than controlled incineration or activated carbon treatment (Thomason and Modell, 1984). The use of SCWO for space applications (to convert human and other aqueous waste to potable water) is also being considered (Timberlake et al., 1982, Hong et al., 1987 & 1988). Waste recycling will be particularly important on long term space missions. The development and current status of the Modar SCWO process has been discussed in a number of recent reviews (Modell, 1989; Thomason et al., 1990; Barner et al., 1991; Tester et al., 1992).
A schematic diagram of the Modar water treatment process is shown in Figure 2.1. The subcritical aqueous organic waste stream is pumped into a tubular reactor, which operates at a pressure usually between 230 and 250 bars. An oxygen or air stream is introduced into the reactor using either a compressor if the feed is a gas or a pump followed by a vaporizer if the feed is a liquid. A caustic feed is used for in-situ neutralization of acidic oxidation products, such as HCl. At the reactor inlet, the feeds rapidly mix with an internal or recycle stream of supercritical water. This direct contact mixing serves to heat the feed above the critical point of pure water, and initiate the kinetic oxidation process.

The bulk reactor temperatures typically range from 500 to 650 °C. Supercritical temperatures are normally maintained by the exothermic oxidation of the organic waste, but auxiliary fuel is required if the waste stream is dilute. After leaving the reactor, the clean water effluent passes through a cooling/heat recovery stage, and finally through a pressure letdown gas/liquid separation stage (see Figure 2.1). If drinkable water is desired, a final polishing step, typically involving ion-exchange, is required to remove the low levels of dissolved metal ions, such as chromium and mercury (Hong et al., 1987, Tester et al., 1992).

At the bulk conditions prevalent in the Modar reactor, water behaves like a non-polar solvent, which leads to total miscibility of most organic compounds and gases in the supercritical water phase (Thomason and Modell, 1984; Thomason et al., 1990; Tester et al., 1992). This complete miscibility combined with the high temperatures results in fast oxidation rates. The primary oxidation products are carbon dioxide and water. Nitrogen (N₂), inorganic acids, and salts are additional products of certain wastes. Oxidation efficiencies above 99.99% are reached at reaction temperatures above 550°C with residence times of less than 1 minute for many organic species (Modell et al., 1982, Tester et al., 1992).

In addition to the near complete destruction of the organic compounds, the oxidation of aqueous waste in supercritical water also provides a pathway for the separation of salts from the waste stream. The non-polar nature of supercritical water at bulk reactor conditions in the SCWO process, results in a very low solubility of salts leading to rapid precipitation of solids. Typical solubility values for some common salts
Figure 2.1  Schematic of MODAR supercritical water oxidation process (Hong et al., 1988).
are shown in Figure 2.2. The solubility of NaCl in water falls from over 25 wt.% at room temperature (Linke, 1958) to approximately 0.02 wt.% or 200 ppm at 550°C and 250 bars (Sourirajan and Kennedy, 1962).

There are two possible sources of salts during the supercritical water oxidation of aqueous wastes. Salts can be contained in the waste stream itself, and thus precipitate once the waste stream becomes supercritical. Salts can also be created by heteroatom reactions in the Modar process. The oxidation of certain compounds, such as chlorinated hydrocarbons, form acidic products. Bases are added to the feed to neutralize the acids, and salt precipitates are formed. One example is the oxidation of methyl chloride and subsequent neutralization of hydrochloric acid with sodium hydroxide, which can be globally represented as:

\[
\text{CH}_3\text{Cl} + 1/2 \text{O}_2 \rightarrow \text{HCl} + \text{H}_2\text{O} + \text{CO}_2 \quad (2-1)
\]

\[
\text{HCl} + \text{NaOH} \rightarrow \text{H}_2\text{O} + \text{NaCl} (s) \quad (2-2)
\]

Depending on the content of the waste, other salts can be formed in a similar matter, such as sodium sulfate and sodium phosphate. The crystallized salts fall to the bottom of the reaction vessel where they are removed (see section 2.3).

### 2.2 Properties of Supercritical Water

The properties of pure water undergo rapid changes as the critical point is approached and exceeded. Figure 2.3 shows the variation of pure water density with temperature along several isobars. For example, as seen in Figure 2.4(a), at a constant pressure of 250 bars, the density of water falls by an order of magnitude as temperature is increased from 100 to 600 °C. In this range, other properties also drastically change as illustrated in Figure 2.4(b-h) where variations in the ion product, static dielectric constant, viscosity, enthalpy, heat capacity and isobaric compressibility of pure water are plotted as a function of temperature at 250 bar. All of the properties plotted in Figure 2.4 were obtained from the semi-empirical equation of state and other compiled equations of Haar et al. (1984), except the ion product which was calculated using the equation of Marshall and Franck (1981). At a pressure of 250 bar, the ion product of water falls from
Figure 2.2  Salt solubility in supercritical water at 250 bar. Data interpolated from: Jasmund (1952) for KCl; Martynova (1976) & Ravich and Borovaya (1964) for Na₂SO₄; Martynova (1976) for CaCl₂ and CaSO₄; and Bischoff and Pitzer (1989) & Pitzer and Pabalan (1986) for NaCl.
Figure 2.3 Temperature-density diagram for pure water (Haar et al., 1984).
Figure 2.4 (a-d) Selected properties of supercritical water at 250 bar (Haar et al., 1984; Marshall and Franck, 1981).
Figure 2.4 (e-h) Selected properties of supercritical water at 250 bar (Haar et al., 1984; Marshall and Franck, 1981).
it's room temperature value of $10^{-14}$ to around $10^{-23}$ at temperatures above 500°C. The static dielectric constant decreases from a room temperature value of 80 to about 2 at temperatures above 500°C. The values of these properties and others have led to the characterization of water as a non-ionic, non-polar solvent at the conditions found in the SCWO process. As shown in Figure 2.4(f), a maximum in the heat capacity occurs at 385°C (see Figure 2.4(f)). This temperature is defined as the pseudo-critical point for a pressure of 250 bar. The isobaric compressibility also has a maximum at this temperature (see Figure 2.4(g)).

Besides having a low solubility in the water at SCWO conditions, most salts also behave as very weak electrolytes. Figure 2.5 shows the dissociation constant of NaCl in water, as a function of temperature at a pressure of 250 bar. This normally strong electrolyte at ambient conditions has a very low dissociation constant in the high temperature range. This extreme change in salt-water interactions from sub- to supercritical conditions leads to difficulty in modeling electrolyte systems.

2.3 Salt Formation and Separation in the SCWO Process

Solid salt separation is a critical engineering design issue in the SCWO process. Although much of the research and process development in this area remain proprietary, salt separator requirements and general design concepts can be found in patents and published process descriptions (eg. Modell, 1985; Hong et al., 1989; Barner et al., 1991). In one proposed separator design (Hong et al., 1989), precipitated salts are redissolved in an aqueous solution at the bottom of the reactor, which is kept at a subcritical temperature. The brine solution is then removed using a pressure letdown valve. A filter is also placed on the effluent line to remove some of the entrained solids. Though this method is workable, several problems still persist, such as, corrosion by the brine solutions, accumulation of sticky salts on reactor walls, and clogging of down stream process lines by fine salt particulates. One unique separation method, which is currently under consideration, is the water-wall reactor (Barner et al., 1991). In this design, a subcritical water solution is used to flush the inner surfaces of the reaction vessel in the locations most prone to salt accumulation.

Some process separator design results have been published. Killilea and co-
Figure 2.5  Dissociation constant for NaCl in water in the limit of infinite dilution (Mesmer et al., 1988).
workers at Modar, Inc. have reported results of a project supported by NASA for studying the separation of inorganic salts from a SCWO reactor under microgravity conditions for possible use in treating waste water on long-term space missions (Killilea et al. 1988). Modar tested both an impingement/filter separator and a cyclone separator on a simulated metabolic waste stream. The impingement method, where solids were collected on a replaceable canister, was found to be more promising than cyclone separation. The cyclone was hindered by solid salt adhesion to the vessel walls, which led to eventual plugging of the unit. Unlike the cyclone, the impingement method took advantage of the inherent stickiness of the high temperature salts. Both a ceramic and a metal mesh filter were used to remove entrained salt particles in the supercritical water effluent from the impingement canister. Though successful, the tests ran for only a few hours, and some fine particles passed through the filters and escaped from the separator. The authors did not state the size of these fine particles.

Other researchers have encountered plugging problems in SCWO reactor/separator units. Dell'Orco and Gloyna (1991) used a vertical tube emptying into a pressure vessel for solids separation on simulated waste streams containing dissolved sodium salts. The effluent from the pressure vessel exited from a top port, which allowed solids to settle to the bottom. Although greater than 95% of the salts in the feed were sometimes removed, a large fraction of the salts remained accumulated on the walls of the vertical tube and pressure vessel as solids. This resulted in plugging during some runs which had feeds containing dissolve sodium sulfate. Dell'Orco and Gloyna also tested a hydrocyclone for removal of fine silica and zirconia particles from a supercritical water stream. They reported high removal efficiencies with the unit, but it was not tested with the much more sticky sodium salts.

In conclusion, salt formation, separation, and removal are integral and critical components of the SCWO process. Very little experimental data exist, and a solid theory explaining precipitation mechanisms is also lacking. Although considerable progress in SCWO salt separation techniques has been made in industry, a fundamental understanding of phase equilibria and solid salt formation in subcritical and supercritical water is needed to optimize performance of current designs and to facilitate the development of the next generation of salt separators.
Chapter 3.
Thesis Objectives and Approach

The primary objective of this research project has been to explore the relationship between phase behavior and precipitation mechanisms in salt-water systems at temperatures (up to 550°C), pressures (100 to 300 bar), and waste stream salt concentrations (up to 10.0 wt%) encountered in the SCWO process. In particular, to:

1) Correlate and evaluate existing thermodynamic models for the NaCl-H₂O system and test the applicability of other conventional approaches for modeling this system under extreme temperatures and pressure.

2) Perform isobaric phase equilibrium experiments on the model salt-water systems of NaCl-H₂O and Na₂SO₄-H₂O to observe phase transitions and verify the phase diagrams.

3) Measure vapor-phase solubilities of the model salts in supercritical water at temperatures and pressures of interest to the SCWO process.

4) Perform experiments to simulate the rapid precipitation of the model salts from supercritical water, thus determining formation mechanisms and providing particle size estimates.

5) Develop a computer model to simulate the mixing of a subcritical water jet with supercritical water.
6) Predict homogeneous nucleation rates and particle growth rates by diffusion limited kinetics and agglomeration by applying the classical theories to salt-water systems at supercritical conditions.

These objectives represent fundamental steps needed to characterize and understand salt formation occurring during the SCWO process. Sodium chloride and sodium sulfate were chosen as the model salts because they are both contained in metabolic waste and many industrial waste streams. An extensive thermodynamic database also exists for the sodium chloride-water system. The approach taken focuses on developing experimental techniques, since little information is available on the precipitation of salts from supercritical water. The theoretical objectives evolved mainly to aid in the interpretation of the experimental results.
Chapter 4.
Phase Equilibrium in Salt-Water Systems

Understanding salt formation during the supercritical water oxidation of aqueous waste first requires characterization of equilibrium phase and solubility relationships in salt-water systems at high temperatures and high pressures. At these extreme conditions, phase behavior is frequently complicated by two-phase, vapor-liquid regions, three-phase equilibrium points, and critical solution points. The conditions required for different phase equilibria are particularly important in the SCWO process near the reactor inlet where severe temperature and composition gradients exist. The general phase behavior of the two principal types of salt-water systems are described in Section 4.1. The two model binary salt-water systems of interest in this study, NaCl-H₂O and Na₂SO₄-H₂O, are described in Sections 4.2 and 4.3, respectively. Finally, the ternary system of the two model salts and water is discussed in Section 4.4.

4.1 General Phase Behavior

Phase equilibrium relationships in binary salt-water systems at high temperatures and pressures can be divided into two general categories (Morey, 1942 & 1957; Ravich, 1970; Valyashko, 1976, 1977 & 1981). Complications involving liquid immiscibilities or solid solutions, which may occur at temperatures and pressures out of the range of this study, will not be considered in this section. Table 4.1 lists examples of the two groupings of salts, designated here as Type I and Type II. In this study, the model Type I salt-water system is NaCl-H₂O, and the model Type II salt-water system is Na₂SO₄-H₂O.
Table 4.1 Examples of Salt-Water System Categories†

<table>
<thead>
<tr>
<th>Type I</th>
<th>Type II</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaCl</td>
<td>Na₂SO₄</td>
</tr>
<tr>
<td>KCl</td>
<td>K₂SO₄</td>
</tr>
<tr>
<td>LiCl</td>
<td>Li₂SO₄</td>
</tr>
<tr>
<td>NaNO₂</td>
<td>Na₂CO₃</td>
</tr>
<tr>
<td>KF</td>
<td>KLiSO₄</td>
</tr>
</tbody>
</table>

† Ravich, 1970; Valyashko, 1977

Figure 4.1 shows the pressure (P)-temperature (T), P-composition (x), and T-x projections of the general three-dimensional (P-T-x) phase diagram of Type I salt-water systems. In these systems, the solubility of the low volatility salt component (in both the liquid and vapor phases) continuously increases with temperature, and terminates at the triple point of the salt. This can be seen in the T-x projection of the general phase diagram (Figure 4.1). As shown in the P-T projection, the vapor pressure curve of saturated solutions goes through a maximum. In this case, saturation refers to three-phase equilibrium (vapor, liquid, and pure solid salt). The maximum is due to increased temperatures, which tend to increase the vapor pressure, and increased aqueous salt concentrations, which tend to lower the vapor pressure (Ravich, 1970). The critical curve is also continuous, and extends from the critical point of pure water to the critical point of the salt. For Type I systems, the three-phase curve does not intersect the critical solution curve (dashed lines in Figure 4.1). Thus, critical phenomena in the Type I systems is only present in unsaturated solutions (no solid salt present). A critical point occurs when the liquid and vapor phase compositions become equal.
Figure 4.1 Projections of P-T-x phase diagram for Type I salt-water systems (adapted from Morey, 1957).
The phase diagram projections for Type II systems are shown in Figure 4.2. For this type of system, the salt solubility falls to very low values as the critical temperature of water is approached, as shown in the T-x projection of Figure 4.2. As a result of these low liquid solubilities at high temperatures, the three phase saturation curve is intersected by the critical curve. Thus, critical phenomena is present in saturated solutions at two points (p and q in Figure 4.2), and there exists lower (T < p) and upper (T > q) two (vapor-liquid) and three (vapor-liquid-solid salt) phase regions. At temperatures between points p and q, only one fluid phase can coexist in equilibrium with solid salt (Ravich, 1970). Type II systems are also referred to as Type p-q systems (Ravich, 1966).

The phase behavior of ternary salt-water systems is very complicated, and requires three-dimensional T-x or P-x projections to illustrate the phase relationships. As with the binary systems, most of the experimental work on ternary systems was performed in Russia between 1940 and 1970. Ravich and Borovaya (1949) reviewed the results for the systems KCl-NaCl-H₂O, KCl-K₂SO₄-H₂O, NaCl-Na₂SO₄-H₂O, and KCl-KBr-H₂O. They found that Type I salts can greatly enhance the high temperature solubility of Type II salts. The ternary system of NaCl-KCl-H₂O has also been studied by Sterner et al. (1988).

The general phase behavior of ternary systems has been described by Valyashko in a series of papers (1971a, b, and c). He placed the ternary systems into three groups, which depended on the binary phase behavior of the individual salt-water systems. Thus, the ternary systems contained either two Type I salts, two Type II salts, or a Type I and Type II salt. When three-phase immiscibility regions were considered, many subsets of the three ternary system groups arose.

The basic generality of the salt-water systems at extreme conditions should allow conclusions based on model systems to be extended to other similar systems, provided the specific system characteristics, such as, the locations of the critical curve and the three-phase curve, are taken under consideration.
Figure 4.2 Projections of P-T-x phase diagram for Type II salt-water systems (adapted from Morey, 1957).
4.2 Type I System Example: NaCl-H₂O

The equilibrium phase behavior of the system NaCl-H₂O at high temperatures and pressures has been frequently researched in the past. This system is of great importance in the design of power plants and SCWO reactors for waste treatment (MODAR process), and in geochemical research. The most extensive studies of this system were conducted by Olander and Liander in 1950, and Sourirajan and Kennedy in 1962. Both investigators used thick walled, large volume vessels with both top and bottom sampling capabilities. Bischoff and Pitzer (1989) have recently published a compilation of vapor-liquid equilibrium in the NaCl-H₂O system to 500°C.

The three-phase line, where pure solid sodium chloride is in equilibrium with both vapor and liquid salt solutions, depends on temperature as shown in Figure 4.3. This is an example a monovariant equilibrium. Since the NaCl-H₂O system is Type I, the saturation pressure curve extends continuously from the water-salt eutectic point to the melting point of pure NaCl (800°C). The values shown in Figure 4.3 correspond to the saturation compositions of NaCl in the vapor and liquid phases, along with the saturation pressure of the system at any given temperature. There is a significant difference in the saturated vapor compositions between the data of the various researchers. The most recent study of Bischoff et al., (1986) seems to verify the early work of Olander and Liander (1950).

Figure 4.4 shows part of the critical curve for the NaCl-H₂O system. Here, a critical point refers those conditions which lead to a vapor and liquid phase with identical composition and other properties. With two components, two phases (vapor and liquid), and the added stoichiometric constraint of equal composition of the phases, the phase rule states that this is a monovariant equilibrium. Thus, the pressure and composition of the system are fixed for each temperature (Figures 4.4(a) and 4.4(b)). The curves shown in Figure 4.4 were calculated using empirical equations of Knight and Bodnar (1988), who fit their experimental data with polynomial equations. Knight and Bodnar (1988) used fluid inclusions to determine points on the NaCl-H₂O critical locus up to a temperature of 820°C (critical solution composition of 30 wt% NaCl). In principle, the NaCl-H₂O critical curve should terminate at the critical point of pure NaCl, which has not been
Figure 4.3 Three-phase equilibrium in NaCl-H₂O system (a) saturated vapor composition, (b) saturated liquid composition, (c) saturation pressure.
Figure 4.4  Liquid-vapor critical equilibrium in the NaCl-H₂O system: (a) lower portion of critical locus, (b) T-x relationship.
measured, but is estimated as 3900°C and 260 bar (Pitzer, 1984).

Figures 4.5 and 4.6 are isothermal pressure-composition phase diagrams for the NaCl-H₂O system at 450 and 550°C, respectively. The composition axis in the figures is shown as a log scale. In these figures, the vapor, liquid and fluid phases are two-component, and the solid phase is assumed to be pure NaCl. The critical point in these diagrams is located at the top of the vapor-liquid dome, and the three-phase point is represented as a horizontal line. There are no data on the effect of pressure on the solubility of NaCl in liquid water at constant temperature (dotted curve in Figures 4.5 and 4.6). Therefore, this phase boundary is only approximated. Above 500°C the data is very scarce. Since the compilation of Bischoff and Pitzer (1989) only extends to 500°C, the Pitzer-Tanger equation of state (PTEOS) (Pitzer and Tanger, 1988; Tanger and Pitzer, 1989) was used to predict the vapor-liquid dome at 550°C (see Figure 4.6). The PTEOS model may still be valid at these conditions, since at lower temperatures it does a good job of representing the compiled data of Bischoff and Pitzer (1989).

Figures 4.7 and 4.8 are isobaric temperature-composition slices of the NaCl-H₂O phase diagram at 250 bars and 300 bars, respectively. The experimental points shown in these figures were interpolated from the isothermal data of the referenced researchers. At 250 bar, the critical solution point occurs at approximately 387°C, and the three-phase temperature is around 450°C. The effect of temperature on the solubility of NaCl in liquid at constant pressure was estimated from the saturation solubility compilation of Linke (1958, solid circles and dotted curve in Figures 4.7 and 4.8).

The dashed curves in Figures 4.5 to 4.8 (vapor-phase solubilities) where generated by a model developed by Pitzer and Pabalan (1986), and do not represent experimental data. These predictions differ greatly from the data of Sourirajan and Kennedy (1962), who may have had problems with their analytic determination of the vapor-phase salt content (Bischoff et al., 1986). Solubility measurements and predictions for the NaCl-H₂O system are further discussed in Chapter 7.
Figure 4.5  Pressure-Composition NaCl-H₂O phase diagram at 450°C.
Figure 4.6 Pressure-Composition NaCl-H₂O phase diagram at 550°C.
Figure 4.7 Temperature-composition NaCl-H$_2$O phase diagram at 250 bar.
Figure 4.8 Temperature-composition NaCl-H₂O phase diagram at 300 bar.
4.3 Type II System Example: Na₂SO₄-H₂O

The system sodium sulfate and water displays Type II phase equilibrium behavior at high temperatures and pressures (Valyashko, 1977). The only extensive study of this system up to 600°C and 1500 bar was conducted by Ravich and Borovaya (1964). Phase boundaries were determined by examining breaks in P-T and P-V curves.

Figure 4.9 shows how the saturated vapor pressure and saturated liquid-phase composition varies with temperature on the monovariant three-phase equilibrium curve. Saturated liquid compositions are shown for the lower three-phase region, and the sodium sulfate percentage sharply falls as the temperature increases. The first intersection of the three-phase curve and the critical solution curve occurs at a temperature and pressure very close to the critical point of pure water, 374°C and 221 bars (point p in Figure 4.9), and the second intersection occurs at approximately 440°C and 1160 bars (point q in Figure 4.9) (Ravich and Borovaya, 1964). At temperatures above 440°C, the upper three-phase region appears. In this region, the liquid salt composition reaches 50% at 450°C and 70% at 500°C (Ravich and Borovaya, 1964). Very little data exists on composition of the saturated vapor phase for the three-phase equilibrium in the Na₂SO₄-H₂O system. Ravich and Borovaya report it to be negligible until pressures exceed 300 bar. The saturated vapor composition must equal the liquid composition in the presence of solid salt at points p and q, since a critical solution exists at these points.

Figure 4.10 shows isothermal slices of the phase diagram of the Na₂SO₄-H₂O system at temperatures of 350°C, 400°C, and 500°C. Since very little data exist for this system, most of the phase boundaries have been qualitatively drawn. The isothermal slice at 350°C (Figure 4.10(a)) intersects the lower two- and three-phase region in the system. The three-phase equilibrium at 350°C occurs at approximately 164 bars. The isothermal slice at 400°C (Figure 4.10(b)) is between the two critical end points (p and q) shown in Figure 4.9. Thus, there can only be one supercritical solution in equilibrium with solid salt (Ravich, 1970). Figure 4.10(c) shows the pressure-composition phase diagram at 500°C. This temperature is above point q, and is in the upper two- and three-phase region.
Three-phase equilibrium in the Na$_2$SO$_4$-H$_2$O system: (a) saturated liquid composition, (b) saturation pressure.
Figure 4.10  Pressure-composition Na$_2$SO$_4$-H$_2$O phase diagram: (a) 350°C, (b) 400°C, (c) 500 °C.
Figure 4.11 shows the lower portion of an isobaric slice of the Na$_2$SO$_4$-H$_2$O phase diagram at a pressure of 250 bars. At this pressure, the system shows much different phase behavior than the NaCl-H$_2$O system. The points on this curve were interpolated from the data of the indicated authors. A key feature of the phase diagram is the rapid fall-off in solubility as the critical point of pure water is approached. At a temperature of 500°C, there is a large discrepancy in the interpolated vapor solubilities of Martynova and Morey. Since the three-phase equilibrium point for this pressure is approximately 830°C (see Figure 4.9), a vapor-liquid two-phase region should appear at temperatures somewhat below 830°C.

4.4 Ternary System Example: NaCl-Na$_2$SO$_4$-H$_2$O

Many mixed salt solutions show interesting behavior at high temperatures and pressures. The solubility of many Type II salts greatly increases in solutions of Type I salts at temperatures and pressures where they are only slightly soluble in pure water (Ravich, 1970). For the NaCl-Na$_2$SO$_4$-H$_2$O system, studies by two groups have confirmed this statement.

The solubility of sodium sulfate in aqueous solutions of NaCl at temperature up to 350°C was examined by Schroeder and co-workers, who used a nickel autoclave with an internal sample chamber (Schroeder et al., 1935). These data are an example of a three-phase equilibrium between three component vapor and liquid phases, and a pure Na$_2$SO$_4$ solid phase. The number of degrees of freedom for this system is two. Schroeder’s results are shown in Figure 4.12, which gives the solubility of Na$_2$SO$_4$ in the liquid phase as a function of NaCl liquid phase composition at various temperatures. In Schroeder’s experiments, the vapor phase compositions and saturation pressures where not measured. At lower temperatures, the effect of NaCl is to decrease the sodium sulfate solubility from its pure water value. At 300°C, the effect is decreased, and at 350°C the effect is reversed. Thus, sodium chloride tends to enhance the solubility of sodium sulfate at high temperatures.
Figure 4.11 Temperature-composition $\text{Na}_2\text{SO}_4$-$\text{H}_2\text{O}$ phase diagram at 250 bar

- Morey and Hesselgesser (1951)
- Ravich and Borovaya (1964)
- Martynova and Samoilov (1962), Martynova (1976)
Data from Schroeder et al. (1935)

Figure 4.12  Solubility of $\text{Na}_2\text{SO}_4$ in aqueous solutions of $\text{NaCl}$ from 150 to 350 °C.
Ravich and his co-workers in the USSR studied phase equilibria in the NaCl-Na$_2$SO$_4$-H$_2$O system at temperatures up to 600°C and pressures up to 1500 bars (Ravich et al., 1951 & 1953). They used an autoclave (filled partially with mercury) to determine phase boundaries by locating breaks in P-T and P-V curves. For some low temperature runs, a visual method (using filled silica tubes) was used to determine salt solubilities, with the pressure being obtained from autoclave experiments conducted in parallel at the same conditions. Ravich’s group performed similar experiments as Schroeder’s group, and examined sodium sulfate solubility in solutions of NaCl at temperatures up to 450°C. Due to the experimental technique used, data were collected at varying temperatures. Figure 4.13 shows the results using a three-dimensional spline surface fit to their 38 experimental data points. Consistent with the tests of Schroeder et al., their measurements indicate that the solubility of sodium sulfate in the liquid phase at high temperatures increases as the liquid phase sodium chloride concentration increases (Figure 4.13(a)). The corresponding vapor pressures for the three-phase equilibrium (Figure 4.13(b)) was also measured by Ravich and co-workers, and these pressures are very low compared to the pressures required to form highly concentrated saturated liquid Na$_2$SO$_4$ solutions in the binary system with water.

Ravich’s group also studied the eutonic solutions in the system NaCl-Na$_2$SO$_4$-H$_2$O (see Figure 4.14). A eutonic solution refers to a four-phase equilibrium between saturated, three-component liquid and vapor phases, and two pure solid salt phases. In a three-component eutonic solution, there is one degree of freedom. As seen in Figure 4.14(a), sodium sulfate concentrations as high as 60 wt% in the liquid phase were found at 570°C and moderate pressures (approximately 200 bar). For the binary system of Na$_2$SO$_4$-H$_2$O, pressures of approximately 1300 bars are required to form concentrated liquid sodium sulfate solutions at a temperature of 500°C (see Figure 4.10(c)). For comparison, the saturation pressures for pure water and the two binary salt-water systems are also shown in Figure 4.14(b). Only the lower portion of the Na$_2$SO$_4$-H$_2$O saturation curve is shown, and it falls on top of the pure water saturation curve. The ternary system curve in Figure 4.14(b) again signifies the high liquid-phase solubility of Na$_2$SO$_4$ in NaCl containing brines, since the saturation pressure in the eutonic system is much lower than the binary NaCl-H$_2$O saturation pressure curve (Ravich et al., 1953).
Figure 4.13 Solubility of Na$_2$SO$_4$ in aqueous solutions of NaCl: (a) liquid-phase compositions, (b) corresponding vapor pressures (data from Ravich et al., 1953).
Figure 4.14  Eutonic solutions in the NaCl-Na₂SO₄-H₂O system. (a) saturated liquid composition (b) saturation pressure curve (pure water and binary salt-water curves are shown for comparison).
Using the binary data for the NaCl-H2O and Na2SO4-H2O systems, and the limited data for the NaCl-Na2SO4-H2O system, a qualitative description of the phase behavior in the ternary system at a pressure relevant to the SCWO process can be formed. Figure 4.15 shows isothermal slices of the NaCl-Na2SO4-H2O phase diagram at 250 bar (adapted from unpublished work of Glenn Hong, Modar Inc., Natick, MA). The shaded regions in these figures represent single phase three-component liquid (L) or vapor (V) solutions. The solid phases are either pure NaCl (S_A) or pure Na2SO4 (S_B).

An important feature of the triangular, isothermal slices shown in Figure 4.15, is the liquid brine compositions. As the temperature increases, the amount of Na2SO4 in the liquid phases also increases. Since no other data exist, the composition of the liquid in equilibrium with solid NaCl and Na2SO4, L-S_A-S_B, at the various temperatures was taken from the eutonic curve, L-V-S_A-S_B, of Ravich and Borovaya (1964). The error introduced in this approximation should be small, since the liquid composition should not be too pressure dependent. In the NaCl-Na2SO4-H2O system, a eutonic solution does not exist at a pressure of 250 bar (Ravich et al., 1953).

In the triangular temperature slices of 400 to 550°C, the vapor-phase compositions contain very low levels of salt. To illustrate this point, the upper corners of the 450 and 550°C slices have been expanded. Also, at higher temperatures, sodium chloride-sodium sulfate melts should appear. The NaCl-Na2SO4 eutectic point occurs at 628°C, with a composition of 31 wt% NaCl and 69 wt% Na2SO4 (Ravich et al., 1953).
Figure 4.15 Isothermal slices of model ternary system phase diagram at 250 bar.
Chapter 5.

Modeling of Phase Equilibrium
from Sub- to Supercritical Conditions

Theoretical modeling of the shock crystallization of salts in supercritical water requires thermodynamic relationships in salt-water systems at both subcritical and supercritical conditions. This includes the prediction of phase boundaries, stability limits, and densities of the stable phases. The complex nature of salt-water systems in both the subcritical and supercritical temperature range leads to difficulties in finding suitable thermodynamic models. Validated thermodynamic relationships for this wide range of conditions exist only for the NaCl-H\textsubscript{2}O system, and they are reviewed in Section 5.1. Attempts to apply existing activity coefficient models and a cubic equation of state to the NaCl-H\textsubscript{2}O system at extreme temperatures and pressures are described in Sections 5.2 and 5.3, respectively. The concluding Section 5.4 discusses modeling of high temperature vapor-liquid regions in salt-water systems using the Pitzer-Tanger equation of state.

5.1 Review of NaCl-H\textsubscript{2}O Thermodynamic Models

The following two sections describe several thermodynamic models for the sodium chloride-water system for both aqueous solutions with "liquid-like" densities and fluid solutions with "vapor-like" densities. Recently, Pitzer and Tanger (1988) have developed a theoretically based equation of state for vapor-liquid equilibrium calculations, and their model is discussed in Section 5.4. Characteristic of most of the NaCl-H\textsubscript{2}O thermodynamic models is a strong temperature and/or density dependence of the fitted parameters. This is unavoidable, due to the highly non-ideal nature of the system.
5.1.1 High-Density Aqueous Solution Models

High-density, aqueous sodium chloride solutions or brines exist at temperatures from ambient to the melting point of the salt. The ability to predict the thermodynamic and physical properties of these solutions is important in the design of the SCWO process. Brine solutions can exist near the reactor inlet where a salt containing waste stream is injected and at the bottom of the reactor where a low temperature section may be used to redisolve the precipitated salts in aqueous solution for removal from the reactor.

Potter and Brown (1976)

In this study, the authors used empirical relationships to regress experimental aqueous NaCl solution density data. The developed equations predict the volumetric properties of aqueous sodium chloride solutions from 0 to 500°C and pressures up to 2000 bars. Salt concentrations range from infinite dilution to vapor-saturated values up to about 8.0 molal (32 wt%). Potter and Brown used simple polynomial expansions in molality and temperature for their density correlations. For temperatures below 100°C, where high accuracy experimental data exists (±10⁻⁶ to ±10⁻⁴ g/cm³), the following equation was chosen,

\[
\rho = \frac{1000 \rho_w + M_2 m \rho_w}{1000 + A_0 m \rho_w + B_0 m^{3/2} \rho_w + C_0 m^2 \rho_w}
\]  (5.1)

where, \(\rho\) is the density of the solution, \(\rho_w\) is the density of pure water, \(m\) is the molality of NaCl (moles per kilogram water), \(M_2\) is the molecular weight of NaCl, and \(A_0, B_0\) and \(C_0\) are temperature dependent, fitted empirical constants. At temperatures above 100°C, the experimental data are less accurate (±0.001 to ±0.005 g/cm³), and the following simpler equation was used,

\[
\rho = A_1 + B_1 m^{1/2} + C_1 m
\]  (5.2)

where \(A_1, B_1\) and \(C_1\) are temperature and pressure dependent parameters. Equations (5.1) and (5.2) can be used to predict solution density as a function of molality at constant pressure and temperature. To correlate volumetric properties as a function of temperature
at constant molality and pressure, a polynomial equation was used,

\[ \rho = A + BT + CT^2 \tag{5.3} \]

where T is temperature in °C, \( \rho \) is solution density in g/cm\(^3\), and A, B and C are empirical constants. Figure 5.1 shows the densities predicted by equation (5.3) for a pressure of 250 bar and three salt concentrations. The constants used in the calculations are also listed in Figure 5.1. These values were interpolated from a table of constants for various molalities and pressures (Potter and Brown, 1976). At higher temperatures, the density curves shown in Figure 5.1 will intersect the vapor-liquid boundary.

*Haas, 1976*

Haas developed a series of empirical equations to represent a preliminary "steam tables" for vapor-saturated NaCl-H\( _2\)O solutions (i.e. boiling brines). The equations are valid between 80 and 325 °C up to saturation compositions. Correlations are presented for calculating density, vapor pressure, enthalpy, entropy and partial molar properties of both the liquid and vapor phases. A total of 11 equations using 64 fit parameters were used.

*Rogers and Pitzer, 1982; Pitzer et al., 1984*

Pitzer and co-workers used an extended Debye-Hückel equation to model aqueous NaCl solutions with liquid-like densities, where the solvent power of water is high enough to fully dissociate the salt. Semi-empirical equations predict the thermodynamic properties of aqueous sodium chloride solutions for temperatures from 0 to 300 °C, pressures up to 1000 bar, and salt compositions from 0 to 6 molal (26 wt%). The model can also be extrapolated with reduced accuracy to saturation molalities. The equations used for excess Gibbs free energy of solution per kilogram of solution were,

\[ \frac{1000 G^\text{EX}}{n_w M_w R T} = -A_\phi \left( \frac{4I}{1.2} \right) \ln (1 + 1.2I^{1/2}) + 2 (m^2B + 2m^3C^\phi) \tag{5.4} \]
Figure 5.1  Densities of aqueous sodium chloride solutions predicted by the empirical equation of Potter and Brown (1976). Pure water density curve from Haar et al. (1984).
\[ B = \beta^{(0)} + 2 \beta^{(1)} \frac{[1 - (1 + 2I^{1/2}) \exp(-2I^{1/2})]}{4I} \] (5.5)

where \( M_w \) is the molecular weight of water, \( \Lambda_v \) is the Debye-Huckel constant for osmotic coefficients on a log e basis (temperature dependent), \( I \) is the ionic strength (equal to \( m \) for NaCl), \( \beta^{(0)}, \beta^{(1)}, \) and \( C^* \) are fit parameters (T and P dependent). The first term in equation (5.4) describes the long-range electrostatic interactions in a Debye-Huckel framework. The remaining two terms describe short-range interactions between two and three ions, and indirect solvent forces. The standard states are pure liquid for water and ideal one molal solution for NaCl (both at the temperature and pressure of the solution). The Haar-Gallagher-Kell (HGK) equation of state was used for the thermodynamic properties of pure water (Haar et al., 1984). Activity coefficients and heat capacities can also be calculated with Pitzer's model.

**Pitzer and Li (1983)**

For higher temperatures, Pitzer and Li developed another semi-empirical model for aqueous sodium chloride solutions. This model is valid from 100 to 550 °C, to 1000 bars, and to saturation compositions. The free energy model contains one Margules term \( (w x_1 x_2) \) and a Debye-Huckel term, and again uses the HGK equation of state for the pure water,

\[ \frac{\Delta G_{\text{mix}}}{(n_1 + 2n_2)RT} = x_1 \ln x_1 + x_2 \ln x_2 + w x_1 x_2 - \left( \frac{4 A_x I}{a} \right) \ln \left( \frac{1 + a I^{1/2}}{1 + 0.7 a} \right) \] (5.6)

Here, \( n_i \) and \( x_i \) are the moles and mole fractions of the components, respectively, and subscript 1 denotes water and 2 denotes NaCl. \( A_x \) is the Debye-Huckel parameter on a mole fraction basis, and \( w \) is a temperature and pressure dependent Margules parameter. Though this equation is simple to use, it is limited to water densities above 0.75 g/cm³, which assures that NaCl is fully dissociated.
5.1.2 Low-Density Fluid Models

In steam and low-density supercritical water, salts are only slightly dissociated. The ionic constant of NaCl in water at the bulk reactor conditions prevalent in the SCWO process is over ten orders of magnitude less than its room temperature value, as was shown in Figure 2.5 (Mesmer et al., 1988). Though these low-density fluid phases exist at temperatures above the critical point of pure water, they are typically referred to as vapor phases, since high-density fluid phases also exist at these conditions (see Section 4.2). A simple solvation model for regressing solubility data for salts in sub- and supercritical water vapor is described in Section 7.2, while a more complicated model is discussed below.

Pitzer and Pabalan, 1986

This model is based on the statistical mechanics theory of a binary imperfect gas, and it predicts the composition of NaCl in a vapor phase which is in equilibrium with solid NaCl. No dissociation of NaCl is considered. The model is valid up to the three-phase saturation pressure for temperatures to 550°C, and can be used to predict NaCl vapor solubilities in regions where accurate experimental data are not available.

The equation of state for a two-component imperfect gas can be written as (Hill, 1960);

\[
\frac{P}{k_B T} = z_1 + z_2 + b_{2,0} z_1^2 + b_{1,1} z_1 z_2 + b_{0,2} z_2^2 + \ldots \tag{5.7}
\]

\[
\rho_1 = z_1 + \sum_{j=2}^\infty j b_{1,j} z_1^j + \ldots \tag{5.8}
\]

\[
\rho_2 = z_2 + \sum_{j=1}^\infty b_{2,j} z_1^j z_2 + \ldots \tag{5.9}
\]

where \(z_i\) is a fugacity of component \(i\) (defined so \(z_i \rightarrow \rho_i\) as \(\rho \rightarrow 0\)), \(\rho_i\) is the density of component \(i\) (molecules per unit volume), while the subscripts 1 and 2 denote water and NaCl, respectfully. The traditional fugacity of an imperfect gas, \(f_i\), is defined such that \(f_i \rightarrow \rho_i\) as \(\rho_i \rightarrow 0\), and is equal to \(z_i\) multiplied by the factor \(k_B T\). In equations (5.8) and
(5.9), \( b_{j,0} \) and \( b_{j,1} \) are cluster integrals which represent the interparticle potentials between a cluster of \( j \) water molecules and 0 or 1 NaCl molecules, respectively. These terms are quite complicated, for example, \( b_{j,1} \) is given by,

\[
b_{j,1} = \int \cdots \int \left\{ \exp \left[ -u_{j,1}(r,\omega_1,\omega_2)/kT \right] - 1 \right\} 4\pi r^2 \partial r \partial \omega_1 \partial \omega_2 \tag{5.10}
\]

where \( u_{j,1} \) is the interaction potential between a \( \text{H}_2\text{O} \) molecule and a NaCl molecule, which is a function of the distance between the molecules, \( r \), the angle of orientation of \( \text{H}_2\text{O}, \omega_1 \), and the angle of orientation of NaCl, \( \omega_2 \). The integral \( b_{j,1} \) can be regarded as equilibrium constants for the hydration reaction;

\[
\text{NaCl}(v) + j\text{H}_2\text{O}(v) \Leftrightarrow \text{NaCl} \cdot j\text{H}_2\text{O}(v) \tag{5.11}
\]

In Pitzer's reformulation, the hydration reaction was first written as series of successive water molecule additions,

\[
\text{NaCl} \cdot (j-1)\text{H}_2\text{O} + \text{H}_2\text{O} \Leftrightarrow \text{NaCl} \cdot j\text{H}_2\text{O} \tag{5.12}
\]

The equilibrium constant for this reaction, \( K_j \), is related to the cluster integral, \( b_{j,1} \), by;

\[
b_{j,1} = \prod_{i=1}^{j} K_i \tag{5.13}
\]

Using this relationship, Pitzer expressed the density of NaCl molecules in the vapor phase, equation (5.9), as;

\[
\sum_{\text{C}} \frac{C}{C_o} = 1 + K_1 f_1 + K_1 K_2 f_1^2 + K_1 K_2 K_3 f_1^3 + \ldots \tag{5.14}
\]

where \( \sum C \) is the concentration of all NaCl containing species, \( C_o \) is the concentration of anhydrous NaCl gas (obtained from properties of pure NaCl given in JANAF tables), and \( f_1 \) is the fugacity of pure water calculated from the HGK equation of state (Haar et al., 1984). Pitzer used experimental solubility data to determine the \( K \) values as a function of temperature and hydration number (\( j \) up to 30 in 5 equal-spaced intervals). As shown in Section 7.1, the model adequately represents much of the available experimental data, which are highly scattered.
5.2 Extension of Condensed Phase Activity Coefficient Models

The aqueous solution models described above for the NaCl-H₂O system all do a respectable job in representing the available experimental data. However, these models tend to be complicated to use, need significant amounts of data to fit parameters, and require modifications and fitting of additional parameters to be applied to the mixed salt systems which prevail during the SCWO of metabolic wastes. Also, very little high-temperature experimental data exist for other salt-water systems. It would be advantageous then, to be able to extend existing electrolyte activity coefficient models to higher temperature and pressure conditions.

5.2.1 Solubility Calculations

Typically, aqueous systems of both single salts and mixed salts are modeled at temperatures below 100°C and moderate pressures using an activity coefficient approach. Three of the more successful models were used in predicting the solubility of sodium chloride in liquid water as one nears supercritical conditions. Under these conditions, an NaCl saturated liquid phase is in equilibrium with a saturated, dilute vapor phase, and pure solid salt. The models developed by Meissner and Tester (1972), Pitzer (1979), and Chen and Evens (1986) were tested. One notes that all three models were extended beyond their recommended temperature and concentration limits.

In the solubility calculations, sodium chloride was assumed to be completely dissociated, which is a good assumption in high density aqueous solutions of NaCl (water density above 0.75 gm/cm³) (Pitzer and Li, 1983). The dissociation reaction for sodium chloride is thus,

\[ \text{NaCl (s)} \leftrightarrow \text{Na}^+ \text{ (aq)} + \text{Cl}^- \text{ (aq)} \]  

(5.15)

The dissociation constant or solubility product for this reaction, which involves a (1:1) strong electrolyte, is,

\[ K_{sp} = \frac{a_{+}a_{-}}{a_{s}} = \frac{\gamma_{+}m_{+}\gamma_{-}m_{-}}{m_{o}^{2}} \]  

(5.16)
where $a$ is the activity, $m$ is the molality, $m_0$ is the reference state, and $\gamma$ is the activity coefficient on a molality basis. The subscripts $+, -,$ and $s$ denote Na$^+$ ions, Cl$^-$ ions, and pure solid salt, respectively. In the derivation of equation (5.16), it was assumed that the solid phase is pure with an activity of one. For the aqueous ions, the reference state is an ideal one molal solution of the ion in water at the temperature and pressure of the system. Thus, the equilibrium constant, $K_{sp}$ is a function of temperature and pressure. Since it is not possible to experimentally evaluate the activity coefficient for a single ion while keeping a solution electronically neutral, a mean ionic activity coefficient ($\gamma_s^\infty$) and a mean ionic molality ($m_s^\infty$) are typically used (Zemaitis et al., 1986). For NaCl (a 1:1 electrolyte), these quantities are,

$$\gamma_s^2 = \gamma_+ \gamma_- \quad \text{and} \quad m_s^2 = m_+ m_-$$  \hspace{1cm} (5.17)

With these definitions and a one molal standard state, equation (5.15) becomes,

$$K_{sp}(T,P) = \gamma_s^2 m_s^2$$  \hspace{1cm} (5.18)

For a 1:1 electrolyte, $m_s$ is also equal to $m$ (the molality of the saturated solution).

The solubility product, $K_{sp}$, was estimated by two different methods. It was first determined using standard thermodynamic relationships and tabulated constants given by Zemaitis et al. (1986). Free energies of formation for the species in equation (5.15) were used to calculate the equilibrium constant at 25$^\circ$C and 1 bar, which was then determined at the desired temperatures and pressures by assuming constant species heat capacities and partial molar volumes. The second method used to determine $K_{sp}$ relied on standard Gibbs energy of solution correlated by Pitzer et al. (1984), with $K_{sp} = \exp(-\Delta G_s^\infty / RT)$. Table 5.1 compares the calculated $K_{sp}$ values from the two methods. The thermodynamic values deviate from the experimental ones by a factor of about two at the highest temperature of 300$^\circ$C. This large deviation is most likely due to the assumption of constant heat capacity for the reaction. In the solubility calculations of this section, the experimental $K_{sp}$ values were used. If similar calculations are made for other salts, where no experimental values are available, theories for the temperature dependence of the species heat capacities could be used to improve the thermodynamic estimates.
Table 5.1  Dissociation constant of NaCl in high temperature brines.

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Pressure* (bar)</th>
<th>$m_{\text{sat}}$ # (molal)</th>
<th>$K_{sp}$ theoretical*</th>
<th>$K_{sp}$ experimental**</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>1</td>
<td>6.10</td>
<td>30.61</td>
<td>30.78</td>
</tr>
<tr>
<td>25</td>
<td>1</td>
<td>6.15</td>
<td>--</td>
<td>38.23</td>
</tr>
<tr>
<td>50</td>
<td>1</td>
<td>6.27</td>
<td>40.38</td>
<td>41.21</td>
</tr>
<tr>
<td>75</td>
<td>1</td>
<td>6.46</td>
<td>--</td>
<td>40.57</td>
</tr>
<tr>
<td>100</td>
<td>1</td>
<td>6.74</td>
<td>35.08</td>
<td>37.52</td>
</tr>
<tr>
<td>125</td>
<td>2.9</td>
<td>6.93</td>
<td>--</td>
<td>32.81</td>
</tr>
<tr>
<td>150</td>
<td>4.8</td>
<td>7.22</td>
<td>24.28</td>
<td>27.23</td>
</tr>
<tr>
<td>175</td>
<td>6.7</td>
<td>7.63</td>
<td>--</td>
<td>21.48</td>
</tr>
<tr>
<td>200</td>
<td>10.8</td>
<td>7.91</td>
<td>14.80</td>
<td>16.02</td>
</tr>
<tr>
<td>225</td>
<td>17.9</td>
<td>8.37</td>
<td>--</td>
<td>11.21</td>
</tr>
<tr>
<td>250</td>
<td>26.4</td>
<td>8.85</td>
<td>8.42</td>
<td>7.32</td>
</tr>
<tr>
<td>275</td>
<td>41.0</td>
<td>9.51</td>
<td>--</td>
<td>4.34</td>
</tr>
<tr>
<td>300</td>
<td>56.8</td>
<td>10.2</td>
<td>4.63</td>
<td>2.28</td>
</tr>
</tbody>
</table>

* For temperatures above 100°C, the system pressure corresponds to the saturation pressure (values interpolated from Keevil, 1942).

# from Linke (1958)

* Calculated using the relationships and constants from Zemaitis et al., 1986 (see text).

** Calculated using $\Delta G^\circ$, values determined by Pitzer et al., 1984 (see text).
Since the mean ionic activity coefficient depends on composition, equation (5.18) was solved iteratively for the solubility at each temperature and corresponding saturation pressure. The activity coefficient models tested are described in the following section.

5.2.2 Activity Coefficient Models

As mentioned above, three activity coefficient models were tested. Pitzer's general activity coefficient model is an extended Debye-Huckel equation with added terms to account for the effect of ionic strength on long range forces (Pitzer, 1979). For a single strong (1:1) electrolyte, Pitzer's model may be written as;

$$\ln \gamma_x = -A_\phi \left[ \frac{\sqrt{I}}{1+1.2I} + 1.67 \ln (1+1.2\sqrt{I}) \right] + m_B + m_C^2 \quad (5.19)$$

where, $A_\phi$ is the Debye-Huckel parameter, I is the ionic strength of the solution (equal to $m_x$ for NaCl), and B and C are empirical parameters, which are strong functions of temperature. The Debye-Huckel parameter is also a function of temperature. Pitzer's NaCl parameters for his model are valid up to 300°C and a maximum molality of 6.0 (Zemaitis et al, 1986).

The second model tested was that of Chen and Evans (1986). Their excess Gibbs free energy model was developed by applying local composition concepts to electrolyte systems. They proposed that the activity coefficient could be written as sum of long and short range force effects,

$$\ln \gamma_x = \ln \gamma_x^{LR} + \ln \gamma_x^{SR} \quad (5.20)$$

For the long range contributions, the Pitzer Debye-Huckel equation was used, and for the short range contributions the nonrandom two-liquid (NRTL) theory of Renon and Prausnitz (1968) was used. For a strong electrolyte, the model requires two binary interaction parameters. For the NaCl-H_2O system at low concentrations, these parameters are a weak function of temperature in the range of 0 to 300°C (Mock et al., 1982). In the solubility calculations, constant values of the parameters, as given by Zemaitis et al. (1986), were used. Therefore, the only temperature dependence included in the
predictions using Chen's model was in the Debye-Huckel parameter, which appears in the long-range force term. The same temperature dependence for $A_e$ was used in the calculations involving Chen's and Pitzer's models (Zemaitis et al., 1986). For NaCl, Chen and Evans' room temperature interaction parameters are valid for a maximum molality of 6.0.

The final model tested was that of Meissner and associates. Meissner and Tester (1972) showed that by plotting the reduced activity coefficient, $\Gamma$, versus the ionic strength, a family of curves results (one for each different salt). The reduced activity coefficient is defined as,

$$\Gamma = \frac{1}{\gamma_z}$$

(5.21)

where $z_+$ and $z_-$ are the absolute charge number of the cation and anion, respectively. Empirical relationships were later developed, which expressed the reduced activity coefficient as a function of ionic strength using one parameter, $q$ (Kusik and Meissner, 1978). Meissner (1980) suggested the following simple equation for the temperature dependence of $q$,

$$q(T) = q(25^\circ C) [1-0.0027(T-25)]$$

(5.22)

where $T$ is in $^\circ C$. The empirical equations relating $q$ to $\gamma_z$, and values of $q$ for many salts, including NaCl, are given by Kusik and Meissner (1978). Meissner's model was also fit to NaCl concentrations up to 6.0 molal.

Computer codes were written for the three models to predict the mean ionic activity coefficients as a function of temperature and were validated by comparing calculated $\gamma_z$ values to listed values given by Zemaitis et al. (1986).

5.2.3 Solubility Predictions

Figure 5.2 shows the prediction of NaCl solubility in saturated aqueous solutions using the three models as compared to experimental solubility values (in molality units) taken from Linke (1958). Both Meissner's and Chen's models show significant deviations from the experimental values above temperatures of 150$^\circ C$. This is most likely due to
Figure 5.2  Predictions of tested activity coefficient models for the saturated liquid composition in the NaCl-H₂O system.
the small temperature correction incorporated in the models, which were originally
developed to be used at moderate temperatures. Pitzer’s model adequately predicts the
solubility up to a temperature of 250°C; primarily as a result of the elaborate temperature
dependence of the model’s fitted parameters. All three models would require significant
modifications and/or additional parameter dependencies to allow prediction of mixed
electrolyte solubilities in aqueous solutions at extreme temperatures and pressures.

5.2.4 ASPEN Simulations

Several simulations using the ASPEN Plus process simulator (Aspen Technology
Inc., Cambridge, MA) were performed to verify the solubility predictions discussed above.
Both Chen’s and Pitzer’s models are part of ASPEN’s electrolyte property model
capabilities. Figure 5.3 illustrates the flow sheet used in the simulations. First, a sodium
chloride solution is fed to an evaporator where salt is precipitated, and then removed
using a filter. The saturated aqueous stream from the filter gives the desired solubility
in molality units, since it contains 1000 grams of water.

A sample ASPEN input file is shown in Table 5.2. The file shown is for a
simulation at 300°C using the model of Chen and Evans. To assure a valid comparison,
the same value of the solubility product used in this study was also used for the ASPEN
Plus simulations. The results of runs at three temperatures are summarized in Table 5.3.
ASPN’s solubility predictions using Chen’s model verifies this studies calculations at
all three temperatures. Due to operational difficulties encountered at the time, Pitzer’s
model predictions could only be verified at 25°C.

5.3 Fluid Phase Modeling Using a Cubic Equations of State

Cubic equations of state are frequently used to model the phase behavior of
supercritical fluid and solute systems (McHugh and Krukonis, 1986). In low density fluid
phases, salts in aqueous solutions remain in their molecular state due to the non-polar
nature of supercritical water. For these vapor-like phases, a PTVN volumetric equation
of state approach may provide a satisfactory model for phase equilibrium estimates. The
Peng-Robinson equation of state, PREOS, (Peng and Robinson, 1976) was used to model
the vapor phase of saturated solutions of sodium chloride over temperature range of 300
Figure 5.3  ASPEN flow sheet used for the sodium chloride solubility simulations.
Table 5.2  Sample ASPEN input file for determining the solubility of NaCl at high temperatures.

TITLE 'NACL SOLUBILITY - TEMPERATURE = 300 C'
DESCRIPTION "CHEN'S EQ. FOR MEAN MOLAL ACTIVITY COEF."
IN-UNITS SI TEMP=C PRES=ATM
COMPONENTS H2O H2O/NA+ NA+/CL- CL-/NACL NACL
DATABANKS AQUEOUS/SOLIDS
PROPERTIES SYSOP15S CHEMISTRY=NACL
;
CHEMISTRY NACL
   PARAM MOLAL=1
   SALT NACL NA+ 1/CL-  1
   ;
   K-SALT = LN(K_sp)
   ;
   K-SALT NACL 3.64357  ; AT 25 C
   K-SALT NACL 2.6905   ； AT 200 C
   K-SALT NACL 0.82418  ； AT 300 C
;
PROP-SET P1 GAMMA PHASE=L
STREAM-REPORT
   SUPPLEMENTARY 1 MOLEFLOW PROPERTIES=P1 INCL-STREAMS=SLURRY
PROP-DATA                     ; CHEN METHOD
   IN-UNITS SI
   PROP-LIST GMELCC
   BPVAL NA+ CL-  8.885
   BPVAL CL- NA+  -4.549
;
FLOWSHEET
   BLOCK EVAP IN=FEED OUT=WATER SLURRY
   BLOCK FILT IN=SLURRY OUT=AQSOUL SOLID
STREAM FEED TEMP=300. VFRAC=0
   MOLE-FLOW H2O 555.25 / NA+ 40/ CL- 40
;
BLOCK EVAP SEP
   PROPERTIES SYSOP15S CHEMISTRY=NACL
   MOLE-FLOW STREAM=WATER COMPS=H2O FLOWS=499.72
   FLASH-SPECS SLURRY TEMP=300. VFRAC=0
   FLASH-SPECS WATER TEMP=300. VFRAC=1
BLOCK FILT SEP
   FRAC STREAM=SOLID COMPS=H2O NA+ CL- NACL &
   FRACS=0 0 0 1
   FLASH-SPECS SOLID NPHASE=1 PHASE=3
Table 5.3 Results of ASPEN simulations (NaCl solubility in molal units).

<table>
<thead>
<tr>
<th></th>
<th>Temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>25</td>
</tr>
<tr>
<td>Experiment Values</td>
<td>6.15</td>
</tr>
<tr>
<td>(Linke, 1958)</td>
<td></td>
</tr>
<tr>
<td>Chen’s Model</td>
<td>6.34</td>
</tr>
<tr>
<td>(this study)</td>
<td></td>
</tr>
<tr>
<td>Chen’s Model</td>
<td>6.34</td>
</tr>
<tr>
<td>(ASPEN)</td>
<td></td>
</tr>
<tr>
<td>Pitzer’s Model</td>
<td>6.16</td>
</tr>
<tr>
<td>(this study)</td>
<td></td>
</tr>
<tr>
<td>Pitzer’s Model</td>
<td>6.14</td>
</tr>
<tr>
<td>(ASPEN)</td>
<td></td>
</tr>
</tbody>
</table>
to 500 °C, and a corresponding pressure range of 58 to 345 bars. This is an example of a two-component (NaCl and H₂O), three-phase (vapor, liquid, and solid salt) equilibrium, which is monovariant. Therefore, specifying the temperature of the system allows one to calculate the pressure of the system and the mole fraction of salt in both the vapor and liquid phases. These three variables can be calculated by solving the following set of phase equilibria constraint equations:

\[ f_i^1(T,P,x_2) = f_i^v(T,P,y_2) \]  \hspace{1cm} (5.23)
\[ f_i^1(T,P,x_1) = f_i^v(T,P,y_1) \]  \hspace{1cm} (5.24)
\[ f_2^v(T,P,y_2) = f_2^s(T,P) \]  \hspace{1cm} (5.25)

In these equations, \( f \) denotes the fugacity and \( x \) and \( y \) represent the mole fractions in the liquid and vapor phases, respectively. Subscript 1 denotes H₂O, 2 denotes NaCl, and superscripts \( v, l, \) and \( s \) denote the vapor, liquid, and solid phases, respectively. By assuming the solid phase is a pure incompressible salt, and using fugacity coefficients to estimate fugacities (\( f_i = x_i \phi_i P \), equations (5.23) to (5.25) can be rewritten as:

\[ x_2 \phi_2^l = y_2 \phi_2^v \]  \hspace{1cm} (5.26)
\[ x_1 \phi_1^l = y_1 \phi_1^v \]  \hspace{1cm} (5.27)
\[ y_2 \phi_2^v P = P_2^v(T) v_2(T,P_2^v) \exp[V_2^s(P-P_2^v)/RT] \]  \hspace{1cm} (5.28)

where \( \phi_i^j \) (\( i=1,2, j=l,v \)) is the fugacity coefficient of component \( i \) in phase \( j \) of the mixture, \( v_2 \) is the fugacity coefficient of pure salt vapor in equilibrium with pure solid salt, \( P \) is the system pressure, \( P_2^v \) and \( V_2^s \) are the vapor pressure and the molar volume of the pure solid salt at temperature \( T \), respectively, and the last term in equation (5.28) represents the Poynting correction. In general, the fugacity coefficients for the mixture are a function of temperature, pressure, and composition, and can be calculated using an equation of state.

The vapor pressure of pure solid sodium chloride as a function of temperature was taken from the compilation of experimental values by O'Knacke (1973), and the specific volume of solid NaCl as a function of temperature was taken from Kaufmann (1960). Using the correlation of O'Knacke (1973), the vapor pressure over pure sodium chloride
at 600°C is 0.001 mmHg (1.3 x 10⁻⁶ bar). Since this vapor pressure is very low, v₂ was assumed to be one (ideal vapor).

The equation of state tested was that of Peng and Robinson (1976), which has been used successfully by researchers to model solute solubilities in supercritical fluids, such as carbon dioxide (McHugh and Krukonis, 1986). The PREOS and suggested mixing rules for a two-component system are,

\[
P = \frac{RT}{V - b_m} - \frac{a_m}{V^2 + 2b_m \sqrt{V - b_m}}
\]

(5.29)

\[a_m = y_1^2 a_1 + 2y_1 y_2 a_{12} + y_2^2 a_2 \quad \text{and} \quad b_m = y_1 b_1 + y_2 b_2\]

where \(a_i\) and \(b_i\) are pure component parameters determined from the critical constants and acentric factors. The binary parameter, \(a_{12}\), is equal to \((1-k_{12})(a_1 a_2)^{1/2}\), where \(k_{12}\) is the binary interaction factor. If the critical constants and acentric factors of each component are known, \(k_{12}\) is the only adjustable parameter for a two-component system. The corresponding fugacity coefficient equation for the PREOS can be found in Modell and Reid (1983).

Since no experimental value of the critical point for NaCl was available, the critical parameters were estimated using the PREOS. Vapor-liquid equilibrium data for pure NaCl (vapor pressures of O'Knacke, 1973, and liquid densities of Kirshenbaum et al., 1962) were fit as a function of temperature using \(T_c\) and \(P_c\) as adjustable parameters. The temperature range in the fit was 1200 to 1600 K. This resulted in values of 4200 K for the critical temperature and 653 bars for the critical pressure. The corresponding acentric factor was -0.100. These values were used in the PREOS binary component calculations which follow. Pitzer (1984) estimated the critical properties of NaCl to be 3900 K and 258 bars by extrapolating vapor and liquid densities of pure NaCl.

In the fit of the three-phase data for the NaCl-H₂O system, an attempt was first made at solving equations (5.26) to (5.28) using the PREOS to calculate the fugacity coefficients for both the vapor and liquid phases. It was found that by varying \(k_{12}\) the experimental salt concentration in the vapor phase could be matched, but the calculated concentration in the liquid phase was in error. For this reason, the PREOS was used only for the vapor phase. An activity coefficient model could have been used for the liquid.
phase, but instead the experimental saturation pressure was specified. This eliminated having to solve all three equations simultaneously.

The following procedure was used to fit the experimental three-phase equilibrium vapor composition of NaCl given by Bischoff et al. (1986). First, the temperature and the corresponding experimental saturation pressure were set. Then, a value for the binary interaction parameter, \( k_{12} \), was assumed. Equation (5.28) was then solved for \( y_2 \) using the successive substitution method. Finally, the parameter \( k_{12} \) was adjusted until the calculated salt mole fraction in the vapor matched the experimental mole fraction. This procedure was repeated at each of Bischoff's experimental temperatures.

The parameter \( k_{12} \) was found to be a strong function of temperature, as shown in Figure 5.4. A fourth-order polynomial was used to empirically represent the variation of \( k_{12} \) with temperature. Figure 5.5 shows the solubility prediction of the PREOS using the fourth order temperature correlation for \( k_{12} \). The calculated weight percent of NaCl in the vapor was very sensitive to the value chosen for \( k_{12} \) at any given temperature. Figure 5.6 shows this relationship. For a 1% change in \( k_{12} \), there was more than a 10% change in the calculated weight percent. This high sensitivity to \( k_{12} \) severely limits the extrapolation of the results to temperatures out of the range of the fitted constant, since large errors will most likely occur. These procedures suggest that the PREOS may not be adequately representing the degree of non-ideality that exists in the saturated vapor phase in the NaCl-H<sub>2</sub>O system at the conditions tested.

5.4 The Pitzer-Tanger Equation of State (PTEOS)

Pitzer and Tanger have recently developed an equation of state for modeling vapor-liquid equilibrium in the NaCl-H<sub>2</sub>O system (Pitzer and Tanger, 1988; Tanger and Pitzer, 1989). The Pitzer-Tanger equation of state (PTEOS) adequately predicts the entire vapor-liquid coexistence surface from the saturation to the critical pressure in the temperature range from 250 to 600 °C using three temperature-dependent parameters. The introduction of another temperature-dependent function enables the prediction of thermodynamic properties, such as, enthalpy, entropy and chemical potential.

Given its success with the NaCl-H<sub>2</sub>O system, it is not surprising that the PTEOS has been shown to adequately model the vapor-liquid region for the KCl-H<sub>2</sub>O system in
Figure 5.4 PR EOS binary interaction parameter $k_{12}$ for the NaCl-H$_2$O system fit along the three-phase curve.

Figure 5.5 PR EOS prediction along the three-phase curve using a 4th order regressed correlation in temperature for $k_{12}$.

Figure 5.6 Sensitivity at one point on the three-phase curve of the PR EOS vapor phase solubility fit for the system NaCl-H$_2$O.
a limited temperature range (300 to 410°C) (Hovey, et al., 1990). The KCl-H₂O system is another example of a Type I system, and it shows phase behavior very similar to the NaCl-H₂O system. It is not known whether the PTEOS can model a Type II salt-water system, which has both a discontinuous three-phase region (vapor-liquid-solid salt) and a discontinuous critical curve. Examples of important Type II solute-water systems include Na₂SO₄-H₂O and SiO₂-H₂O.

The goal of this section is to explore the development and use of the PTEOS for modeling vapor-liquid equilibrium (VLE) in salt-water systems at extreme temperatures and pressures. This includes, stating the theoretical basis of the equation of state, assumptions required in its development, and its limitations, writing computer codes for fitting the parameters of the equation of state to isothermal VLE data, and testing the programs by reproducing the parameter fit of Pitzer and Tanger for the NaCl-H₂O system, and exploring the ability of the equation of state to model the Type II salt-water system, Na₂SO₄-H₂O, using the limited VLE data which is available. These topics are discussed in the following sections.

### 5.4.1 Theoretical Basis

An analytical function can be approximated using a Taylor series expansion in its independent variables around a specific point. The Pitzer-Tanger equation of state (PTEOS) is based on an expansion around the critical point of pure water, which has a critical temperature of 374.2°C, a critical pressure of 220.5 bar and a critical density of 0.322 g/cm³. Using temperature, pressure and composition (expressed as mole fraction) as the independent variables, the following expansion is derived for a binary mixture:

\[
P(T, \rho, x) = P_c + (\delta T)P_T^{\rho} + \{ (\delta \rho)P_T^{\rho} \} + xP_x^{\rho} + \frac{1}{2}[((\delta T)^2P_T^{\rho} + (\delta \rho)^2P_T^{\rho}) + x^2P_T^{\rho} + 2(\delta T)(\delta \rho)P_T^{\rho} + 2(\delta T)xP_T^{\rho} + 2(\delta \rho)xP_T^{\rho}] + \ldots
\]

with,
\[
\delta T = T - T_c \quad \delta \rho = \rho - \rho_c
\]

\(P_c, T_c, \) and \(\rho_c\) = the critical pressure, temperature, and density of pure water
\(P, T, \) and \(\rho\) = the pressure, temperature, and density of the solution
and, \(x = \) mole fraction of NaCl.
The subscripts $T$, $\rho$ or $x$ indicate partial differentiation of $P(T,\rho,x)$ with respect to that variable, and the superscript $cp$ indicates evaluation at the critical point of water, for example, $P_{T,x}^{cp}=(\partial P/\partial T)_{\partial x}$ evaluated at $P=P_c$, $T=T_c$, and $\rho=\rho_c$. Since only a few terms of the Taylor expansion have been written, the expansion is only strictly valid for near-critical, dilute mixtures. The bracketed terms in equation (5.30) contain partial derivatives which are zero due to the critical point stability constraints for the pure solvent.

In their derivation of an equation of state for the NaCl-H$_2$O system, Pitzer and Tanger used two newly defined variables, the reduced density ($d$) and the NaCl to H$_2$O mole ratio ($y$). They then performed a similar expansion around the critical point of pure water using these new variables,

$$P(T,d,y) = P_{H_2O} + y b_{10} + y(d-1)b_{11} + y^2 b_{20} + \ldots$$  \hspace{1cm} (5.31)

where the reduced density ($d$) is equal to $\rho_r/\rho_c$, $\rho_r$ is the density of water on salt free basis (equal to $\rho$ (1 - wt. frac. NaCl)), $\rho$ is the density of the solution, $P_{H_2O}$ is the pressure of pure water at $T$ and $d$, $y$ is the mole ratio of NaCl to H$_2$O = $x/(1-x)$, and $b_{10}$, $b_{11}$, and $b_{20}$ are temperature dependent parameters.

The $P_{H_2O}$ term in equation (5.31) is evaluated at a given temperature and reduced density using the pure water equation of state of Haar, Gallagher and Kell (1984) (HGK). This approximation may be justified because the expansion is in the density of water in the solution, and not the total solution density. In comparing equation (5.31) with equation (5.30), the $P_{H_2O}$ term must represent all composition independent terms in the rigorous expansion of equation (5.30), since all other terms in equation (5.31) are composition dependent.

Pitzer and Tanger then went on to derive common thermodynamic properties from their pressure explicit equation of state. In general, Helmholtz free energy is related to pressure by,

$$P = \rho^2 \left( \frac{\partial A}{\partial \rho} \right)_{T,x}$$  \hspace{1cm} (5.32)
Pitzer and Tanger used the following equation to obtain the density dependent terms of the Helmholtz free energy per mole of water (Hovey, 1990),

$$P = \frac{d^2}{V_c} \left( \frac{\partial A}{\partial d} \right)_T$$  \hspace{1cm} (5.33)

where $V_c$ is the critical molar volume of water. If one transforms equation (5.32) from a derivative with respect to the solution density to one with respect to Pitzer's defined reduced density, $d = \rho(1-z)/\rho_w$ (where $z$ is the weight fraction of NaCl), a factor of $(1-z)^{-1}$ should appear on the right side of equation (5.33). Because the pressure expansion is expressed in terms of the density of water in the system and the derived Helmholtz free energy is per mole of water, one infers that the $(1-z)^{-1}$ factor is not required. Once the density dependent terms of the Helmholtz free energy were derived, Pitzer and Tanger then added the composition dependent terms which included an ideal mixing term and a term linearly proportional to amount of NaCl present in the solution. The Gibbs free energy per mole of solution was obtained by adding a PV term to the Helmholtz free energy, and then multiplying the resulting equation by the ratio of moles of water to moles of solution. The following equation was obtained by Pitzer and Tanger for the Gibbs free energy per mole of solution,

$$G = (1-x)g_{H_2O}(T,d) + RT\left[x\ln x + (1-x)\ln(1-x)\right] + xV_c b_{11}(1 + \ln d) + x g_{NaCl}(T)$$  \hspace{1cm} (5.34)

where, $g_{H_2O}$ is the Gibbs free energy of pure H$_2$O (from HGK EOS) and $g_{NaCl}$ is the Gibbs free energy of pure NaCl.

It is important to note that the ideal mixing term in equation (5.34) is on an undissociated basis. Pitzer comments that this is a good approximation near the critical density of pure water and at lower densities, but at higher densities ionization must be considered (Tanger and Pitzer, 1989). Although the PTEOS can be used to predict saturated liquid compositions up to 73.6 wt% NaCl at a temperature of 600°C ($P_{sat}=390$ bar), the predicted solution densities and heat capacities are reasonably accurate only up to sodium chloride concentrations of approximately 10 wt% (Tanger and Pitzer, 1989).

Pitzer and Tanger determined the compositions of vapor and liquid phases in
equilibrium by locating the double tangent on an isothermal, isobaric plot of Gibbs free energy versus mole fraction. The construction of this plot first requires the iterative calculation of density as a function of mole fraction (or mole ratio) from equation (5.31). To evaluate the three parameters in equation (5.31), Pitzer and Tanger used trial and error to fit the vapor-liquid coexistence curve as a function of pressure at various fixed temperatures. They paid special attention to the compositions of the saturated vapor and liquid solutions and the critical composition and pressure (Pitzer and Tanger, 1988). This is reasonable, since those three composition points define the boundaries of the vapor-liquid coexistence surface at a given temperature.

The temperature variations obtained by Pitzer and Tanger for their three equation of state parameters, $b_{10}$, $b_{11}$ and $b_{20}$, are shown in Figure 5.7. The most significant temperature dependence is in the parameter $b_{20}$. The $b_{20}$ term in equation (5.30) becomes important at high salt concentrations, as it accounts for binary solute interactions (Tanger and Pitzer, 1989).

5.4.2 Vapor-Liquid Calculations for NaCl-H$_2$O system

This section describes a computer program written to predict vapor-liquid equilibrium (binodal curve) in the NaCl-H$_2$O system. The code used to solve the PTEOS for the properties of a sodium chloride solution at a specified temperature, pressure and NaCl wt% was provided by John Tanger (Simulation Sciences, Fullerton, CA). The use of the PTEOS for predicting spinodal curves is discussed in the next section.

The number of degrees of freedom for a two component, two-phase mixture in equilibrium is two. Thus, at a given temperature and pressure, the compositions of the phases are fixed. For vapor-liquid equilibrium in the NaCl-H$_2$O system the equilibrium relationships are,

$$
\mu_2^v(T,P,x_2^v) = \mu_2^l(T,P,x_2^l) 
$$

(5.35)

$$
\mu_1^v(T,P,x_1^v) = \mu_1^l(T,P,x_1^l) 
$$

(5.36)
Figure 5.7  Temperature dependency of PTEOS parameters for the NaCl-H$_2$O system (correlation of Pitzer and Tanger, 1988).
In these equations, $\mu$ denotes the chemical potential, with subscript 1 denoting $\text{H}_2\text{O}$, 2 denoting $\text{NaCl}$, and superscripts $v$ and $l$ denoting the vapor and liquid phases, respectively. Also, $x$ represents the mole fraction. The PTEOS computer code provided the chemical potentials for $\text{H}_2\text{O}$ and $\text{NaCl}$ directly, so a fugacity representation of the equilibrium criteria was not used.

The simultaneous solution of equations (5.35) and (5.36) was performed numerically using a Newton-Raphson multi-dimensional root finding technique (Press et al., 1986). The equilibrium criteria equations were first rewritten as,

$$F'(T,P,x^v_2,x^l_2) = \mu^v_2 - \mu^l_2 = 0 \quad (5.37)$$

$$G'(T,P,x^v_2,x^l_2) = \mu^v_1 - \mu^l_1 = 0 \quad (5.38)$$

The common root of the functions, $F'$ and $G'$, was the desired equilibrium composition. The Newton-Raphson solution of equations (5.37) and (5.38) proceeded by first making an initial guess of the equilibrium composition, and then a matrix equation was solved to obtain the corrections to the initial guess. Iterations were performed until the vapor and liquid compositions converged. The matrix equation for the composition corrections was obtained by applying a linear Taylor expansion to the functions shown in equations (5.36) and (5.37) (in the neighborhood of the equilibrium composition), and then the expansions were set to zero. This resulted in,

$$\begin{bmatrix}
\frac{\partial F'}{\partial x^v_2} & \frac{\partial F'}{\partial x^l_2} \\
\frac{\partial G'}{\partial x^v_2} & \frac{\partial G'}{\partial x^l_2}
\end{bmatrix}
\begin{bmatrix}
\delta x^v_2 \\
\delta x^l_2
\end{bmatrix} =
\begin{bmatrix}
-F' \\
-G'
\end{bmatrix} \quad (5.39)$$

where $\delta x_2$ denotes the change in the composition used in the iteration loop. The partial derivatives in equation (5.39) are taken with respect to the indicated phase mole fraction while holding the mole fraction of the other phase constant. Since the chemical potential of a component in a given phase is not dependent on the composition of the other phase, equation (5.39) can be rewritten as,
\[
\begin{bmatrix}
\frac{\partial \mu_2}{\partial x_2} & \frac{\partial \mu_1}{\partial x_2} \\
\frac{\partial \mu_1}{\partial x_2} & \frac{\partial \mu_1}{\partial x_2}
\end{bmatrix}
\begin{bmatrix}
\delta x_2^y \\
\delta x_2^1
\end{bmatrix} = 
\begin{bmatrix}
-F' \\
-G'
\end{bmatrix}
\] (5.40)

In the actual solution of equation (5.40), the partial derivative of the chemical potentials with respect to the mole fraction of NaCl in the vapor or liquid phase were determined numerically.

The procedure outlined above for predicting vapor-liquid equilibrium was tested for the NaCl-H₂O system at a temperature of 450°C and from the saturation pressure (250.4 bar) to the critical pressure (421.3 bar). The vapor and liquid compositions stated by Tanger and Pitzer (1989) were reproduced up to a pressure of 413.6 bars. At higher pressures, the computer code would not converge, most likely because the chemical potential versus mole fraction curves developed an inflection point as the critical pressure was approached. Figure 5.8 shows the NaCl-H₂O pressure-composition phase diagram at a temperature of 450°C. The three parameter fit of Pitzer and Tanger (1988) does an adequate job of representing the equilibrium data.

### 5.4.3 Spinodal prediction in the NaCl-H₂O System

At the limit of stability for binary mixture, the following relationships hold,

\[
\left( \frac{\partial \mu_2}{\partial x_2} \right)_{T,P} = \left( \frac{\partial \mu_1}{\partial x_2} \right)_{T,P} = 0
\] (5.41)

Thus, spinodal points can be found be locating the maximum and minimum on a plot of the chemical potential versus of mole fraction at a specific temperature and pressure. Figure 5.9 shows the predicted chemical potentials of NaCl and H₂O versus NaCl wt% at a temperature of 450°C and a pressure of 400 bar. The curves were generated using the PTEOS. The equilibrium vapor and liquid compositions on the binodal as predicted by the PTEOS at the conditions of Figure 5.9 are 1.88 wt% and 16.8 wt%, respectively. The spinodal points are given by the extrema of the curves in Figure 5.9, and thus, the
Figure 5.8  Binodal prediction of the PTEOS shown on the pressure composition NaCl-H₂O phase diagram at 450°C.
Figure 5.9  Chemical potentials for the NaCl-H₂O system at 450°C and 400 bar predicted by the PTEOS.
limit of stability for the vapor and liquid phases at 450°C and 400 bars are 3.5 wt% and 11.2 wt%, respectively. The chemical potentials plotted in Figure 5.9 are for a water standard state of 273 K (aqueous) and a NaCl standard state of 298 K (solid).

Similar plots were generated at other pressures at the temperature of 450°C. The predicted spinodal points are listed in Table 5.4. The spinodal points listed in Table 5.4 are plotted on the NaCl-H₂O phase diagram shown in Figure 5.10. The vapor leg of the spinodal shows a unexpected bend toward higher wt% as the pressure is decreased from the critical pressure to the three-phase pressure. The spinodal curve calculations were also made at a few pressure below the three-phase pressure, which extended the predictions into the vapor-solid region of the phase diagram (out of the valid pressure and temperature range of the model). This was performed to test if the vapor spinodal curve would bend back toward the binodal vapor curve. This does appear to be occurring, although the program did not converge for all of the runs at these lower pressures.

5.4.4 VLE Modeling of Na₂SO₄-H₂O System

As discussed in Section 4.3, the Na₂SO₄-H₂O system is as a Type II binary system. The intersection of the critical curve of the mixture with the three-phase curve (liquid, vapor and solid salt) results in two critical end points. The first critical end point occurs very close to the critical pressure and temperature of pure water, while the second critical end point occurs approximately at a temperature of 440°C and a pressure of 1140 bar (Ravich and Borovaya, 1964). At temperatures below the first critical end point and above the second critical end point, regions of vapor-liquid, two-phase equilibrium exist. At temperatures between the critical ends points, only a single fluid phase can exist in equilibrium with solid salt (Ravich, 1970). The only available isothermal vapor-liquid equilibrium data for this system is in the upper two-phase region at temperatures of 450 and 475 °C (Ravich and Borovaya, 1964). Although the data at these temperatures are very sparse and scattered, they are sufficient for a preliminary parameter estimation.

Algorithm for Parameter Fit

To fit the PTEOS parameters at a given temperature, the experimental saturation compositions and critical composition were used. The criteria for vapor-liquid phase
Table 5.4  Predictions of the PTEOS for the binodal and spinodal curves in the NaCl-H$_2$O system at 450°C (compositions given in wt% NaCl).

<table>
<thead>
<tr>
<th>Pres. (bars)</th>
<th>Binodal</th>
<th>Spinodal</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>vapor</td>
<td>liquid</td>
</tr>
<tr>
<td>421.3 (critical)</td>
<td>6.44</td>
<td>6.44</td>
</tr>
<tr>
<td>413.6</td>
<td>3.21</td>
<td>11.8</td>
</tr>
<tr>
<td>400.0</td>
<td>1.88</td>
<td>16.8</td>
</tr>
<tr>
<td>375.0</td>
<td>0.89</td>
<td>24.5</td>
</tr>
<tr>
<td>350.0</td>
<td>0.46</td>
<td>31.3</td>
</tr>
<tr>
<td>325.0</td>
<td>0.24</td>
<td>37.4</td>
</tr>
<tr>
<td>300.0</td>
<td>0.13</td>
<td>42.9</td>
</tr>
<tr>
<td>250.4 (3-phase)</td>
<td>0.031</td>
<td>52.5</td>
</tr>
<tr>
<td>200.0*</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>150.0*</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>100.0*</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>50.0*</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

# extrapolation into vapor-solid region of phase diagram.
Figure 5.10   Spinodal prediction of the PTEOS shown on the pressure-composition NaCl-H$_2$O phase diagram at 450$^\circ$C.
equilibrium at the saturation vapor pressure for a given temperature are,

\[ \mu_2^y(T, P_{\text{sat}}, x_2^y, \text{sat}) = \mu_2^l(T, P_{\text{sat}}, x_2^l, \text{sat}) \]  (5.42)

\[ \mu_1^y(T, P_{\text{sat}}, x_2^y, \text{sat}) = \mu_1^l(T, P_{\text{sat}}, x_2^l, \text{sat}) \]  (5.43)

The subscript or superscript, sat, in equations (5.42) and (5.43) identifies that pressures and compositions are at their equilibrium values. At the critical point for a mixture, the chemical potential of each component must go through an inflection point; thus both the first and second partial derivatives with respect to mole fraction of one of the components must vanish,

\[ \left. \frac{\partial \mu_2}{\partial x_2} \right|_{P_{\text{sat}}, x_2^y} = \left. \frac{\partial^2 \mu_2}{\partial x_2^2} \right|_{P_{\text{sat}}, x_2^y} = 0 \]  (5.44)

To fit the parameters \( b_{10}, b_{11} \) and \( b_{20} \), equations (5.42) through (5.44) were rewritten as,

\[ F'(b_{10}, b_{11}, b_{20}) = \mu_2^{y, \text{sat}} - \mu_2^{l, \text{sat}} = 0 \]  (5.45)

\[ G'(b_{10}, b_{11}, b_{20}) = \mu_1^{y, \text{sat}} - \mu_1^{l, \text{sat}} = 0 \]  (5.46)

\[ H'(b_{10}, b_{11}, b_{20}) = \left. \frac{\partial \mu_2}{\partial x_2} \right|_{P_{\text{sat}}, x_2^y} + \left. \frac{\partial^2 \mu_2}{\partial x_2^2} \right|_{P_{\text{sat}}, x_2^y} = 0 \]  (5.47)

The partial derivatives in equation (5.47) were determined numerically at the critical pressure and composition for a specific set of \( b \)’s. Since this equation represents a relaxed form of the constraint in equation (5.44), the fitting method will first be tested on the NaCl-H₂O system. The common root of equations (5.45) to (5.47) determines the set of \( b \)’s which fit the saturation and critical point experimental compositions at the specified temperature. A Newton-Raphson non-linear, multi-dimensional, root finding technique was used to solve these equations (Press, et al., 1986). First an initial guess of the parameters was made, and then the following matrix equation was solved for the
parameter corrections,

\[
\begin{bmatrix}
\frac{\partial F'}{\partial b_{10}} & \frac{\partial F'}{\partial b_{11}} & \frac{\partial F'}{\partial b_{20}} \\
\frac{\partial G'}{\partial b_{10}} & \frac{\partial G'}{\partial b_{11}} & \frac{\partial G'}{\partial b_{20}} \\
\frac{\partial H'}{\partial b_{10}} & \frac{\partial H'}{\partial b_{11}} & \frac{\partial H'}{\partial b_{20}}
\end{bmatrix}
\begin{bmatrix}
\delta b_{10} \\
\delta b_{11} \\
\delta b_{20}
\end{bmatrix}
= 
\begin{bmatrix}
-F' \\
-G' \\
-H'
\end{bmatrix}
\]  

(5.48)

The partial derivatives in equation (5.48) were also determined numerically by introducing a small change in the relevant parameter while keeping all the other parameters constant.

**Na$_2$SO$_4$-H$_2$O Parameter Fit**

The technique outlined above for fitting Pitzer and Tanger's parameters was tested on the system NaCl-H$_2$O at temperatures of 450 and 600 °C. For the experimental points, the predicted saturation and critical data from the PTEOS were used (Tanger and Pitzer, 1989). For both temperatures, the difference between Pitzer and Tanger's b parameters and the parameters fit using the above technique was less than 0.1%. This verified the code written to fit the PTEOS to VLE data.

The data used to fit the PTEOS to the Na$_2$SO$_4$-H$_2$O system is listed in Table 5.5. These data are only an estimate of the actual equilibrium values, since Ravich and Borovaya used interpolation and extrapolation to draw their isothermal vapor-liquid coexistence curves at the specified temperatures.

The results of the computer fit to the data at both temperatures are in Table 5.6. The Na$_2$SO$_4$-H$_2$O system parameters show a strong temperature dependence. The fitted values of the b$_{11}$ parameter are also positive, unlike the corresponding parameter for the NaCl-H$_2$O system. In discussing the physical significance of the terms in his equation of state, Pitzer states that the b$_{10}$ term arises from the hydration of the solute by water of critical density, while the b$_{11}$ term arises from the hydration of the solute by water including the change in density effect (Tanger and Pitzer, 1989). The higher pressures required for vapor-liquid equilibrium in the Na$_2$SO$_4$-H$_2$O system may have caused the reversal of the density effect on hydration shown in b$_{11}$ parameter, or it may just be an
Table 5.5  Experimental data used in PTEOS fit of the Na$_2$SO$_4$-H$_2$O System (Ravich and Borovaya, 1964)

<table>
<thead>
<tr>
<th>Temp. (°C)</th>
<th>Saturation Pres (bar)</th>
<th>Sat. Vapor (wt% Na$_2$SO$_4$)</th>
<th>Sat. Liquid (wt% Na$_2$SO$_4$)</th>
<th>Critical Pres (bar)</th>
<th>Crit. Compo. (wt% Na$_2$SO$_4$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>450.</td>
<td>1165.</td>
<td>13.4</td>
<td>48.9</td>
<td>1245.</td>
<td>32.</td>
</tr>
<tr>
<td>475.</td>
<td>1226.</td>
<td>3.7</td>
<td>63.</td>
<td>1490.</td>
<td>30.</td>
</tr>
</tbody>
</table>

Table 5.6  Results of PTEOS fit to part of the upper three-phase region in the Na$_2$SO$_4$-H$_2$O System.

<table>
<thead>
<tr>
<th>Parameter (bar)</th>
<th>450 °C</th>
<th>475 °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>$b_{10}$</td>
<td>-37697.</td>
<td>-52194.</td>
</tr>
<tr>
<td>$b_{11}$</td>
<td>6746.6</td>
<td>17017.</td>
</tr>
<tr>
<td>$b_{20}$</td>
<td>-6605.1</td>
<td>-1673.9</td>
</tr>
</tbody>
</table>
artifact of the parameter fit.

The parameters listed in Table 5.6 were tested by using the method described in Section 5.4.2 to predict the vapor-liquid coexistence curve for the Na$_2$SO$_4$-H$_2$O system at a temperature of 475°C and pressures from saturation (1226 bars) to critical (1490 bars). For pressures above 1486 bar, the computer code for predicting vapor-liquid equilibrium did not converge, but a simplified code written to predict the critical pressure and composition by solving the two constraints in equation (5.44) did verify the critical point location. The result of this simulation is shown in Figure 5.11. The predicted binodal curve (using the three-phase compositions and the critical composition) does an adequate job of representing the interpolated experimental data of Ravich and Borovaya (1964).

5.5 Summary and Recommendations

Some of the many thermodynamic models available for the NaCl-H$_2$O system have been reviewed. Two of the more promising models, the Pitzer-Pabalan equation of state for low-density vapor solutions, and the Pitzer-Tanger equation of state for vapor-liquid phases in equilibrium, do a adequate job at representing the scattered high temperature data.

Two conventional thermodynamic approaches have been applied to the NaCl-H$_2$O system at extreme conditions. The Peng-Robinson equation of state was fit to vapor-phase solubility data, and three activity coefficient models were used to predict high-temperature aqueous solution solubilities. In their present form, these approaches do not satisfactorily describe the very non-ideal nature of the NaCl-H$_2$O system in the temperature, pressure, and composition ranges tested.

The semi-theoretical Pitzer-Tanger equation of state (PTEOS) was used to predict vapor-liquid equilibrium in the Type I NaCl-H$_2$O system at 450°C. The calculations used a Newton-Raphson algorithm to solve the equilibrium equations with the appropriate values for the empirical parameters given by Pitzer and Tanger (1988). The PTEOS was also used to estimate spinodal curves, which predicted that a large metastable region exists in the NaCl-H$_2$O system at a temperature of 450°C. Experimental verification of
Figure 5.11  Results of PTEOS three parameter fit of the upper vapor-liquid region in the $\text{Na}_2\text{SO}_4$-$\text{H}_2\text{O}$ system at 475$^\circ$C.
this region is still needed.

The PTEOS was also used to empirically fit the upper vapor-liquid surface for the Type II Na₂SO₄-H₂O system at temperatures of 450 and 475 °C. The temperature dependence of the parameters in this fit is much greater than the reported fit for the NaCl-H₂O system (Pitzer and Tanger, 1988), and this suggests that one or two more fitted parameters may be required in the pressure expansion to adequately represent the vapor-liquid coexistence surface for this system. More data is required before the full phase diagram (both upper and lower two-phase regions) can be empirically simulated.
Chapter 6
Isobaric Phase Equilibrium Experiments

An experimental procedure was developed for observing phase transformations and estimating phase boundaries in salt-water systems at constant pressure. Testing in an isobaric mode is desirable, since the oxidation and salt separation steps in the SCWO process occur at constant pressure. Furthermore, salt formation mechanisms may depend on phase behavior. To evaluate this technique, static isobaric experiments were performed on the NaCl-H₂O, Na₂SO₄-H₂O, and NaCl-Na₂SO₄-H₂O systems at the typical process pressure of 250 bar.

6.1 High Temperature and Pressure Optical Cell

A cell was designed and constructed in cooperation with Harwood Engineering (Walpole, Ma.) for direct optically accessible, in-situ measurements of phase equilibria and solid salt formation in supercritical water. Although the cell was designed for service to 340 bar (5000 psig) at temperatures up to 700°C, the maximum conditions used in this study were 300 bar and 600°C. The cell was constructed from a corrosion resistant, high strength nickel alloy, Inconel 625, and the windows were optically clear, synthetic sapphire (α-Al₂O₃). The composition of Inconel 625 is shown in Table 6.1. Similar view cells have been used in the past by Franck’s group at the University of Karlsruhe in Germany (Japas and Franck, 1985; Schilling and Franck, 1988).

A cross-sectional diagram of the optical cell is show in Figure 6.1. The cell was cubic in shape with an outer length of 12.7 cm (5 in.), and an inner volume of approximately 25 cm³. All six faces of the cell contained threaded ports, in which either Inconel 625 window holders, plugs or flow tubes were inserted. All the ports were interchangeable, which allowed for many different cell configurations. The cell was designed for both side and forward light scattering measurements up to angles of 10° from the centerline.
Figure 6.1 Cross-sectional view of high temperature and pressure optically accessible cell.
Table 6.1 Chemical composition of Inconel 625 (wt\%)†.

<table>
<thead>
<tr>
<th>Element</th>
<th>Composition</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nickel (Ni)</td>
<td>58.0 max</td>
</tr>
<tr>
<td>Chromium (Cr)</td>
<td>20.0 - 23.0</td>
</tr>
<tr>
<td>Iron (Fe)</td>
<td>5.0 max</td>
</tr>
<tr>
<td>Molybdenum (Mo)</td>
<td>8.0 - 10.0</td>
</tr>
<tr>
<td>Tantalum (Ta)</td>
<td>3.15 - 4.15</td>
</tr>
<tr>
<td>C, Mg, Si, Al, and Ti</td>
<td>&lt; 0.5</td>
</tr>
</tbody>
</table>

† Inco Alloys International, 1985

The cell body contained two drilled holes in the top and bottom faces, which served as thermowells. The holes extended 2.54 cm into the cell body, and had diameters of approximately 1.7 mm. During the experiments, type K thermocouples, sheathed in stainless steel 316 (0.79 mm diameter), were placed in the thermowells.

Copper gaskets made the high pressure seals at all the ports (see Figure 6.1). The gaskets were circular rings with a square cross-section. During early testing of the cell, undesirable corrosion of the gaskets occurred. Corrosion was minimized by plating the rings with a thin layer of nickel (1/2 mil) and an outer layer of gold (2 mils). After each temperature cycle of the cell, all the port retainers were retightened to assure proper sealing during the next experiment. After 4 to 6 runs, the gaskets usually could no longer be compressed to produce a satisfactory seal, and they were replaced.

A schematic of the sapphire window assembly is shown in Figure 6.2(a). The sapphire windows had a diameter of 1.91 cm (3/4 in.), and a thickness of 0.953 cm (3/8 in.). The actual diameter of the circular viewing area was about 1.27 cm (1/2 in.). The cell’s internal pressure sealed the windows by mating the optically flat surface of the window with a similar surface on the closure. These surfaces were polished flat within one light band. Following suggested procedures used by Franck and his colleagues at Karlsruhe, a gold foil spacer (0.025 mm thick) was compressed between the two flat surfaces to reduce the effects of any imperfections in the surfaces. The initial loading of the assembly was achieved by tightening the window cap with a wrench.
Figure 6.2  Sapphire window seals, (a) window holder assembly, (b) one of the tools used for pressing out the gold washers.
The gold foil washers were pressed out of a thin gold sheet using specially fabricated stainless steel 316 tools. One of the tools was constructed by Franck's group at the University of Karlsruhe. A schematic of the tool used to cut the ID of the gold foil washers is shown in Figure 6.2(b). A similar tool was used to cut the OD of the washer. The tools were machined out of a solid rod using a lathe. The 10° bevel was machined first, and then the OD of the rod was taken down to the desired value (0.510"), which created a razor sharp edge. The tools were placed in a drill press to allow a smooth downward load to be applied by hand to press out the washers.

6.2 Apparatus and Procedures

A schematic of the experimental setup incorporating the optical cell for examining phase behavior in salt-water systems at extreme temperatures and pressures is shown in Figure 6.3. For the static experiments, only one flow tube was inserted in the top port of the cell, and it was used for internal temperature measurement and solution bleed-off during heating. The flow tube had an inner diameter of 0.318 cm, and the thermocouple which passed through it had an outer diameter of 0.159 cm. Inconel 625 plugs were placed in the bottom and two side ports of the cell, while window holders were inserted in the remaining two side ports (front and back).

The cell was heated by twelve electrical resistance strip heaters. The strip heaters had Incoloy sheathing for operation up to 800°C, and had heating areas of 1.3 cm x 14 cm. Each heater had a maximum power output of 125 W at 120 V, which gave a total power of 1500 W available for heating the cell. The strip heaters were wired in parallel in two groups of six, and power to each group was regulated with a variable transformer. The heaters were attached to the cell using stainless steel strapping, with two heaters connected to each outer face of the cell to provide uniform heating.

The cell was supported on the optical table using a steel stand. For safety, a LEXAN enclosure was constructed on top of the optical table. The enclosure had a base of 1.22 x 1.83 meters and was 0.91 meters high. The LEXAN shield was 1.91 cm. thick. Ceramic fiber insulation was used to encase the cell. Two pieces of 2.54 cm. thick, high-strength, Kaowool ceramic board (Babcock and Wilcox) were placed under the cell, and three to four layers of 2.54 cm thick high-temperature Kaowool ceramic blanket was
Figure 6.3 Schematic of apparatus for isobaric phase equilibrium experiments.
packed around the other faces of the cell. The ceramic insulation could withstand a maximum temperature of around 1000°C. Clear circular glass plates were sometimes attached to the outer face of the window holder retainers to reduce heat losses from the window ports.

A high-performance liquid chromatography (HPLC) pump with a self-flushing head was used to pressurize the cell. Pressure was measured with a transducer, which was rated to 517 bar (7500 psi) with an accuracy of ±0.5 bar. A chart recorder was used to monitor the pressure during a run.

In a typical static isobaric experiment, the cell was first filled with a homogeneous solution of known salt concentration at room temperature. The cell was then slowly heated at constant pressure. A phase transformation was identified visually or by light extinction. The temperature of the inner solution and of the cell block was recorded when the nucleation of the new phase was first identified. The inner solution temperature was measured using a thermocouple inserted through the flow tube, and the cell block temperature was measured with thermocouples placed in the top and bottom thermowells in the cell body.

Since a salt solution expands as it is heated, the pressure in the cell could have been kept constant by varying the bleed-off rate with temperature, using a pressure control loop and a solenoid micrometering valve. Due to the small fluid volume contained in the optical cell (=25 cm³) and the nonlinear variation of water density at these temperatures and pressures, the required bleed-off rates would vary widely and be too small to make this method practicable. For example, in order to heat 25 cm³ of pure H₂O isobarically at 250 bar and a rate of 1.5 °C/min, the calculated required average bleed-off rate changes from 0.022 g/min between 50 to 100 °C to a high of 0.51 g/min between 375 to 400 °C, and finally to 0.006 g/min between 550 to 600 °C.

A simpler technique was developed for conducting the isobaric experiments. During an experiment, the high pressure pump was used to flow pure water through a straight length of tubing, while the pressure was held constant using a back pressure regulator. The optical cell was connected to the system using a high-pressure cross (as shown in Figure 6.3), and as the cell was heated the bleed-off combined with the pumped pure water. Since the flow rate of the pump was kept appreciably above the required
bleed-off rate for isobaric heating, the total pressure in the system remained nearly constant. For a typical isobaric run with a heating rate between 1.0 and 2.0 °C/min, the pressure varied by only 1 to 2 bar if the flow rate of the pure water was kept at 2.0 g/min.

6.3 Results and Discussion

The experimental procedure described above was first tested on the NaCl-H2O system. After verification of the method, experiments were performed on the Na2SO4-H2O and NaCl-Na2SO4-H2O systems.

6.3.1 NaCl Experiments at 250 bar

Solutions of known sodium chloride concentration were heated at a rate of approximately 1.5 °C/min, while maintaining a constant pressure of 250 bar. The initial concentration of the solutions ranged from 0.1 to 20.0 wt% NaCl. As each solution was heated from room temperature, it passed from the one-phase fluid region into the vapor-liquid region of the phase diagram (the NaCl-H2O phase diagram at 250 bar is shown in Figure 4.7). Video taping was routinely carried out to document observations.

In the isobaric runs with initial concentrations of 0.1 and 0.3 wt% NaCl, a sharp phase transformation was not visually observed in the cell. For these initial concentrations, a new phase with liquid-like density should have nucleated as the solutions were heated. Nucleation of the droplets most likely occurred on the inner walls of the cell, and then flowed downward out of the view provided by the windows in the cell. In the 0.3 wt% run, a haze did slowly developed in the solution, but no distinct initial nucleation temperature could be obtained.

For solutions of concentration of 1.0 wt% or greater, a well-defined phase transformation was identified visually, and appeared as a burst of very small vapor bubbles nucleated from the homogeneous fluid. The vapor bubbles seemed to emerge from the inner walls of the cell, which were hotter than the bulk solution because the cell was heated externally. Neglecting any significant penetration into the metastable region, the temperature at which the bubbles first appeared locates the vapor-liquid boundary in the phase diagram at the concentration of the initial solution. The initial nucleation of
the vapor bubbles from a 3.0 wt% NaCl solution can be seen in Figure 6.4(a). The dark region in the video prints was caused by the scattering of light from the small bubbles. After continued heating, the co-existence of the low-density vapor phase, which rose to the top of the cell, and the high-density liquid phase, which collected at the bottom of the cell, was observed. An example of this is shown in Figure 6.4(b). The liquid phase appears dark because of the continuous nucleation of vapor bubbles which occurred as the solution was heated. The numbers in the photos are the run times, which were recorded by the video camera.

Table 6.2 lists the measured nucleation temperatures for all the isobaric experiments. The NaCl-H$_2$O results are listed first. Figure 6.5 compares the results of the NaCl isobaric runs at a pressure of 250 bar, which are plotted as solid triangles with error bars, with interpolated data from isothermal experiments reported by other investigators. The bottom error limit corresponds to the measured bulk solution temperature as the initial vapor bubbles nucleated, and the top error limit corresponds to the cell block temperature at the onset of nucleation. Averages of the upper and lower experimental temperatures are plotted as the solid triangular points. Since nucleation occurred consistently on the inner walls of the cell, it is believed that the bulk solution temperature and the block temperature provide an upper and lower bound for the actual phase nucleation temperature. The excellent agreement of our data with others along the vapor-liquid binodal line for the NaCl-H$_2$O system confirms that the isobaric experimental technique can accurately estimate phase boundaries. Also, since the isobaric method can be performed directly at the pressure of interest, measurement and interpolation of isothermal data is not required.

In the isobaric experiments, heating was continued up to a temperature of approximately 550°C. As the solution was heated through the vapor-liquid region, the liquid-phase decreased in volume as it became more concentrated in NaCl. Finally, at the three-phase temperature of 450°C, another phase transformation should have occurred with solid salt crystallizing from the concentrated liquid brine. Since not all of the internal volume in the cell can be viewed through the sapphire windows, this second phase transformation could not be observed.

A few runs were performed in an attempt to observe the crystallization of the solid
(a) initial nucleation of vapor-phase (average temperature = 390°C)

(b) two-phase, vapor-liquid equilibrium (average temperature = 392°C)

Figure 6.4 View inside optical cell during an isobaric experiment at 250 bar with an initial NaCl concentration of 3.0 wt%.
<table>
<thead>
<tr>
<th>Initial Conc. (wt%)</th>
<th>Nucleated Phase</th>
<th>Temperatures at Nucleation</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Bulk Solution (°C)</td>
</tr>
<tr>
<td>0.1 NaCl</td>
<td>liquid</td>
<td>*</td>
</tr>
<tr>
<td>0.3 NaCl</td>
<td>liquid</td>
<td>*</td>
</tr>
<tr>
<td>1.0 NaCl</td>
<td>vapor</td>
<td>384</td>
</tr>
<tr>
<td>3.0 NaCl</td>
<td>vapor</td>
<td>385</td>
</tr>
<tr>
<td>5.0 NaCl</td>
<td>vapor</td>
<td>385</td>
</tr>
<tr>
<td>10.0 NaCl</td>
<td>vapor</td>
<td>388</td>
</tr>
<tr>
<td>20.0 NaCl</td>
<td>vapor</td>
<td>395</td>
</tr>
<tr>
<td>1.0 Na$_2$SO$_4$</td>
<td>solid</td>
<td>*</td>
</tr>
<tr>
<td>3.0 Na$_2$SO$_4$</td>
<td>solid</td>
<td>362</td>
</tr>
<tr>
<td>10.0 Na$_2$SO$_4$</td>
<td>solid</td>
<td>342</td>
</tr>
<tr>
<td>3.0 Na$_2$SO$_4$ &amp; 3.0 NaCl</td>
<td>solid</td>
<td>366</td>
</tr>
<tr>
<td></td>
<td>vapor</td>
<td>388</td>
</tr>
</tbody>
</table>

* No distinct nucleation temperature was observed
Figure 6.5  Results of sodium chloride static isobaric experiments shown on the temperature-composition NaCl-H₂O phase diagram at 250 bar.
phase at the three-phase point and to obtain an estimate of the growth rate of the crystals. In the runs, sapphire windows were placed in the top and bottom ports of the cell, and the dead volume around the bottom window cap was decreased by using a 90/10 nickel/chromium sleeve. These changes were performed to hopefully crystallize the solid salt on the bottom window, but as the temperature rose above 450°C, solid formation was not observed. This was most likely a result of the window being sightly cooler than the rest of the cell, since its outer surface was exposed to air.

At the end of the isobaric experiments, the pressure in the cell was lowered, and it was then cooled to room temperature. During cooling, the cell was flushed out with nitrogen by inserting a small stainless steel tube down the flow tube. This was performed to remove any residual water vapor which remained in the cell. Once cooled, the cell was opened, and white solid salt was visible on the bottom inside surface. The salt was usually caked around the lower Inconel 625 plug with a few wafer-like crystals on the surface. In the runs with the sapphire windows in the top and bottom faces of the cell, the solid salt was caked around the bottom window cap, and none was formed on the window surface.

A Hastelloy C256 disk was placed at the bottom of the cell to collect some of the solids. After cooling, the disk was removed and mounted on a stub for analysis with a scanning electron microscopy (SEM). Figure 6.6 shows two SEM’s of solids collected after an isobaric experiment at 250 bar with an initial NaCl concentration of 5.0 wt%. The surface of the solid contained both cubic-like crystals (Figure 6.6(a)) and step-like growth patterns (Figure 6.6(b)).

6.3.2 Na₂SO₄ Experiments at 250 bar

As discussed in Section 4.3, in the sodium sulfate-water system at a pressure of 250 bar and temperatures encountered in the supercritical water oxidation process, only a single-phase, saturated fluid solution can exist in equilibrium with solid Na₂SO₄. This conclusion was based on the Russian study of Ravich and Borovaya (1964). Thus, if a sodium sulfate solution is heated isobarically at this pressure, pure Na₂SO₄ should be nucleated once the solid-fluid phase boundary is crossed (see Figure 4.11).

Three isobaric experiments with varying initial sodium sulfate concentrations were
Figure 6.6 SEM photomicrographs of NaCl crystals grown during an isobaric experiment at 250 bar.
performed to verify the 250 bar phase behavior for this salt. Table 6.2 lists the results of the experiments. For two of the runs with initial concentrations of 3.0 and 10.0 wt% Na$_2$SO$_4$, solid nucleation was observed during the heating, and the solids appeared as fine particles settling inside the optical cell and salt crystals with needle/dendrite morphology on the inner window surface. These results are plotted on the sodium sulfate-water phase diagram in Figure 6.7. The error limits on the points represent the temperature of the inner solution (lower limit) and the cell block (upper limit) at the first observation of solid phase nucleation, and the solid triangle is the arithmetic average of the two temperatures. Both points fall above the Russian data. This could be a result of difficulties in detecting the first nucleated solids, which most likely occurred on the hot inner walls of the vessel. Alternatively, a significant metastable zone may exist. For the most dilute run with an initial loading of a 1.0 wt% Na$_2$SO$_4$ solution, not enough particles were formed to allow visual detection, but dendrite needles were observed attached to the inner walls of the vessel after the cell was cooled and opened.

The 250 bar Na$_2$SO$_4$ results confirm the Russian study. Solid nucleation occurred directly from the homogeneous fluid, and a no vapor-liquid, two-phase region was observed. Also, solid salt formed at temperatures below the critical temperature of water.

After all the Na$_2$SO$_4$ runs, the cell was flushed with nitrogen, cooled, and opened to remove crystal samples. Figure 6.8 shows optical microscope photomicrograph of the dendrite needles which grew on the inner surface of the back sapphire window during the 3.0 wt% Na$_2$SO$_4$ run (the back window was illuminated with white light during videotaping). The photos were taken using reflective light to illuminate the removed window. The dendrites are arranged in branch or fern-like structures with primary and secondary branches aligned perpendicular to the main stems.

Dendrite growth is frequently observed during crystallization of water, salts from aqueous solution, and metals (Buckley, 1951). While no clear explanation for the regularity of the branches exist, the primary cause of dendrite growth is high-supersaturation (Strickland-Constable, 1968). One theory proposes that diffusional limitations cause abnormal, rapid growth in a single direction into the bulk solution where high supersaturation endures, and side branches end once the supersaturation decreases (Buckley, 1951). Typically, the main dendrite stems grow rapidly into the supersaturated
Figure 6.7  Results of sodium sulfate isobaric experiments shown on the temperature-composition $\text{Na}_2\text{SO}_4 \cdot \text{H}_2\text{O}$ phase diagram at 250 bar.
Figure 6.8  Light microscope photos of sodium sulfate dendrites grown during an isobaric experiment at 250 bar.
solution, while the primary and secondary branches grow at slower rates. Near the end of the crystal growth, the spaces between the branches begin to fill. In the isobaric sodium sulfate experiments described above, the high-supersaturation was caused by the sharp drop in solubility as the critical temperature of water was approached. The high-temperatures may also have contributed to the abnormal growth.

**Sodium Sulfate Morphology**

Figure 6.9 shows SEM photomicrographs of dendrites collected after the 10.0 wt% isobaric run. Though amorphous impart, the dendrites have a distinct elongated hexagonal morphology. Sodium sulfate has been reported to exist in five polymorphic forms (Kracek, 1929; Kracek and Gibson, 1930) as listed in Table 6.3. Of these forms, only three are stable at ordinary pressures, Phases I, III, and V (Kracek and Ksanda, 1930). Anhydrous hexagonal crystals are the stable form of sodium sulfate at temperatures above 241°C, while at temperatures below 185°C, thenardite, or the common orthorhombic from, is stable. The rates of transformation between the phases depend on the environment. Kracek and co-workers report that in the presence of a trace amounts of moisture or other catalyst, such as H₂SO₄, the salt inverts rapidly. If the salt is totally dry, the inversions are more sluggish, and metastable phases exist, such as Phase III at temperatures below 185°C. Because the dendrites were formed at temperatures above 241°C (the first solids were detected at approximately 344°C), the original crystal structure should have been hexagonal. During cooling, inversion to Phase III and then Phase I (if some moisture remained in the cell) should have occurred. This inversion in the presence of traces of water vapor could account for the amorphous appearance of the crystals.

**X-ray Diffraction Analysis**

To determine the actual crystal form of the collected dendrites, X-ray powder diffraction tests were performed. Powder diffraction is a powerful tool for identifying crystalline substances. The theory of x-ray diffraction is well known (Glusker and Trueblood, 1985; Atkins, 1982). Samples are first ground to a powder and placed into a thin rectangular mold. A collimated x-ray beam is then directed at the sample, and the
Figure 6.9  SEM photomicrographs of sodium sulfate dendrites grown during an isobaric experiment at 250 bar.
Table 6.3  Anhydrous phases of sodium sulfate.†

<table>
<thead>
<tr>
<th>Phase</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>High temperature modification, hexagonal, low birefringence, stable above 241°C.</td>
</tr>
<tr>
<td>II</td>
<td>High birefringence phase, unstable at low pressures</td>
</tr>
<tr>
<td>III</td>
<td>&quot;Altered thenardite&quot;, orthorhombic, low birefringence, stable between 241°C and 185°C, metastable below 185°C.</td>
</tr>
<tr>
<td>IV</td>
<td>Monoclinic, high birefringence, unstable at low pressures</td>
</tr>
<tr>
<td>V</td>
<td>Thenardite, orthorhombic, moderate birefringence, stable below 185°C.</td>
</tr>
</tbody>
</table>

† (Kracek, 1929; Kracek and Ksanda, 1930)
diffracted radiation is measured at various angles with a Geiger counter. At certain angles, the diffracted beam undergoes constructive interference due to scattering off atoms in different planes of the crystal. This occurs when the Bragg condition is met,

$$\sin \theta_{hkl} = \frac{\lambda}{2d_{hkl}}$$  \hspace{1cm} (6.1)

where $\theta$ is the incident angle of the x-ray, $\lambda$ is the wavelength of the beam, and $d_{hkl}$ is the spacing between planes in the crystal with Miller indices of $h$, $k$, and $l$. In the powder sample, many tiny crystals are randomly oriented, and some will be so oriented to satisfy the Bragg relationship for a given set of planes. Many spectra have been collected for known substances, and computer searches are used to identify unknown substances.

Two powder samples were tested. The first was a sodium sulfate standard obtained from Mallinckrodt (analytic grade salt). The second sample was the dendrites collected from the 10.0 wt% isobaric run. Figure 6.10 shows the X-ray spectras. The spectra are plotted as relative intensity of the diffracted X-ray beam versus the scattering angle, $2\theta$. Both spectra are practically identical, and were identified in the computer search as thenardite (Phase V). Kracek and Ksanda (1930) have reported X-ray spectra for both orthorhombic forms of Na$_2$SO$_4$ (Phases III and V), and the spectra are distinct. Thus, the dendrites were the stable orthorhombic form of anhydrous Na$_2$SO$_4$ (Phase V), and not the metastable form (Phase III).

Schroeder et al. (1935) also collected elongated crystals with a hexagonal outline from Na$_2$SO$_4$ solubility experiments at temperatures above 241°C. They used a petrographic microscope to determine the phase of the salt, and identified mostly the Phase V form with small amounts of Phase III present. It was noted that the crystals had a mosaic appearance, which was attributed to phase inversion during cooling.

6.3.3 Mixed Salt Experiment at 250 bar

A single static experiment with the ternary system, NaCl-Na$_2$SO$_4$-H$_2$O, was performed at a pressure of 250 bar. The initial composition of the homogeneous solution loaded into the cell was 3.0 wt% NaCl and 3.0 wt% Na$_2$SO$_4$. As the solution was slowly heated, both types of nucleated phases (solids and vapor bubbles) were observed with no
Figure 6.10  Powder X-ray diffraction spectra of Na$_2$SO$_4$ salt samples.
appreciable differences in nucleation temperatures from the experiments with the binary salt-water systems at similar concentrations. The nucleated temperatures are listed at the bottom of Table 6.2. The first nucleated phase occurred at an average temperature of 368°C, and appeared as solids settling to the bottom of the cell and dendrite crystals growing on the inner surface of one of the sapphire windows, similar to the pure Na₂SO₄ experiments. The second nucleated phase appeared as small vapor bubbles rising to the top of the cell, and at higher temperatures a vapor-liquid interface emerged (at an average temperature of approximately 396°C), similar to the pure 3.0 wt% NaCl run. Both of these transitions are consistent with the ternary system phase diagram shown in Figure 4.15. The initial concentration of the solution (94.0 wt% H₂O, 3.0 wt% NaCl, and 3.0 wt% Na₂SO₄) is located in the upper corner of the triangular diagrams. At temperatures of 300 and 350 °C, the solution was in the homogeneous liquid region (L), while between about 350 and 400 °C two phase boundaries (Sₜ-L and V-L) should have been crossed.

In the isobaric experiments, the only known composition is that of the homogeneous solution loaded into the cell. Once an additional phase is nucleated, the total composition will change as one of the phases is removed in the bleed-off stream. Thus, in the isobaric experiment described above, only the first phase boundary crossed could be obtained (provided no significant metastable region exists).

Some additional information from the mixed salt experiment can be inferred. During solid nucleation, the total amount of solids settling in the cell did not appear as intense as in the pure 3.0 wt% Na₂SO₄ experiment. Also, the dendrites which grew on the window surface began to redissolve as the vapor-liquid interface came into view. Finally, the collected solids were caked on the bottom surface of the cell, and did not have a dendritic appearance. These results suggest that the sodium sulfate dendrites, which initially formed, were redissolved in the concentrated liquid brine. As discussed in Section 4.4, sodium sulfate solubility in high-temperature aqueous brines increases with NaCl content.
Chapter 7.

Dense Vapor Phase Solubility Measurements
at Sub- and Supercritical Conditions

The objective of the work described in this section was to obtain solubilities of two common salts, sodium chloride and sodium sulfate, at conditions prevalent in the supercritical water oxidation process. Subcritical pressures were examined for sodium chloride to help resolve some of the discrepancies in the data reported in the literature. Salt solubility at lower pressures is also important to a recently proposed modification of the SCWO process (Hong, 1992). The solubility predictions of two thermodynamic models for NaCl were also compared to experimental results. The next section describes the earlier experimental and theoretical work related to our study.

7.1 Previous Work

7.1.1 NaCl Vapor-Phase Solubility

Seven studies measuring sodium chloride solubility in aqueous, vapor phases were examined. Table 7.1 outlines the parameter ranges of these studies, and the experimental techniques used. Figure 7.1 shows representative examples of previously reported NaCl solubilities (in ppm by weight) measured at a temperature of 500°C. The differences in the data are striking, particularly at lower pressures, providing substantial motivation for the present work. By examining the various experimental methods used in these studies, possible sources for the discrepancies may be identified.

NaCl solubility has been measured using flow methods by Styrikovich et al. (1955), Martynova and Samoilov (1962), and Galobardes et al. (1981a,b). Of these studies, only Galobardes and his co-workers provide a detailed description of their
Table 7.1 Summary of previous studies of NaCl solubility in water vapor

<table>
<thead>
<tr>
<th>Investigators</th>
<th>T Range (°C)</th>
<th>P Range (bar)</th>
<th>Experimental Technique</th>
</tr>
</thead>
<tbody>
<tr>
<td>Olander and Liander (1950)</td>
<td>380-475</td>
<td>150-300 (to saturation)</td>
<td>Batch sampling system, 5 L copper-lined steel vessel, Titration for Cl⁻ concentration.</td>
</tr>
<tr>
<td>Styrikovich et al. (1955)</td>
<td>400-550</td>
<td>30-180</td>
<td>Continuous system, Volumetric analysis for Cl⁻ concentration.</td>
</tr>
<tr>
<td>Martynova and Samoilov (1962)</td>
<td>350-600</td>
<td>30-300</td>
<td>Continuous system, Colorimetric analysis for Cl⁻.</td>
</tr>
<tr>
<td>Martynova (1964)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Galobardes et al. (1981a,b)</td>
<td>400-550</td>
<td>14-103</td>
<td>Continuous system, Na⁺ conc. by flame spectroscopy.</td>
</tr>
<tr>
<td>Bischoff et al. (1986)</td>
<td>300-500</td>
<td>at saturation (58-328)</td>
<td>Batch system, 25 ml titanium vessel, Cl⁻ conc. by ion chromatography.</td>
</tr>
</tbody>
</table>
Figure 7.1 Previous studies of sodium chloride solubility in water vapor at 500 °C.
experimental apparatus and procedures. Galobardes found that varying salt-water contact times from 20 to 350 seconds did not significantly affect the sodium ion concentration in their samples, which were obtained using flame spectroscopy coupled with a preconcentration step to measure Na⁺ levels below 0.2 ppm. In the Russian studies of Styrikovich et al. and Martynova and Samoilov, the primary method of analysis was determination of the Cl⁻ ion concentration of samples using a colorimetric technique. Their results agree well with each other, but significantly differ from Galobardes et al. at pressures below 100 bar.

A number of studies have used sampling followed by a direct measurement of Na⁺ and/or Cl⁻ concentration. These include, Olander and Liander (1950), Sourirajan and Kennedy (1962), and Bischoff et al. (1986). Bischoff and co-workers sampled and measured the vapor composition along the three-phase (vapor-liquid-solid NaCl) curve. Sourirajan and Kennedy determined NaCl concentration using flame spectroscopy for sodium. Sample sizes ranged from 0.05 to 0.15 g, and were collected by condensing the steam into 25 cm³ of pure water. Thus, the samples were diluted between 167 and 500 times, which most likely magnified detection errors. Their data shows little pressure dependence until very low values, and is over an order of magnitude greater than the data from the flow studies under comparable temperature and pressure conditions.

Alekhin and Vakulenko (1988) have recently reported solubilities measured in-situ using a radioactive tracer. Though this method is unique, the analytical procedures used by the authors were not well described. In the study, gamma radiation from ²²NaCl molecules in the vapor phase was detected through a 4 mm thick titanium wall in a vessel with a inner volume of 180 cm³. No mention of the calibration technique was given. Also, the possibility of errors due to absorbed NaCl molecules to the inner walls of their vessel was not discussed. These shortcomings shed doubt on the reported results. This conclusion is further supported by the study of Galobardes et al. (1981b), who used the absorption of NaCl molecules on a hot Inconel 600 wall to concentrate their most dilute samples. They calculated that the metal wall had an equivalent of 80 monolayers of absorbed salt molecules on it. Thus, Alekhin and Vakulenko may not have measured true vapor-phase solubilities.
7.1.2 NaCl Vapor-Phase Solubility Models

In some of the studies described above, a simple solubility model was adopted to correlate the experimental data (Styrikovich, 1969; Martynova, 1964; Galobardes et al., 1981b). The model is semi-empirical in nature, and has a straightforward derivation from classical equilibrium thermodynamics (Martynova, 1964). It is first assumed that the equilibrium between solid NaCl and its vapor phase component occurs as a solvation-type reaction:

\[ \text{NaCl}_{(s)} + n \text{H}_2\text{O}_{(v)} = \text{NaCl} \cdot n \text{H}_2\text{O}_{(v)} \]  \hspace{1cm} (7.1)

where \( n \) is the number of hydrated water molecules attached to the dissolved NaCl molecule, and (s) and (v) refer to the solid and vapor phases, respectively. Due to the low density of the water vapor, its solvation power is low, and the dissolved NaCl exists as ion pairs (Mesmer et al. 1989). The equilibrium relationship for equation (7.1) is then written as,

\[ K_c = \frac{a_{\text{hyd}}}{a_w^n a_s} = \frac{C_{\text{NaCl}}}{\rho_w^n} \]  \hspace{1cm} (7.2)

where \( a \) is the activity, \( \rho \) is the density, and the subscripts hyd, w, and s represent hydrate NaCl-nH\text{H}_2\text{O}, water, and pure solid NaCl components, respectively. \( C_{\text{NaCl}} \) is the concentration of NaCl in the vapor phase. In the approximation shown in equation (7.2), the activity of solid NaCl was assumed to be one, and the vapor phase was taken as ideal. The water activity is approximated by its concentration expressed in terms of the density of pure water (\( \rho_w \)). To arrange equation (7.2) in a form suitable for regression of experimental data, the logarithm of both sides is taken with a Gibbs-Helmholtz type relationship for the temperature dependence of the equilibrium constant utilized:

\[ \log C_{\text{NaCl}} = n \log \rho_w + \log K_c = n \log \rho_w - \frac{A}{T} + B \]  \hspace{1cm} (7.3)
Thus if A and B are approximately constant, isothermal plots of $\log C_{\text{NaCl}}$ vs. $\log \rho_w$ should yield straight lines with slopes equal to the hydration number, $n$. This behavior has been reported by Styrikovich (1969) and Galobardes et al. (1981b), whose regressed parameters ($n$, A, B) were very close to each other, and did not show a specific dependence on temperature or density. Martynova (1964), on the other hand, reported a strong dependence of $n$ on density. Galobardes’ parameters were used to calculate the predicted solvation model curve shown in Figure 7.1. Since the abscissa of the isothermal plot is pressure and not $\log \rho_w$, the curve is non-linear. Although the prediction using Galobardes’s fitted parameters was extrapolated beyond the range of the data used to fit the parameters, the solvation model does an adequate job of representing some of the solubility data at the higher pressures.

Pitzer and Pabalan (1986) have recently developed a theoretically-based equation with empirically fitted parameters which predicts NaCl solubility in water vapor from low pressures up to saturation pressures. Their model is based on the statistical mechanics theory for a two-component imperfect gas (see Section 5.1.2). The Haar, Gallagher and Kell equation of state (Haar et al. 1984) was used to calculate the fugacity of pure water. The prediction of the Pitzer and Pabalan equation shown in Figure 7.1 was based on a fit to the data of Galobardes et al. (1981b) and Bischoff et al. (1986). Though more complicated than the solvation approach, the form of the Pitzer and Pabalan equation of state can easily be used for predictions of other thermodynamic properties.

### 7.1.3 NaCl Hydrolysis

A few researchers have studied the high temperature hydrolysis of solid sodium chloride (Martynova and Samoilov, 1957; Hanf and Sole, 1970). This reaction can be written as,

$$\text{NaCl}_{(s)} + \text{H}_2\text{O}_{(l)} = \text{NaOH}_{(s)} + \text{HCl}_{(g)} \quad (7.4)$$

In this reaction, a solid phase solution of NaCl and NaOH is proposed to be formed resulting in HCl. Thus, HCl may be another source of chlorine in the vapor phase, in addition to dissolved NaCl.

Martynova and Samoilov (1957) studied the hydrolysis of NaCl by passing high
pressure steam (10-141 bar) through a solid salt bed at temperatures ranging from 450-600 °C. They established that the hydrolysis reaction occurred significantly at temperatures above 500°C. The solid NaCl removed from their vessel was also found to have between 0.013-0.015 % NaOH in it (the authors do not state the concentration basis, i.e. whether it is mole or weight percent). The amounts of NaOH were obtained by testing the pH of the dissolved salt in water. Galobardes et al. (1981b) have also reported slight levels of hydrolysis at 450°C and 103.4 bar.

A more comprehensive study on NaCl hydrolysis was performed by Hanf and Sole (1970). In their study, humidified N₂ was passed through solid NaCl at temperatures between 600-800 °C and liquid NaCl at temperatures between 800-950 °C. The partial pressure of H₂O ranged from 0.11 to 0.22 bar. The system pressure was not stated, but it was most likely near atmospheric.

In Hanf and Sole’s experiments, the moles of HCl in the effluent gas were monitored as a function of time. For the hydrolysis of liquid NaCl, they found that equilibrium was rapidly achieved, and a simplified equilibrium representation of the hydrolysis reaction, which assumed unit activity for solid NaCl and an ideal vapor phase, adequately represented their experimental results. For the hydrolysis of solid NaCl, the equilibrium relationship did not hold at short times, and this was explained by diffusional limitations of NaOH into the solid NaCl phase. This conclusion was also supported by experiments where the evolution rate of HCl increased as the size of the solid NaCl crystals was decreased.

7.1.4 Na₂SO₄ Vapor-Phase Solubility

Table 7.2 lists the previous studies of Na₂SO₄ that we reviewed. The number and range of these studies are much less than those for sodium chloride. All of the researchers used continuous methods. Figure 7.2 shows the results of these studies at 500°C where the reported solubilities differ by over two orders of magnitude.

Morey and Hesselgesser (1951) flowed water through a bed of Na₂SO₄ contained in an Inconel X vessel with an inner volume of 74 cm³. No quantitative value for the water flow rate range was given. It was only mentioned to be between 10-25 drops per minute, which most likely corresponds to about 1 to 2 g/min. The salt concentration was
<table>
<thead>
<tr>
<th>Investigators</th>
<th>Temperature Range (°C)</th>
<th>Pressure Range (bar)</th>
<th>Experimental Technique</th>
</tr>
</thead>
<tbody>
<tr>
<td>Morey and Hesselgesser (1951)</td>
<td>500</td>
<td>67-1000</td>
<td>Continuous system, Gravimetric analysis</td>
</tr>
<tr>
<td>Styrikovich et al. (1955)</td>
<td>350-550</td>
<td>30-200</td>
<td>Continuous system, Radioactive tracer ($^{35}$S)</td>
</tr>
<tr>
<td>Martynova and Samoilov (1962)</td>
<td>500</td>
<td>180</td>
<td>Continuous system, Radioactive tracer ($^{35}$S) and cation-exchange resin</td>
</tr>
<tr>
<td>Martynova (1976)</td>
<td>425-600</td>
<td>300</td>
<td>not given</td>
</tr>
</tbody>
</table>
Figure 7.2  Previous studies of sodium sulfate solubility in water vapor at 500 °C.
determined by dividing the weight of salt by the total weight of the samples, whose size ranged from 500-1800 grams. The authors did not mention how the weight of salt was measured nor did they give any error analysis. It is presumed that the water was evaporated and the residual salt weighed.

In the studies of Styrikovich et al. (1955) and Martynova and Samoilov (1962) the dissolved sodium sulfate concentrations were too low to be measured by standard techniques. Styrikovich et al. used a radioactive tracer (Na$_2^{35}$SO$_4$) to detect the salt concentration in their samples. Martynova analyzed for sulfate ion gravimetrically on samples concentrated on a cation-exchange resin. Using these methods, concentrations as low as 0.03 ppm were measured. No mention of contact times between the salt and the water were given.

7.2 Experimental Techniques

7.2.1 Apparatus and Procedures

The apparatus used in this study is shown in Figure 7.3. The heated parts of the unit were constructed from high Nickel alloys (Inconel 625, 600 and Hastelloy C276) for both corrosion resistance and high-temperature strength. Periodic tests of the effluent for dissolved metals, showed that small levels of corrosion did occur (see Section 7.3.4 for exact levels). In the experiments, pure deionized water was flowed continuously through a salt bed using a high-pressure liquid chromatography pump. A back pressure regulator was used to control system pressure, and a pressure gauge was placed after the pump to measure the up-stream pressure during a run. The feed was heated using two electrical resistance heating units. The tubing in the heaters was coiled to increase total heat exchanger area. In the first low-temperature heating unit, stainless steel 316 tubing was used. In the second high-temperature heating unit, Hastelloy C276 tubing was used.

The salt bed was packed loosely in an Inconel 625 tube, which was 42 cm long with an OD of 1.43 cm and an ID of 0.91 cm. The length of the salt bed was typically 20 to 25 cm. The salt crystals were analytical grade and sieved to give a size range of 0.25 to 0.5 mm or 0.5 to 0.8 mm. Inert spherical ceramic beads (0.2 cm diameter) were
Figure 7.3  Schematic of apparatus for solubility experiments.
placed above and below the salt bed to hold it in place. The tube was placed in a Lindberg tube furnace (2.54 cm ID), and connected to the inlet and outlet lines using high-pressure Inconel 625 crosses. In order to compensate for unequal heating in the furnace, ring heaters were attached to the crosses, which were also insulated.

After exiting the top high-pressure cross, the hot, vapor salt solution was cooled using a shell-and-tube heat exchanger. The pressure of the cool fluid was then measured with a high-accuracy transducer which was rated to 517 bar with an accuracy of ±0.5 bar. After passing through the back-pressure regulator, the liquid effluent was collected in polyethylene bottles for off-line ion analysis. For most of the runs, water was passed through the salt bed overnight to assure that steady-state operation was reached.

A three-zone temperature control scheme was used to ensure that the water temperature at the bottom of the salt bed (T₂ in Figure 7.3) and the exit temperature at the top of the salt bed (T₁ in Figure 7.3) were kept within ±1 °C of the desired temperature. All the thermocouples used were Type K (Chromel-Alumel) with Inconel 600 sheathing. The 0.16 cm diameter T₁ and T₂ thermocouples passed though the high-pressure crosses above and below the furnace, respectively (see Figure 7.3). The temperature at the bottom of the salt bed (T₂) was used to control the power to the ring heaters attached to the bottom high-pressure cross, while the temperature at the top of the bed (T₁) was used to control the electric power to the furnace. The electric power to the ring heaters attached to the top high-pressure cross was controlled using the temperature measured by T₃, which was in contact with the effluent stream in the top high-pressure cross. Temperature T₃ was also held at the desired experimental temperature for a particular run.

7.2.2 Analytical Techniques

The collected samples were analyzed for all expected dissolved ions. In the sodium chloride experiments, concentrations of hydrogen, sodium, and chlorine ions were determined. The hydrogen concentration was measured using a pH electrode. The sodium ion concentration was determined using an Inductively Coupled Plasma (ICP) atomic emission spectroscopy instrument. The typical detection limit for the ICP instrument was 0.1 ppm sodium (by weight), which corresponds to an NaCl concentration
of 0.25 ppm. A colorimetric method was used to analyze for chlorine (ASTM standard method D512c-81). In this method, ferric thiocyanate is formed and analyzed photometrically at a wavelength of 463 nm. Chlorine levels down to around 0.2 ppm could be accurately detected.

In the sodium sulfate experiments, sodium ion was measured using the ICP instrument. A turbidimetric method for sulfate ion (ASTM standard method D516-88) was also tested. In this method the sulfate ion is converted to a barium sulfate suspension, and the absorbance of the suspension is measured with a spectrophotometer at a wavelength of 390 nm. We found the detection limit of the method to be approximately 1.0 ppm of sulfate ion with an error of ±1.0 ppm.

**7.3 Results and Discussion**

**7.3.1 NaCl Solubility Experiments and Solvation Model Regression**

Sodium chloride solubility experiments were conducted at temperatures of 450, 500 and 550 °C and pressures ranging from 100 to 250 bar. Water flow rates varied from 0.2 to 3.0 g/min, which corresponds to water-salt contact times in the tube from 10-200 seconds. With these flow rates, no significant pressure drop occurred through the bed. This was within the accuracy of the up-stream pressure gauge which was ± 5 bar. The experimental pressure was measured using the down-stream pressure transducer. Throughout the experiments, the dependence of the measured concentrations on flow rate was tested. Figure 7.4 shows the accumulated results of flow rate tests at three experimental temperatures and pressures. Two values for the calculated NaCl concentration in the samples are given, one based on the measured Na⁺ concentration and one based on the measured Cl⁻ concentration. For most of the experiments, the chlorine based measurements were higher than the sodium based measurements. This is believed to be a result of NaCl hydrolysis, and is discussed below. As can be seen in Figure 7.4, no uniform dependence of concentration on flow rate was observed. For all the NaCl experiments, the solubility was based on sodium ion concentration, since the excess chlorine ions were a result of the hydrolysis reaction.

The solubility results for sodium chloride measured in this study agree well with
Figure 7.4(a) Effect of water flow rate on NaCl solubility measurements

a) 450°C and 100 bar  b) 500°C and 200 bar, 550°C and 250 bar.
Figure 7.4(b) Effect of water flow rate on NaCl solubility measurements
a) 450°C and 100 bar  b) 500°C and 200 bar, 550°C and 250 bar.
the reported data of other researchers who used similar continuous flow experimental techniques. Table 7.3 lists the results of the sodium chloride solubility experiments. For each temperature and pressure, the listed solubility is based on an average of the measured sodium ion concentration in runs at various flow rates. Figure 7.5 shows the results on isothermal plots for comparison with data from other researchers. At pressures of 150 bar and above, our results fall close to those of Styrikovich et al. (1955) and Martynova (1964). At a pressure of 100 bar, our results are closer to those of Galobardes et al. (1981b). For all of our experiments, solubilities were about one to two orders of magnitude below those reported by Sourirajan and Kennedy (1962) or Alekhin and Vakulenko (1988).

The solvation model described above and shown in equation (7.3) was used to regress our data. In the fit, we included a subset of Galobardes's data (three points at each temperature) and also the data of Bischoff et al (1986). The resulting equation is:

$$\log C_{NaCl} = 3.866 \log \rho_w - \frac{1233.4}{T} + 7.772$$

(7.5)

where log is the logarithm in base 10, $C_{NaCl}$ is the saturated NaCl concentration in ppm, $\rho_w$ is the pure water density in g/cm$^3$, and $T$ is the temperature in Kelvins. As shown in Figure 7.5, the simple solvation model represents our solubility data reasonably well over the full temperature and pressure range examined. The Pitzer and Pabalan (1986) model also provides a reasonable representation of our data.

### 7.3.2 Extent of NaCl Hydrolysis

In our experiments, hydrolysis was detected at all temperatures and at several of the experimental pressures. Hydrolysis was most significant at a pressure of 100 bar. This can be seen in the last column of Table 7.3, which lists the ratio of the molar concentration of chlorine ion to sodium ion. One conceivable reason for this is that at these low pressures, NaCl solubility is also low and thus, the relative amount of chlorine produced by the hydrolysis reaction was greater. The pH of the samples typically ranged from 4 to 5, which is additional evidence for the occurrence of the hydrolysis reaction.

The solid salt from the tube was also analyzed for NaOH at the end of a group
Table 7.3  Results of NaCl Solubility Experiments

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Pressure (bar)</th>
<th>Density† (g/cm³)</th>
<th>NaCl solubility ‡ (ppm)*</th>
<th>[Cl]/[Na] (molar ratio)</th>
</tr>
</thead>
<tbody>
<tr>
<td>450</td>
<td>100</td>
<td>0.03361</td>
<td>1.5</td>
<td>1.5</td>
</tr>
<tr>
<td></td>
<td>150</td>
<td>0.05420</td>
<td>12.5</td>
<td>1.1</td>
</tr>
<tr>
<td></td>
<td>200</td>
<td>0.07873</td>
<td>63.6</td>
<td>1.0</td>
</tr>
<tr>
<td>500</td>
<td>100</td>
<td>0.03050</td>
<td>0.9</td>
<td>5.5</td>
</tr>
<tr>
<td></td>
<td>150</td>
<td>0.04808</td>
<td>13.7</td>
<td>1.2</td>
</tr>
<tr>
<td></td>
<td>200</td>
<td>0.06771</td>
<td>31.4</td>
<td>1.1</td>
</tr>
<tr>
<td></td>
<td>250</td>
<td>0.08990</td>
<td>101</td>
<td>1.0</td>
</tr>
<tr>
<td>550</td>
<td>100</td>
<td>0.02807</td>
<td>0.9</td>
<td>8.3</td>
</tr>
<tr>
<td></td>
<td>200</td>
<td>0.06043</td>
<td>33.8</td>
<td>1.2</td>
</tr>
<tr>
<td></td>
<td>250</td>
<td>0.07864</td>
<td>98</td>
<td>1.1</td>
</tr>
</tbody>
</table>

† calculated from pure water equation of state (Haar et al., 1984)
‡ based on measured Na⁺ concentrations in samples
* ppm = parts per million by weight throughout
Figure 7.5(a-b) Comparison of isothermal sodium chloride solubility experimental results and model predictions, a) $450^\circ$C, b) $500^\circ$C, and c) $550^\circ$C.
Figure 7.5(c) Comparison of isothermal sodium chloride solubility experimental results and model predictions, a) 450°C, b) 500°C, and c) 550°C.
of runs, which typically lasted over two weeks. First, a small quantity of the removed salt was dissolved into a known volume of water. The pH of the water was then determined to be very basic (around 10). From this measurement, the wt% of NaOH in the solid was estimated. The NaOH wt% in the salt taken from the bottom half of the bed was 0.023 (0.035 mole %), while the top half of the bed had a NaOH wt% of 0.014 (0.020 mole %). These values represent bulk NaOH concentrations in the solid NaCl, which may be different than the actual surface concentrations.

The equilibrium relationship for the hydrolysis reaction (equation 7.4) was used to estimate the contribution of chlorine ions from hydrolysis at a pressure of 100 bar. The equilibrium constant is given as,

$$K_{\text{Hydro}} = \left( \frac{\hat{f}_{\text{NaOH}}^{(s)} / f_{\text{NaOH}}^{o}}{\hat{f}_{\text{HCl}}^{(v)} / f_{\text{HCl}}^{o}} \right) \left( \frac{\hat{f}_{\text{NaCl}}^{(s)} / f_{\text{NaCl}}^{o}}{\hat{f}_{\text{H}_{2}\text{O}}^{(v)} / f_{\text{H}_{2}\text{O}}^{o}} \right)$$  \hspace{1cm} (7.6)

where $\hat{f}_i$ represents a mixture fugacity, and $f^o$ represents a reference fugacity. The reference state for H$_2$O and HCl was taken as the ideal gas at 1 bar (unit fugacity), while the reference state for NaCl and NaOH was taken as the pure crystalline solid at 1 bar. Since the solid phase is nearly pure NaCl and the vapor phase is nearly pure H$_2$O, the Lewis and Randall rule was used to express the mixture fugacities for NaCl and H$_2$O in terms of pure component fugacities ($\hat{f}_i = x_i f_i$). Also, since the mole fractions of NaCl in the solid phase and water in the vapor phase are both approximately 1.0, this further reduces to $x_i f_i = f_i$. Using these approximations and expressing the mixture fugacity for NaOH in terms of an activity coefficient ($\gamma_{\text{NaOH}}$) and the mixture fugacity of HCl in terms of a fugacity coefficient ($\Phi_{\text{HCl}}$), equation (7.6) becomes:

$$K_{\text{Hydro}} = \left( \frac{\gamma_{\text{NaOH}} \gamma_{\text{NaOH}}^{(s)} / f_{\text{NaOH}}^{o}}{\Phi_{\text{HCl}} \gamma_{\text{HCl}}^{o} P / (f_{\text{NaCl}}^{(v)} f_{\text{H}_{2}\text{O}}^{o})} \right)$$ \hspace{1cm} (7.7)

where $x_{\text{NaOH}}$ is the mole fraction of NaOH in the solid phase, $\gamma_{\text{HCl}}$ is the mole fraction of HCl in the vapor phase, and P is the system pressure. The ratio of the pure component fugacities to the reference fugacities for NaCl and NaOH in the solid phase can be evaluated using a Poynting correction factor. For the moderate pressure of 100 bar, this
term was neglected. Also, as a first approximation, the fugacity coefficient for HCl was taken as one, since no experimental data for dilute aqueous HCl solutions at conditions of interest could be found. Equation (7.7) thus becomes:

\[
K_{\text{Hydrol}} = \frac{\gamma_{\text{NaOH}} \times_{\text{NaOH}} \gamma_{\text{HCl}} \ P}{f_{\text{H}_2\text{O}}}
\]  

(7.8)

In the equilibrium calculations, the activity of NaOH in solid NaCl was obtained using the empirical equation of Hanf and Sole (1970), the pure water fugacity was calculated using the HGK equation of state (Haar et al., 1984), and the equilibrium constant was calculated using the JANAF tables (Chase et al., 1986). The mole fraction of NaOH in the solid phase was estimated from the bulk solid salt analysis described above. An average value of 0.028 mole % was used. Three sample calculations at temperatures of 450, 500, and 550 °C and a pressure of 100 bar are shown in Table 7.4. Predicted equilibrium chlorine concentrations become significant at temperatures above 500°C. The chlorine ion concentrations shown in Table 7.4 (units of ppm by weight) were converted from the equilibrium mole fraction of HCl calculated using equation (7.8).

By plotting sodium chloride solubility at 100 bar, using the results of our experiments and those of Galobardes et al. (1981b) and Martynova (Martynova and Samoilov, 1962; Martynova, 1964), a possible explanation for the discrepancies in the data can be developed. As Figure 7.6 shows, if one uses measured chlorine concentration to calculate the solubility of NaCl (as done by Martynova and Samoilov), the estimated solubility will be too high due to the hydrolysis reaction. This is verified by our results showing the calculated NaCl solubility from Cl⁻ measurements versus Na⁺ measurements. A predicted NaCl solubility curve is also plotted showing the effect of using total chlorine concentration to determine NaCl solubility. The contribution of the hydrolysis reaction was obtained using the approximations outlined above, while the contribution of chlorine from the actual dissolved NaCl was obtained using the solvation model parameters of Galobardes et al. (1981). Styrikovich et al. (1966) do mention that their solubilities at low densities (low pressures) and high temperatures may be too high due to hydrolysis of NaCl.
Table 7.4  Predicted chlorine concentrations due to hydrolysis of NaCl at a pressure of 100 bar.

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>$K_{\text{Hydrol}}$</th>
<th>water fugacity $f^*_{\text{H}_2\text{O}}$ (bar)</th>
<th>Activity coefficient$^\dagger$ $\gamma_{\text{NaOH}}$</th>
<th>Cl$^-$ (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>45°C</td>
<td>1.2 x 10^{-10}</td>
<td>89.0</td>
<td>7.2</td>
<td>0.10</td>
</tr>
<tr>
<td>500</td>
<td>5.9 x 10^{-10}</td>
<td>91.2</td>
<td>5.8</td>
<td>0.63</td>
</tr>
<tr>
<td>550</td>
<td>24.0 x 10^{-10}</td>
<td>92.9</td>
<td>4.8</td>
<td>3.13</td>
</tr>
</tbody>
</table>

$^\dagger$ defined in equation (7.7)
Figure 7.6  Extent of measured sodium chloride hydrolysis at 100 bar,  
— solvation model of Galobardes et al. (1981b),  
—- model of Pitzer and Pabalan (1986),  
—- calculated NaCl concentration based on total Cl\textsuperscript{-} from solvation and hydrolysis (see text).
As discussed by Hanf and Sole (1970) the hydrolysis of solid NaCl is a process which may have diffusional limitations. This could lead to unsteady behavior, and hydrolysis levels which depend on experimental parameters such as salt particle sizes and the previous history of the salt bed. These factors could contribute to researchers observing different levels of hydrolysis during their experiments. For example, Galobardes et al. (1981b) report testing for hydrolysis at a temperature of 450 °C and a pressure of 103.4 bar. At these conditions, they measured a chlorine to sodium molar ratio of 1.2. In our study, we measured this ratio to be 1.5 at the identical temperature and a pressure of 100 bar. Galobardes and co-workers do not report if hydrolysis tests were made at higher temperatures, where one would expect more significant contributions.

### 7.3.3 Na₂SO₄ Solubility Experiments

Sodium sulfate solubility experiments were conducted at temperatures of 450 and 500 °C and pressures of 250 and 300 bar. Water flow rates were varied from 0.5 to 1.5 g/min. The sodium ion concentrations in the samples were measured using an Inductively Coupled Plasma (ICP) atomic emission spectroscopy instrument. Due to the low concentrations in the effluent samples, the turbimetric test could not be used to analyze for sulfate ion concentration. An attempt was made to concentrate some of the samples by evaporation of water. Though we were able to verify that the samples did contain some sulfate ions, the levels were too small to allow accurate comparison to the sodium ion measurements.

The measured sodium concentrations in the effluent samples showed a unsteady nature, which hindered the determination of sodium sulfate solubility. An example of this unsteady behavior is shown in Figure 7.7, where the effluent sodium sulfate concentration (based on Na⁺) is plotted versus time for the temperature of 500°C and a pressure of 250 bar. The falloff in concentration may have been a result of bed degradation, which could then lead to channeling of the water through the bed. After the run, the salt bed was caked in the tube, and had to be scraped out. After one series of runs, the salt removed from the tube had a slight dark appearance to it, which may have signified the contamination of corrosion products on the salt surface.

In spite of these experimental difficulties, an estimate for the solubility can be
Figure 7.7 Measured sodium sulfate effluent concentrations at 500°C and 250 bar as a function of time during a continuous flow experiment.
obtained if one assumes that the high concentration values shown in Figure 7.7 represent saturation conditions reasonable well. This would give a value of around 0.9 ppm sodium sulfate solubility in supercritical water at 500°C and 250 bar. Due to the difficulty of continuous measurements with sodium sulfate, a batch experimental system to determine solubilities is recommended for this salt.

7.3.4 Corrosion Tests

Effluent samples from some of the experiments with sodium chloride and sodium sulfate were analyzed for metal ion content to determine the level of corrosion which occurred during the runs. ICP spectroscopy was used to detect the presence and concentration of specific elements in the samples. With this technique, only the soluble corrosion products are measured. In our experiments, the main metals in contact with the high temperature and high pressure water vapor were Inconel 625 and Hastelloy C276. Inconel 625 has a primary atom composition of approximately 60% Ni, 20% Cr, 9% Mo, 3.5% Nb and < 5% Fe. Hastelloy C276 has a primary atom composition of approximately 56% Ni, 16% Mo, 16% Cr, 5% Fe, 2% Co, and 4% W.

Table 7.5 lists the average concentration of the five metal atoms analyzed. In the runs with sodium chloride the predominate corrosion products were nickel with an average concentration of 0.36 ppm and iron with an average concentration of 0.12 ppm. For the sodium sulfate runs, the corrosion products with the highest concentration in the effluent were chromium (0.53 ppm) and molybdenum (0.43 ppm). No correlation between the run conditions (temperature, pressure, or flow rate) and corrosion levels could be inferred from our test data. Though the concentrations of some of the metal atoms are significant, it is unlikely that the corrosion products had a measurable effect on the determined salt concentrations.

7.4 Summary and Recommendations

The solubility results for sodium chloride measured in this study agree well with the reported data of other researchers who used similar continuous flow experimental techniques. Our work has also determined that the hydrolysis of sodium chloride may be the cause of some of the discrepancies at lower pressures reported in the literature. The
Table 7.5  Results of inductively coupled plasma (ICP) analysis for corrosion ions during solubility experiments at various temperatures and pressures.

<table>
<thead>
<tr>
<th>Salt Type</th>
<th>Average Concentration in ppm (std. dev., σ)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Mo</td>
</tr>
<tr>
<td>NaCl</td>
<td>0.093</td>
</tr>
<tr>
<td>(15 samples)</td>
<td>(0.051)</td>
</tr>
<tr>
<td>Na₂SO₄</td>
<td>0.429</td>
</tr>
<tr>
<td>(14 samples)</td>
<td>(0.344)</td>
</tr>
</tbody>
</table>
solvation model used by some researchers in the past does reasonably well in modeling our data.

Experiments with sodium sulfate were hindered by unsteady measurements in the continuous flow apparatus. These uncertainties notwithstanding, it appears that the solubility of sodium sulfate at a temperature of 500°C and 250 bar may be over two orders of magnitude less than that of sodium chloride. Due to the difficulty of continuous measurements with sodium sulfate, a batch experimental system to determine true solubilities may be preferred for this salt.
Chapter 8.
Shock Crystallization Experiments

Flow experiments were performed to characterize salt formation at temperatures, pressures, and supersaturation values similar to those found in the actual SCWO process. In the experiments, high levels of supersaturation were achieved by injecting a cool aqueous salt solution into a coaxially flowing supercritical water stream. This resulted in a rapid or "shock-like" precipitation of solid salts. These experiments were used to identify important mechanisms of salt growth and estimate particle sizes of the solids formed in the process.

The chapter begins with a description of the experimental apparatus and procedures (Section 8.1) and the general jet characteristics (Section 8.2). The results of the particle collection runs (Section 8.3), laser extinction runs (Section 8.4), and the in-situ size distribution tests (Section 8.5) are then described. Section 8.6 summarizes the experiments and the proposed precipitation mechanisms, while future research directions are addressed in Section 8.7.

8.1 Apparatus and Procedures

8.1.1 Flow System Description

The dynamic experiments were designed to simulate the rapid mixing of a waste stream containing dissolved salts with supercritical water in the SCWO process. The two feeds in the experiments were a pure supercritical water (SCW) stream (typically at 550°C, 250 bar, and flowing at 10.2 g/min) and a cool salt solution (0.5 to 10.0 wt%, typically at 150°C, 250 bar, and flowing at 0.5 g/min). Figure 8.1 shows the apparatus for the shock crystallization experiments. The Inconel 625 optical cell was configured with two large flow tubes (0.912 cm ID) in the top and bottom ports, two window holders
Figure 8.1 Schematic of apparatus for flow/shock crystallization experiments.
in the front and back ports for photographic documentation and light scattering measurements, and two Inconel 625 plugs in the other side ports. The cell was designed to operate to temperatures of 700°C at 300 bar (see Section 6.1).

The supercritical water feed stream is shown in the upper right corner of Figure 8.1. Cold distilled water was fed using a high pressure liquid chromatography pump, and an electrical resistance heater was used to raise the temperature of the water to supercritical. A schematic of the SCW feed heater is shown in Figure 8.2. The heater consisted of two semi-cylindrical, 850 W, hard refractory heating units (Lindberg). The half-shell units had an inner diameter of 7.6 cm and a length of 20.3 cm, with a maximum temperature of 1200°C. A variable transformer was used to regulate voltage to one unit for baseline heat, while the other unit was connected to a temperature controller. The temperature inside the heater was typically held at 630°C. The coiled Hastelloy C276 tubing in the heater was constructed from a 6.1 m (20 ft.) straight piece with a 0.158 cm OD and 0.108 cm ID. Once heated, the SCW stream entered the optical cell through an annular space in the top flow tube. The tubing which connected the feed heater to the cell was wrapped with high temperature heating tape and insulation.

A low-pulse HPLC pump was used to deliver the jet feed to the cell (upper left of Figure 8.1). This feed was either pure deionized, distilled water or a salt solution. For the pure water feed, salt solution samples were introduced into the jet feed stream with a six-port injection valve. The operation of this valve is shown in Figure 8.3. In the load position, the sample loop was filled with the salt solution using a syringe, and in the injection position water from the jet feed pump flushed out the loop. The injection valve was positioned close to the cell to reduce dispersion of the sample as it traveled to the cell. The salt solution was injected co-axially into the SCW stream as a jet using a cooled nozzle (described in section 8.1.2), which passed down the center of the top flow tube.

Three primary temperature measurements were made during a flow experiment. The temperature of the supercritical water feed was measured by a thermocouple in contact with the feed in the high-pressure cross above the cell. The exit temperature of the salt solution jet was estimated with a small OD thermocouple (0.051 cm.) which passed down the center of the nozzle to its tip. The tip of the thermocouple was located
Legend

1. Heater shell (Al sheet metal, 10" dia. and 12" length)
2. Ceramic board insulation
3. Ceramic blanket insulation
4. Cylindrical heating unit (two half shells)
5. Coiled Hastelloy 1/16" tubing
6. Thermocouple
7. Insulated high temperature heating tape
8. 316SS fitting (1/16" to 1/8")
9. 316SS fitting (1/8" to 3/8")
10. 316SS tubing nipple (connects to high pressure cross of injection nozzle)

Figure 8.2  Schematic of cylindrical supercritical water feed heater.
Figure 8.3 Injection valve for introducing salt solution samples into jet feed.
approximately 1.5 mm. before the exit of the nozzle. The temperature of the mixed stream was measured with a 0.159 cm. OD thermocouple, which passed through the bottom flow tube of the cell. All three thermocouples were Type K (Chromel-Alumel) with Inconel 600 sheathing. The temperature of the cell block was also monitored, and used to regulate power to the strip heaters.

After the mixed stream exited the cell, it was quickly quenched using a water-cooled shell-and-tube heat exchanger. The inner tube, which contained the hot cell effluent, had an active length of 1.52 m and was made from Inconel 625 tubing with an ID of 0.158 cm and an OD of 0.953 cm. The outer tube was made from thin walled, 1.27 cm OD stainless steel tubing. Filtered cooling water flow rates of around 1000 cc/min easily lowered the temperature of the cell effluent from its typical exit value of 550°C (flowing at rates between 10 to 15 g/min) to a final temperature below 30°C.

A transducer was located after the heat exchanger for the primary pressure measurement. The transducer was rated to 517 bar (7500 psi) with an accuracy of ±0.5 bar. The pressure was controlled using a hand loaded, low flow back pressure regulator, which was rated to 345 bar (5000 psig). A micrometering valve, located before the back pressure regulator, was used to make fine pressure adjustments during a run.

8.1.2 Water-cooled Nozzle

As discussed above, the salt solution was injected into the cell using an actively cooled nozzle to keep the solution's temperature sub-critical and thus prevent solid salt from precipitating in the nozzle. The internal coolant flow for the nozzle was finely controlled to provide ample insulation of the salt solution jet, while not removing a significant amount of heat from the SCW feed stream. For most of the runs, distilled water was used as the coolant, while nitrogen gas was used in a few early tests. The distilled water was stored in a pressurized stainless steel tank, and the flow rate was controlled using a fine metering valve. Typical nozzle cooling water flow rates ranged from 0.5 to 3.0 g/min.

A schematic of a nozzle assembly is shown in Figure 8.4. The nozzle tip thermocouple was sealed in the upper compression fitting using a drilled out Vespel ferrule. The two brass elbows served as the cooling water hookup lines, and they were
Figure 8.4  Schematic of water cooled nozzle assembly and optical cell flow tube.
drilled out at one end to allow tubing to pass through them. The tubing was soldered to the elbows to seal in the low pressure cooling water. Various size adapters were connected to the medium pressure Inconel 625 cross for the thermocouple, nozzle, and SCW feed connections. The outer nozzle tube was connected to the top adaptor fitting using a compression seal, which fixed its position. The bottom opening of the cross connected to the flow tube, which was inserted into the optical cell.

Figure 8.5 shows a cross section schematic of the coned nozzle tip. The inner and outer tubes were made from Hastelloy C276, while the thermocouple was sheathed with Inconel 600. The flow of the cooling water inside the nozzle is also shown in Figure 8.5. The coned tip of the nozzle was machined from a solid rod of Hastelloy C276. The tip was then connected to the two Hastelloy tubing pieces using an electron beam welding device. In the welding procedure, the nozzle exit was usually partially closed off, and it was reopened using a small drill. The drill size determined the exit diameter of the nozzle.

Table 8.1 lists the various nozzles which were used in the shock crystallization experiments. A total of four nozzles were constructed. Some nozzles are listed twice in Table 8.1, since the exit position of the tip in the cell was altered after a few runs. For an individual nozzle, the first listing, designated with the letter A, represents the original location of the nozzle tip in relationship to the center of the cell. The second listing is the location of the nozzle after it was moved upward and the compression fitting was reconnected, which swaged a second ferrule on the outer tube of the nozzle (below the original ferrule).

### 8.1.3 Operating Procedures

The general operating procedure for a typical flow experiment is outlined in this section. A more detailed step-by-step procedure is given in Appendix 11.2. The system was typically setup the day before a run. The cell was first assembled with both flow tubes inserted in their ports, and a particle collection device secured at the bottom of the cell. The cell was then placed on the optical table, and the nozzle assembly was connected to the top flow tube. The feed lines and exit line were then connected, and the system was pressure tested. Finally, the cell was insulated, and any analytical devices
Figure 8.5  Diagram of coned nozzle tip.
<table>
<thead>
<tr>
<th>Nozzle #</th>
<th>Tip Type</th>
<th>Tip ID (mm)</th>
<th>Tip Location</th>
<th>Distance † (cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1A</td>
<td>flat</td>
<td>0.64</td>
<td>top of window</td>
<td>0.5</td>
</tr>
<tr>
<td>1B</td>
<td>&quot;</td>
<td>&quot;</td>
<td>top of flow tube</td>
<td>10.8</td>
</tr>
<tr>
<td>2A</td>
<td>flat</td>
<td>0.84</td>
<td>at flow tube</td>
<td>2.0</td>
</tr>
<tr>
<td>2B</td>
<td>&quot;</td>
<td>&quot;</td>
<td>in flow tube</td>
<td>5.8</td>
</tr>
<tr>
<td>3</td>
<td>cone</td>
<td>0.84</td>
<td>top of window</td>
<td>0.5</td>
</tr>
<tr>
<td>4A</td>
<td>cone</td>
<td>0.71</td>
<td>at flow tube</td>
<td>2.8</td>
</tr>
<tr>
<td>4B</td>
<td>&quot;</td>
<td>&quot;</td>
<td>in flow tube</td>
<td>5.8</td>
</tr>
</tbody>
</table>

† Distance is measured from tip of nozzle (jet exit) to the center of the cell (middle of window view).
were setup and aligned.

At the beginning of an experiment, the two feed pumps were turned on, and the pressure of the system was raised using the back pressure regulator. Pressures ranged from 200 to 300 bar. The pure water feed heater and the cell's strip heaters were then turned on to slowly heat the system until the desired temperatures were reached. The cell block was continuously heated, typically up to a final temperature between 580 and 600°C (determined by the set-point of the cell temperature controllers). During the heating period, pure water was fed though the nozzle. After a steady state was obtained, a salt solution was introduced into the nozzle feed, and the various light scattering or photographic measurements were performed. At the end of an experiment, the pumps and heaters were turned off, and the system pressure was slowly lowered. During cooling, the system was flushed with nitrogen to remove water vapor, which when condensed would dissolve any formed solids. After reaching ambient temperature, the cell was opened, and the solid salt was collected for scanning electron microscopy (SEM) and X-ray analysis.

8.1.4 Equipment for Video and Photographic Documentation

Video documentation was performed using a Panasonic digital camera connected to a 19" television monitor and a video tape recorder. A 50 mm lens with a 14 mm teleconverter was placed on the camera, and a white light was shinned through the cell for illumination. The camera was focused near the center of the cell, which corresponded to a working distance of around 15 cm. (distance from focal plane to front surface of lens). Since the camera lens was close to the hot cell, a box fan was used to keep the lens cool during a run. A summary of the jets documented on video tape is listed in Appendix 11.3.

Photographs were taken with a 35 mm camera, using both a normal telephoto lens and a stereomicroscope for magnification. In one set of photos, a 135 mm lens and a total of 87 mm of teleconverter spacers were used to provide the correct working distance (over 15 cm.) and ample magnification. With 3x5 inch prints, the final magnification was 2.9x. Photos were also taken with a 50 mm lens and a 21 mm teleconverter, which gave a smaller magnification on the negative. The prints from these negatives were made with
an enlarger in a darkroom. For safety, a sheet of LEXAN (1 cm thick) was placed between the cell and the camera. A fast shutter speed (1/500 s) was used to freeze the jet, while a 60 W light, focused through the rear window of the cell, provided enough illumination for the photos.

A series of photographs were taken using a Wild M8 stereomicroscope in a monocular assembly with a phototube camera attachment. The microscope working distance with a 0.4x objective lens was 18.0 cm (7 in.). The zoom feature of this microscope allowed the total magnification to be continuously varied from 4.8x to 40x (with a 20x eyepiece), while keeping the working distance constant. The microscope required a bright light source. A 200 W light with fiber optic probes was used for illumination. The shutter speed was 1/250 sec.

A schematic of the inside of the cell during the photographic documentation experiments is shown in Figure 8.6. The supercritical water feed flowed along the outer surface of the nozzle, until it mixed with the jet. Nozzle #3 (see Table 8.1) was used, which had its tip situated at the top of the view provided by the windows in the optical cell, which enabled the observation of the initial mixing region of the two streams.

8.1.5 Particle Collection Methods

Four different particle collection methods were used throughout the shock crystallization experiments. The particles were collected inside the cell, after a cooling period under a nitrogen atmosphere. In the initial experiments, the solid salts were carefully gathered from the bottom inner surface of the cell. The bottom flow tube had a fairly sharp contraction, which caused many of the particles in the effluent stream to impinge and stick to it.

The three additional collection methods are shown in Figure 8.7. In the first method, a short section of sapphire tubing was secured at the bottom of the inner cell chamber using a piece of thin nickel-chromium wire. Sapphire was chosen because of its corrosion resistance to supercritical water. The wire was first inserted through the tubing, and then coiled and fitted into the bottom flow tube. Although this procedure did not rigidly fasten the tube, it did keep it from shifting as the cell was assembled. The tubing piece was mounted directly on an SEM stub for particle size and morphology
Figure 8.6  Schematic of cell interior during the shock crystallization experiments. Nozzle tip is shown positioned near the center of the cell.
Figure 8.7  Particle collection methods.
analysis following the experiment. Low-resistance contact cement and silver paint were used to attach the tubing to the stub.

The second particle collection method shown in Figure 8.7 is a thin disk, which also trapped particles in the cell by impingement. The disks were punched out of a 1 mm thick sheet of Hastelloy C276, and had diameters of either 2.38 or 2.22 cm. Two slots were cut in the disk, so it could be secured at the bottom of the cell with a piece of wire. The disk was slightly bent (around ten degrees) to allow the effluent to flow out of the cell. As with the sapphire tube pieces, the disks were attached to SEM stubs for post-mortem particle analysis.

The final particle collection method used was a 1.6 mm thick Hastelloy C276 frit. The purchased frits were made from sintered metal powder, and were listed as being able to trap 2.0 μm particles. The diameter of the frit was reduced from approximately 2.57 to 2.51 cm with a belt sander. As shown in Figure 8.7, the frit laid on top of the bottom flow tube during an experiment.

8.1.6 Extinction Equipment and Procedures

The ancillary equipment used for the extinction measurements is shown in Figure 8.8. The laser and detector were arranged around the optical cell, which was configured to perform the shock crystallization experiments. The laser was a 10 mW, 632.8 nm, unpolarized, Helium-Neon laser with a 5x beam expander, which enlarged the beam diameter to approximately 3.5 mm. A silicon photodiode detector with an active area of 1 cm² was used to measure the laser power. The diode was connected to a picowatt power meter. A chart recorder was used to record the power readings as a function of time.

Ambient light was excluded from the detector with an aperture and a narrow band filter, which only passed light at 0.633 μm (He-Ne wavelength). Early tests using a 5 mm aperture were unsuccessful, because the transmitted laser beam frequently hit the aperture edge. The beam steering was caused by density and refractive index gradients in the cell. The power fluctuations were reduced to acceptable levels (about 5% of the total transmitted power) by using a larger aperture (12.7 mm) and also by attaching clear glass plates to the outer surface of the window retainers, which lowered heat losses from
Figure 8.8  Schematic of equipment used for laser transmission measurements.
the window ports. Average power values were graphically obtained from the strip chart recorder output, which was connected to the power meter.

For safety, eye protection was worn when positioning the laser. The eye goggles were designed to block out He-Ne radiation. A black felt cover was also placed over the frame of the optical table to protect laboratory personnel against a stray reflected laser beam.

8.2 General Jet Characteristics

Observations of pure water and mixed salt solution jet characteristics within the cell were recorded on video tape and photographed. This documented the initial mixing region of the jet with the coaxially flowing supercritical water stream. The effects of jet flow rate, composition and pressure were explored.

8.2.1 Pure Water Jets at 250 bar

Figure 8.9 shows photos of pure water jets mixing with a pure supercritical water stream at a pressure of 250 bar taken with the stereomicroscope. The first four jets appear dark due to the density differences between the subcritical water in the core of the jet and the external supercritical water stream. The bright, collimated light from the fiber optic probe also intensified the "shadow" of the jet. In Figures 8.9(a) to 8.9(d) the exit temperature of the jet was approximately 110 to 130 °C with a density of around 0.95 g/cm³, and the temperature of the supercritical water stream was approximately 545°C with a density of 0.08 g/cm³. The corresponding refractive indices for the jet and the SCW feeds were approximately 1.31 and 1.02, respectively (Schiebener et al., 1990). For the final jet shown in Figure 8.9(e), there was no nozzle cooling, and the jet feed was allowed to heat-up in the nozzle to a supercritical exit temperature of approximately 490°C with a corresponding density of 0.09 g/cm³ and refractive index of 1.03.

Table 8.2 lists the measured mixed stream temperature and the calculated Reynolds number of the jets shown in Figure 8.9. The position of the mixed stream thermocouple in the cell was shown in Figure 8.6. For all the jets, the measured mixed stream temperature range was close to the calculated fully mixed temperature using an enthalpy
Figure 8.9 (a-c) View of pure water jets at various flow rates and temperatures (250 bar, SCW feed: 10.2 g/min, 545°C, Nozzle #3).
(d) 2.0 g/min
110-130 °C

(e) 0.5 g/min
485-495 °C

Figure 8.9 (d-e) View of pure water jets at various flow rates and temperatures (250 bar, SCW feed: 10.2 g/min, 545°C, Nozzle #3).
Table 8.2  The effect of jet flow rate and temperature on the measured mixed stream temperature.†

<table>
<thead>
<tr>
<th>Jet flow, pure H₂O (g/min)</th>
<th>Nozzle cooling (g/min)</th>
<th>Jet exit temperature (°C)</th>
<th>Measured Mixed Temperature # (°C)</th>
<th>Enthalpy Balance Mixed Temperature (°C)</th>
<th>Jet Reynolds number ‡ (4w/πμdₚₒₓ)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.25</td>
<td>2.0</td>
<td>120-145</td>
<td>526-528</td>
<td>530</td>
<td>30</td>
</tr>
<tr>
<td>0.5</td>
<td>1.8</td>
<td>110-140</td>
<td>515-520</td>
<td>512</td>
<td>60</td>
</tr>
<tr>
<td>1.0</td>
<td>1.6</td>
<td>110-130</td>
<td>470-490</td>
<td>480</td>
<td>120</td>
</tr>
<tr>
<td>2.0</td>
<td>1.4</td>
<td>110-145</td>
<td>440-460</td>
<td>437</td>
<td>240</td>
</tr>
<tr>
<td>0.5</td>
<td>0.0</td>
<td>485-495</td>
<td>550-560</td>
<td>546</td>
<td>420</td>
</tr>
</tbody>
</table>

†  Flow Run 45; Pressure = 250 bar; SCW feed: T=550°C, 10.2 g/min; Cell block: T=585°C; Nozzle #3
‡  Nozzle diameter equal to 0.84 mm., wᵢ is the mass flow rate of jet.
#  Mixed stream thermocouple located 2.0 cm below nozzle tip.
balance, which is also listed in Table 8.2. Though all of the jets with a subcritical exit temperature appear turbulent (Figure 8.9(a-d), their exit Reynolds numbers were less than 240, presumably placing them in the laminar region. According to Streeter (1961), the critical Reynolds number for circular jets with uniform properties is 1000, below which turbulent flow cannot be sustained. The jet with a supercritical exit temperature (Figure 8.9(e)), had the highest exit Reynolds number, but appears fairly laminar. This suggests that the turbulence seen in the cool jets resulted from density gradients which caused the jet to break up. There also seems to be a dependence of the mixing rate on the jet flow rate. As the flow was increased, the potential core of the jet (or the unmixed region) appears to lengthen (compare Figure 8.9(a) with 8.9(d)).

8.2.2 Salt Solution Jets at 250 bar

Figure 8.10 shows photos of various salt jets at 250 bar. A pure water jet is also shown for comparison. The photos were taken using 35 mm film, a camera shutter speed of 1/500 sec, and white light entering through the rear window of the cell for illumination. The SCW to jet feed ratio was 20:1, which resulted in a mixed stream temperature of approximately 530°C. Additional heating was also provided by the cell body, which was held at approximately 600°C. The pure water jet shown in Figure 8.10(a) appears fairly unstable due to the density differences in the two feeds. Although the water jets shown in Figures 8.9(b) and 8.10(a) had identical properties, they appear somewhat different, due to the photo lighting. The white bulb used for illumination in the photos shown in Figure 8.10 provided very diffuse light compared to the collimated light from the fiber optic probe used for the photos in Figure 8.9.

The 3.0 wt% NaCl jet shown in Figure 8.10(b) appears somewhat more stable than the pure water jet. The third jet shown in Figure 8.10(c) had an initial concentration of 10.0 wt% NaCl. This jet appears much narrower and more focused than the pure water jet, and can be seen breaking up into droplets with diameters of approximately 0.7 mm. The large vapor-liquid equilibrium region in NaCl-H₂O phase diagram at 250 bar (see Figure 4.7), most likely caused the apparent two-phase flow seen in Figure 8.10(c). In the more dilute 3.0 wt% NaCl jet, the volume of the nucleated liquid phase may have been too small to coalescence into droplets large enough to be visible.
Figure 8.10  View of jets mixing with a coaxially flowing supercritical water stream at 250 bar.

Pressure: 250 bar
Jet Feed: 0.5 g/min
    100 - 110 °C
SCW Feed: 10.2 g/min
    550 °C
Mixed Temperature = 530 °C
Nozzle #3, 0.84 mm diameter
The 3.0 wt% Na\textsubscript{2}SO\textsubscript{4} jet shown in Figure 8.10(d) appears much darker than the previous ones. Possibly, this was caused by small particles which nucleated homogeneously from the solution, scattering the light. This conclusion is also supported by the results of particle collection runs and laser light scattering experiments. In the Na\textsubscript{2}SO\textsubscript{4}-H\textsubscript{2}O system at 250 bar, there is a continuous falloff in solubility as the critical temperature of water is approached, and no vapor-liquid region in the temperature range of interest (see Figure 4.11). Since the solution around the jet also appeared cloudy, some recirculation occurred during the experiment.

The final jet shown in Figure 8.10(e), is a mixed solution containing 3.0 wt% NaCl and 3.0 wt% Na\textsubscript{2}SO\textsubscript{4}. The appearance of the jet is closer to that of the 3.0 wt% NaCl jet, and no noticeable scattering from fine particles is evident, as was the case for the 3.0 wt% Na\textsubscript{2}SO\textsubscript{4} jet. As discussed in Section 4.4, Na\textsubscript{2}SO\textsubscript{4} shows increased solubility in high temperature NaCl brines. This could explain the mixed jet appearance, since no Na\textsubscript{2}SO\textsubscript{4} precipitation was observed in the initial mixed region of the jet.

### 8.2.3 Salt Solution Jets at 200 bar

A number of jets were examined at a pressure of 200 bar. This pressure is below the critical point of pure water (221 bar), and significant changes in the appearance of the jets were observed. The pure water jet shown in Figure 8.11(a) appears much different than the 250 bar pure water jet shown in Figure 8.10(a). As the 200 bar water jet was heated, it passed through the two-phase, vapor-liquid region in the phase diagram for pure water (see Figure 2.3). This resulted in a narrow liquid jet which appears to become narrower as it flows downward, possibly due to water being vaporized as the jet was heated. The exit Reynolds number of the jet was approximately 62, and it does indeed appear laminar, unlike the 250 bar water jet with a similar Reynolds number of 60.

A 200 bar, 10.0 wt% NaCl jet is shown in Figure 8.11(b). Like the 250 bar NaCl jet shown in Figure 8.10(c), the 200 bar jet also appears to breakup into liquid droplets, but the droplets form closer to the nozzle exit. This could be due to a shift to lower temperature of the vapor-liquid region in the NaCl-H\textsubscript{2}O system as the pressure decreases from 250 to 200 bar (discussed in Section 8.6.1). The initial droplet sizes measured from the photo are approximately 0.8 mm.
(a) Pure $\text{H}_2\text{O}$

(b) 10.0 % NaCl

(c) 5.0% Na$_2$SO$_4$

Pressure: 200 bar
Jet Feed: 0.5 g/min
130 - 150 °C
Pure Water: 10.2 g/min
Feed: 550 °C
Mixed Temperature = 530 °C
Nozzle #3, 0.84 mm diameter

Figure 8.11 View of jets mixing with a coaxially flowing subcritical water stream at 200 bar.
The final jet shown in Figure 8.11(c) is a 5.0 wt% Na₂SO₄ jet, which appears much different than the 250 bar Na₂SO₄ jet (see Figure 8.10(d)). There seems to be no rapid precipitation of fine solids in the 200 bar jet. Also, two-phase, vapor-liquid flow is evident. This later observation is consistent with the Na₂SO₄-H₂O phase diagram, which contains both a three- (V-L-S) and two-phase (V-L) region at pressures below 221 bar (see Section 4.3). These effects will be further explored in future experiments in our laboratory.

8.3 Size and Morphologies of Collected Particles

8.3.1 Collection Efficiencies and Effluent Analysis

Particle collection runs were typically conducted at a pressure of 250 bar with a supercritical water feed rate of 10.2 g/min. The collection techniques were described in Section 8.1.5. For the majority of the runs, a nozzle with its exit in the upper flow tube was used, which is believed to have assured complete mixing of the jet with the supercritical water feed before the stream left the inner chamber of the cell. The relative position of the nozzle and the mixed temperature thermocouple used in the particle collection runs was shown in Figure 8.7. The main parameters varied were the jet composition and flow rate. A limited number of runs with a system pressure of 200 bar and with different SCW feed rates were also conducted.

Table 8.3 summarizes the particle collection runs. In some of the runs, laser transmission measurements were also performed. These values are listed on page 2 of Table 8.3, and are discussed in Section 8.4. The last part of Table 8.3 gives a rough particle size range of the collected solids obtained from SEM analysis. Loose particles were not collected for some runs, and a size range could not be determined. The morphology and size of many of the collected particles are discussed in Sections 8.3.2 and 8.3.3.

The collection characteristics and efficiencies of the various methods depended partly on the type of salt precipitated and the run conditions. The collection efficiency is defined here as the mass of salt deposited on the collection device divided by the total
Table 8.3 Summary of particle collection runs (page 1 of 3).

<table>
<thead>
<tr>
<th>Flow Run # (FR)</th>
<th>Nozzle a</th>
<th>Particle collection method</th>
<th>Pres. (bar)</th>
<th>Jet Feed composition b (wt%)</th>
<th>flow (g/min)</th>
<th>Temp (°C)</th>
<th>Delivery method c</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>#1A</td>
<td>nozzle tip</td>
<td>244</td>
<td>3.0 NaCl</td>
<td>0.5</td>
<td>374-376</td>
<td>cont. 34 min</td>
</tr>
<tr>
<td>2</td>
<td>#1A</td>
<td>bottom of cell</td>
<td>245</td>
<td>3.0 NaCl</td>
<td>2-1.6</td>
<td>265-278</td>
<td>cont. 15 min</td>
</tr>
<tr>
<td>4</td>
<td>#2A</td>
<td>bottom of cell</td>
<td>249</td>
<td>3.0 NaCl</td>
<td>1.0</td>
<td>240-268</td>
<td>cont. 14 min</td>
</tr>
<tr>
<td>5</td>
<td>#2A</td>
<td>bottom of cell</td>
<td>250</td>
<td>3.0 NaCl</td>
<td>0.5</td>
<td>166-212</td>
<td>cont. 24 min</td>
</tr>
<tr>
<td>6</td>
<td>#2B</td>
<td>bottom of cell</td>
<td>251</td>
<td>3.0 NaCl</td>
<td>1.0</td>
<td>110-140</td>
<td>cont. 10 min</td>
</tr>
<tr>
<td>7</td>
<td>#2B</td>
<td>bottom of cell</td>
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<td>115-125</td>
<td>s.l., 0.25 ml</td>
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<td>cont. 60 min</td>
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<td>0.5</td>
<td>275-325</td>
<td>s.l., 5 ml</td>
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<td>1.5</td>
<td>130-150</td>
<td>s.l., 5 ml</td>
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<td>s.l., 2 ml</td>
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<td>0.5 Na₂SO₄</td>
<td>0.3</td>
<td>120-145</td>
<td>s.l., 2 ml</td>
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a) see Table 8.1 for nozzle descriptions
b) i/j Mixed represents i wt% Na₂SO₄ and j wt% NaCl in jet
c) delivery methods: cont. = continuous feed; s.l. = sample loop
Table 8.3 Summary of particle collection runs (page 2 of 3).

<table>
<thead>
<tr>
<th>Flow Run# (FR)</th>
<th>SCW Feed Temp (°C)</th>
<th>Mixed Temp. (°C)</th>
<th>Block Temp. Top (°C)</th>
<th>Bot. (°C)</th>
<th>Nozzle Type</th>
<th>Cooling rate (d) (cc/min)</th>
<th>(I/I_0) (percent)</th>
<th>Turbidity - (\ln (I/I_0))/L</th>
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<td>549</td>
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\(d\) nozzle cooling rates given as cc/min at STP.
Table 8.3 Summary of particle collection runs (page 3 of 3).

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<th>Flow Run# (FR)</th>
<th>Particle size range (μm)</th>
<th>Notes f</th>
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<tr>
<td>1</td>
<td>large porous solid crystallized on nozzle tip (see Figure 8.12)</td>
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<tr>
<td>2</td>
<td>large agglomerate formed on bottom of cell, hard to discern primary particles</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>large agglomerate formed on bottom of cell, hard to discern primary particles</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>large agglomerate formed on bottom of cell, some fine particles collected</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>20 - 80 particle clusters collected, primary particle size range given (Fig. 8.14)</td>
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</tr>
<tr>
<td>7</td>
<td>some particles on window surface, not enough for size analysis</td>
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</tr>
<tr>
<td>8</td>
<td>1 - 3 large agglomerate collected, primary particle size range given (Fig. 8.19)</td>
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</tr>
<tr>
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<td>1 - 25 teardrop shaped large particles and some larger agglomerated solids (8.23)</td>
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</tr>
<tr>
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<td>0.5 - 10 partial collection of particles which stuck to tube surface (Fig. 8.25)</td>
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</tr>
<tr>
<td>16</td>
<td>too few particles collected</td>
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<td>2 - 8 large solid collected, splattered appearance</td>
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</tr>
<tr>
<td>19</td>
<td>1 - 10 partial collection of particles which stuck to tube surface</td>
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</tr>
<tr>
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<td>blank run, no significant pitting of sapphire tube surface occurred</td>
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</tr>
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<td>0.5 - 1 very small number of particles collected (Fig. 8.26)</td>
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</tr>
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<td>10 - 50 many kernal shaped particles collected</td>
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</tr>
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<td>24</td>
<td>5 - 30 many large teardrop shaped agglomerates collected</td>
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</tr>
<tr>
<td>25</td>
<td>hard solid salt formed on bottom walls of cell, glassy appearance</td>
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<tr>
<td>27</td>
<td>20 - 100 many particles collected (Fig. 8.13)</td>
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<tr>
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<td>5 - 25 many large teardrop shaped agglomerates collected (Fig. 8.20)</td>
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<tr>
<td>30</td>
<td>5 - 25 small flaky particles (Fig. 8.15)</td>
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<tr>
<td>32</td>
<td>1 - 30 collected agglomerates on disk and in fitting before heat exchanger (8.21+22)</td>
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</tr>
<tr>
<td>33</td>
<td>20 - 100 particle clusters and one large agglomerate collected (Fig. 8.16)</td>
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</tr>
<tr>
<td>34</td>
<td>hard solid salt formed on bottom walls of cell, glassy appearance</td>
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</tr>
<tr>
<td>35</td>
<td>1 - 4 particles packed together to form a filter cake on surface of frit (Figs. 8.27+37)</td>
<td></td>
</tr>
<tr>
<td>36</td>
<td>hard solid salt formed on bottom walls of cell, glassy appearance</td>
<td></td>
</tr>
<tr>
<td>37</td>
<td>20 - 90 particles piled-up near center of frit (Fig. 8.17)</td>
<td></td>
</tr>
<tr>
<td>38</td>
<td>0.5 - 2 particles packed together to form a filter cake on surface of frit (Fig. 8.37)</td>
<td></td>
</tr>
<tr>
<td>40</td>
<td>0.5 - 2 particles stuck to top surface of frit, not enough fed to form filter cake (8.28)</td>
<td></td>
</tr>
<tr>
<td>41</td>
<td>1 - 3 few particles on disk surface, most collected between disk and cell wall (8.25)</td>
<td></td>
</tr>
<tr>
<td>42</td>
<td>2 - 50 particles piled-up near center of frit (Fig. 8.29)</td>
<td></td>
</tr>
<tr>
<td>47</td>
<td>10 - 50 agglomerates deposited on bottom of cell walls (flow tube surface) (Fig. 8.24)</td>
<td></td>
</tr>
<tr>
<td>48</td>
<td>1 - 3 particles packed on top surface of frit, partially coalesced (Fig. 8.40)</td>
<td></td>
</tr>
<tr>
<td>49</td>
<td>1 - 3 particles packed on top surface of frit, partially coalesced (Fig. 8.40)</td>
<td></td>
</tr>
<tr>
<td>51</td>
<td>500 - 1000 large particles on frit surface, porous (Fig. 8.18)</td>
<td></td>
</tr>
<tr>
<td>52</td>
<td>1 - 3 particles packed on top surface of frit, partially coalesced (Fig. 8.42)</td>
<td></td>
</tr>
<tr>
<td>53</td>
<td>1 - 3 particles packed on top surface of frit, partially coalesced (Fig. 8.42)</td>
<td></td>
</tr>
</tbody>
</table>

e) typical particle size range from SEM analysis (not all particles collected in some runs).

f) figure number of SEM photomicrographs given in parentheses
mass of salt in the jet feed. In the runs where solids were collected on the bottom inner surface of the cell or on a piece of sapphire tubing, exact collection efficiencies could not be easily determined. The sodium chloride solids tended to stick to the bottom flow tube, and then buildup on top of each other. After cooling, the particles appeared white and were easily removed. Usually, fewer sodium sulfate particles were trapped by the sapphire tube or stuck to the bottom flow tube. This is believed to be partly due to the smaller size of the sodium sulfate particles precipitated from the supercritical water. In the mixed salt solution runs, loose particles were not be collected. The salt appeared as a hard, caked solid, on and around the bottom flow tube or on the surface of the sapphire tube or Hastelloy disk.

When particles were gathered on a Hastelloy disk or frit, collection efficiencies could easily be determined. Table 8.4 lists typical efficiencies for various jet compositions and pressures. The efficiencies for the NaCl runs were all very high, and the particles were usually concentrated in a pile near the center of the circular disk or frit. In addition to the solids gathered on the collection device, a small fraction of particles also stuck to the inner walls of the cell.

High collection efficiencies for the sodium sulfate particles precipitated from supercritical water at 250 bar were only obtained with the Hastelloy frit, as shown in Table 8.4 for Flow Run 35 (FR35) and FR38. The collection efficiencies of the Hastelloy disk or sapphire tube were significantly lower, while also being concentration dependent (see FR32 and FR41 in Table 8.4). The sodium sulfate experiment at 200 bar (FR42) showed a marked increase in collection efficiency for the Hastelloy disk. This is believed to be due a change in the precipitation mechanism, which caused larger particles to be formed (discussed in Section 8.6.2).

Effluent samples were taken during many of the particle collection runs to test for soluble corrosion products and sodium ion content. The effluent collection was started near the moment of salt solution injection, and continued for around 10 minutes after all of the solution flowed through the cell. This assured that any salt not precipitated would be collected. The samples were analyzed with an Inductively Coupled Plasma (ICP) atomic emission spectroscopy instrument. Table 8.5 lists the results. In addition to sodium (Na), the effluent was tested for molybdenum (Mo), chromium (Cr), nickel (Ni),
<table>
<thead>
<tr>
<th>Flow run #</th>
<th>Jet Composition</th>
<th>Collection Method</th>
<th>Collection efficiency ‡ (%)</th>
<th>Appearance of solids</th>
</tr>
</thead>
<tbody>
<tr>
<td>32</td>
<td>3.0 wt% Na₂SO₄</td>
<td>bent disk</td>
<td>&lt; 30</td>
<td>other particles were collected on cell walls and in downstream fitting</td>
</tr>
<tr>
<td>33</td>
<td>10.0 wt% NaCl</td>
<td>bent disk</td>
<td>96.2</td>
<td>concentrated near center of disk</td>
</tr>
<tr>
<td>35</td>
<td>3.0 wt% Na₂SO₄</td>
<td>2.0 μm frit</td>
<td>88.7</td>
<td>filter cake on frit surface</td>
</tr>
<tr>
<td>37</td>
<td>3.0 wt% NaCl</td>
<td>2.0 μm frit</td>
<td>88.0</td>
<td>concentrated near center of disk</td>
</tr>
<tr>
<td>38</td>
<td>0.5 wt% Na₂SO₄</td>
<td>2.0 μm frit</td>
<td>94.5</td>
<td>filter cake on frit surface</td>
</tr>
<tr>
<td>41</td>
<td>1.0 wt% Na₂SO₄</td>
<td>bent disk</td>
<td>&lt; 5</td>
<td>most salt packed around edge of disk, little on surface</td>
</tr>
<tr>
<td>42</td>
<td>1.0 wt% Na₂SO₄</td>
<td>bent disk</td>
<td>&gt; 90.0</td>
<td>loose particles on disk surface</td>
</tr>
<tr>
<td>51</td>
<td>3.0 wt% NaCl</td>
<td>2.0 μm frit</td>
<td>&gt; 90.0</td>
<td>large loose particles on disk surface</td>
</tr>
</tbody>
</table>

† Unless otherwise noted, Pressure = 250 bar; SCW feed: T = 550°C, 10.2 g/min; Jet feed: 0.5 g/min, T = 110-140°C, nozzle #4B (in flow tube), see Table 8.3 for complete run conditions.
‡ Collection efficiency defined as weight of solid on collection device divided by total weight of salt in jet feed.
Table 8.5  ICP metal ion analysis of effluent from particle collection runs.

<table>
<thead>
<tr>
<th>Flow Run†</th>
<th>Mo</th>
<th>Cr</th>
<th>Ni</th>
<th>Fe</th>
<th>Au</th>
<th>Na</th>
</tr>
</thead>
<tbody>
<tr>
<td>32 (SS)</td>
<td>0.227</td>
<td>0.263</td>
<td>0.039</td>
<td>0.018</td>
<td>0.044</td>
<td>2.5</td>
</tr>
<tr>
<td>33 (SC)</td>
<td>0.046</td>
<td>0.055</td>
<td>1.969</td>
<td>0.019</td>
<td>0.044</td>
<td>25.6</td>
</tr>
<tr>
<td>34 (Mix)</td>
<td>0.115</td>
<td>0.059</td>
<td>0.812</td>
<td>0.022</td>
<td>0.038</td>
<td>53.7</td>
</tr>
<tr>
<td>35 (SS)</td>
<td>0.067</td>
<td>0.026</td>
<td>0.265</td>
<td>0.015</td>
<td>0.038</td>
<td>0.14</td>
</tr>
<tr>
<td>36 (Mix)</td>
<td>0.040</td>
<td>0.051</td>
<td>0.973</td>
<td>0.016</td>
<td>0.024</td>
<td>16.9</td>
</tr>
<tr>
<td>37 (SC)</td>
<td>0.044</td>
<td>0.031</td>
<td>1.860</td>
<td>0.343</td>
<td>0.030</td>
<td>19.2</td>
</tr>
<tr>
<td>38 (SS)</td>
<td>0.136</td>
<td>0.022</td>
<td>0.291</td>
<td>0.011</td>
<td>0.025</td>
<td>0.17</td>
</tr>
<tr>
<td>40 (SS)</td>
<td>0.067</td>
<td>0.020</td>
<td>0.161</td>
<td>0.010</td>
<td>0.025</td>
<td>0.25</td>
</tr>
</tbody>
</table>

† Salt type for run given in parentheses with SS = sodium sulfate, SC = sodium chloride, and Mix = SS and SC.
and iron (Fe), which are all elements found in Inconel 625 and Hastelloy C276, and for gold (Au), which was used to plate the copper gaskets and seal the windows. The only appreciable corrosion product in the effluent was Nickel, which in some samples reached levels up to 2.0 ppm. All of the effluent samples were clear.

The sodium ion content of the effluent samples was very low for all of the analyzed runs, while being lowest in the experiments with sodium sulfate jets. As discussed in Chapter 7, sodium sulfate has a solubility of less than 1 ppm in supercritical water at 250 bar and 550°C, while NaCl has a solubility of approximately 130 ppm at identical conditions. The Na\(^+\) analysis agrees with the general solubility trends, with the sodium ion content in the samples from runs with sodium sulfate typically two orders-of-magnitude less than observed in the sodium chloride runs. It is not possible to quantitatively compare the sodium content in the cell effluent with the solubility values, since fine nucleated particles may have been entrained in the effluent and redissolved before analysis. This could explain the high sodium ion content measured in the sample from FR32. Additionally, the effluent was collected over a period encompassing the salt solution sample injection. This caused some dilution of the effluent samples (never more than 50%), due to collection of pure water.

### 8.3.2 NaCl Solids

This section discusses morphologies and sizes of typical solids collected during the rapid crystallization of sodium chloride from supercritical water. One run at a subcritical pressure of 200 bar is also described. Much of the mechanistic interpretation of these results will be reserved until the end of this chapter (Section 8.6.1). The complete run conditions for the particle collection experiments discussed below were listed in Table 8.3.

In the initial shock crystallization runs, nitrogen was used as the internal cooling fluid for the nozzle. Although the nitrogen provided enough cooling to prevent solid precipitation inside the nozzle, the jet feed did exit at temperatures close to the vapor-liquid region in the NaCl-H\(_2\)O system at 250 bar. This was evident during the first shock crystallization run with a 3.0 wt\% NaCl solution. As the solution exited the nozzle, which was in the view provided by the sapphire windows in the optical cell, a rapid
growth of solid salt occurred on the nozzle tip. It is believed that the observed solid growth was a phase transformation from a concentrated liquid brine into pure solid NaCl. Since the measured exit temperature of the jet was 380°C and the inner walls of the nozzle were most likely hotter, it is feasible that the dense brine formed in the nozzle and crystallized as it came in contact with the SCW stream. Figure 8.12 shows two scanning electron microscope (SEM) photomicrographs of the solid which formed on the nozzle tip. The solid piece was over 3 mm long, with many cavities in its surface (top photo in Figure 8.12). At higher magnifications, the pores appear to penetrate deep into the solid (bottom photo in Figure 8.12).

In the majority of the shock crystallization experiments, water was used as the nozzle coolant, which enabled the jet exit temperature to be keep relatively low compared to the supercritical water feed temperature. Typical feed exit temperatures were between 100 to 150 °C. Figure 8.13 shows the particles formed from a 3.0 wt% NaCl jet flowing at 0.5 g/min. The particles were grouped in clusters of amorphous kernel shaped particles with lengths between 10 and 100 μm. At higher magnification, the particles appeared to have many hollow inner regions. Similar particles were formed from a 3.0 wt% NaCl jet flowing a 1.0 g/min, as shown in Figure 8.14. Solid growth from concentrated brine droplets could account for the morphology of the particles.

The size of the collected sodium chloride particles was affected by the jet concentration. Figures 8.15 and 8.16 show SEM photomicrographs of particles formed from a 0.5 wt% NaCl jet and a 10.0 wt% jet, respectively. Many of the solids formed from the dilute, 0.5 wt% jet appear shell-like, and are much smaller than the solids collected from the more concentrated jet. Although the solids formed from the 10.0 wt% jet had a similar size range as those formed from the 3.0 wt% jets, the fraction of particles with diameters over 50 μm seemed to increase.

The solids shown in Figures 8.13 to 8.16 were all trapped at the bottom of the optical cell by impingement on the flow tube, a piece of sapphire tubing, or a Hastelloy disk. Once a few particles stuck to the collection device surface, others were readily trapped. With the 2.0 μm Hastelloy frit or disk, the NaCl particles usually formed a pile concentrated near the surface. Figure 8.17 shows the upper surface a frit, which was used to collect solids formed from a 3.0 wt% jet. Most of the loose particles, which were piled
Figure 8.12  SEM photomicrographs of porous NaCl particle deposited on nozzle tip (FR1, Jet feed: 3.0 wt% NaCl, 0.5 g/min, 370-380°C; SCW feed: 10.2 g/min, 550°C; Pressure = 250 bar; see Table 8.3 for complete run conditions).
Figure 8.13  SEM photomicrographs of NaCl particles precipitated from a 3.0 wt% jet flowing at 0.5 g/min (FR27, Jet feed: 115-135°C; SCW feed: 10.2 g/min, 538°C; Pressure = 250 bar).
Figure 8.14  SEM photomicrographs of NaCl particles precipitated from a 3.0 wt% jet flowing at 1.0 g/min (FR6, Jet feed: 110-140°C; SCW feed: 10.2 g/min, 534°C; Pressure = 251 bar).
Figure 8.15  SEM photomicrographs of NaCl particles precipitated from a 0.5 wt% jet flowing at 1.0 g/min (FR30, Jet feed: 110-125°C; SCW feed: 10.2 g/min, 550°C; Pressure = 249 bar).
Figure 8.16  SEM photomicrographs of NaCl particles precipitated from a 10.0 wt% jet flowing at 0.5 g/min (FR33, Jet feed: 115-130°C; SCW feed: 10.3 g/min, 556°C; Pressure = 250 bar).
Figure 8.17  SEM photomicrographs of NaCl particles trapped on frit surface (FR37, Jet feed: 3.0 wt%, 0.5 g/min, 120-145°C; SCW feed: 10.3 g/min, 562°C; Pressure = 253 bar).
on the surface, were removed by taping side of the frit, and only the particles lodged in the cracks remained.

The particles shown in Figure 8.18 were collected at 200 bar, and formed from a 3.0 wt% NaCl jet flowing at 0.5 g/min. The top SEM photomicrograph shows the overall morphology of the particles, whose lengths ranged from 0.5 to 1.0 mm. The lower SEM in Figure 8.18 is a magnification of the surface of one of the particles, which appears very porous. The particles formed at 200 bar were over an order-of-magnitude larger than the particles formed from similar jets at 250 bar.

8.3.3 Na₂SO₄ Solids

This section discusses morphologies and sizes of typical solids collected during the rapid precipitation of sodium sulfate from supercritical water. One run at a subcritical pressure of 200 bar is also described. Much of the mechanistic interpretation of these results will be reserved until the end of the chapter (Section 8.6.2).

The dark appearance of the sodium sulfate jet shown in Figure 8.10(d) was attributed to light scattering by fine particles. Many of the particle collection runs verified that small micron-size particles were precipitated, though with some particle collection methods only the largest particles were gathered. The large particles appeared as partially coalesced agglomerates of micron-size primary particles.

Figure 8.19 shows a magnified view of a large agglomerate collected from the bottom of the optical cell during a flow run in which a cool, jet of 3.0 wt% Na₂SO₄ flowing at 1.0 g/min was mixed with a supercritical water stream flowing at 10.2 g/min. The nozzle tip for this run was situated in the upper flow tube, and the downstream fully mixed region of the jet and SCW appeared extremely dark. Since salt particles at these conditions tend to be "sticky", the small particles which caused the turbidity most likely agglomerated together at the bottom of the cell. As with the NaCl runs, extreme levels of supersaturation were achieved during the experiment. The Na₂SO₄ solid shown in Figure 8.19 comprised many small particles which were fused together. Most of the primary particles were between 1 and 2 μm long.

Similar runs to that described above, with a jet feed of 0.5 g/min, were conducted with either a sapphire tube or a Hastelloy disk secured in the cell to collect the
Figure 8.18  SEM photomicrographs of NaCl particles precipitated from a 3.0 wt% jet mixed with subcritical water at 200 bar, (a) overall morphology, (b) surface of particle, (FR51; Jct feed: 0.5 g/min, 115-130°C; Pure water feed: 10.2 g/min, 553°C).
Figure 8.19  SEM photomicrographs of Na$_2$SO$_4$ particles precipitated from a 3.0 wt% jet flowing at 1.0 g/min; collected at bottom of cell (FR8, Jet feed: 107-141°C; SCW feed: 10.2 g/min, 532°C; Pressure = 249 bar).
precipitated solids. It is believed that only the larger particles were trapped, while the finer solids flowed around the collection devices and escaped in the effluent. Figure 8.20 and 8.21 show the particles collected on the sapphire tube and the Hastelloy disk, respectively. The particles appear fairly spherical with long tails, and widths between 5 and 25 μm. It is possible that the particles were formed by agglomeration and partial coalescence of smaller primary particles with diameters of approximately 1 to 3 μm. This is consistent with calculated average particle sizes from laser extinction measurements (discussed in Section 8.4.3) and measured sizes of particles collected on a Hastelloy frit (discussed below). The agglomerates most likely formed near the jet exit where high salt concentrations existed. The tails of the particles may have been caused by shear forces from velocity gradients in the jet, which deformed the soft, sticky solids.

In many runs (except those using a Hastelloy frit to collect particles), sodium sulfate solids accumulated in the Inconel fitting located after the cell and before the downstream cooling water heat exchanger. One such particle was cylindrical with a diameter of approximately 2 mm and a length of nearly 1 cm. As shown in the SEM photos in Figure 8.22, the solid consisted of small primary particles with diameters between 1 to 5 μm. The particles were collected during the same run as the solids shown in Figure 8.21. Most likely, the Hastelloy disk only collected particles with dimensions above approximately 5 μm, while the smaller particles flowed out of the cell in the effluent stream. Other fine particles, which may have been smaller than 1 μm, were visible in the tubing beyond the Inconel fitting.

Spherical, tailed agglomerates were also collected on the bottom surface of the optical cell during an experiment with the nozzle tip situated near the center of the cell (FR9). The residence time of the mixed solution in the cell during this run was approximately 5 seconds, compared to about 10 sec for FR32. The collected particles from FR9 are shown in Figure 8.23, and the general size and shape of the agglomerates are similar to those collected during FR32 (shown in Figure 8.21). Thus, the particles most likely formed near the jet exit, and not further downstream.

A single run was conducted with the cell block temperature held at approximately 400°C, and the nozzle tip located at the top of the window (Flow Run #47, FR47). The jet feed was 3.0 wt% Na₂SO₄ flowing at 0.5 g/min, while the supercritical water feed rate
Figure 8.20  SEM photomicrographs of Na$_2$SO$_4$ particles precipitated from a 3.0 wt% jet flowing at 0.5 g/min; collected on sapphire tube (FR28, Jet feed: 110-130°C; SCW feed: 10.2 g/min, 548°C; Pressure = 248 bar).
Figure 8.21 SEM photomicrographs of Na₂SO₄ particles precipitated from a 3.0 wt% jet flowing at 0.5 g/min; collected on a Hastelloy disk (FR32; Jet feed: 110-130°C; SCW feed: 11.0 g/min, 555°C; Pressure = 250 bar).
Figure 8.22  SEM photomicrographs of Na₂SO₄ particles precipitated from a 3.0 wt% jet; collected in the high pressure fitting located between the optical cell and the heat exchanger (FR32, Jet feed: 0.5 g/min, 110-130°C; SCW feed: 11.0 g/min, 555°C; Pressure = 250 bar).
Figure 8.23  SEM photomicrographs of Na$_2$SO$_4$ particles precipitated from a 3.0 wt% jet with the nozzle tip located near the center of the cell; collected on bottom inner surface of cell (FR9, Jet feed: 0.5 g/min, 104-125°C; SCW feed: 10.2 g/min, 552°C; Pressure = 249 bar).
was 10.2 g/min. The low cell block temperature caused significant cooling of the SCW stream and also a low mixed stream temperature of about 395°C, which led to a delay in solids precipitation. During the other runs with cell block temperatures near 600°C and mixed temperatures of about 550°C, solids precipitation occurred immediately as the jet exited the nozzle. In FR47, the jet became cloudy approximately 1 cm downstream. Figure 8.24 shows Na₂SO₄ particles collected from the bottom of the cell during this run. Although the particles are as large as those shown in Figure 8.23, the long tails observed earlier are missing, which suggests that the particles were not formed in the high shear regions existing near the jet exit.

Na₂SO₄ agglomerate size decreased as the initial jet concentration was lowered. Figure 8.25(a) shows particles collected on a piece of sapphire tubing and formed from a jet with an initial concentration of 1.0 wt% flowing at 0.5 g/min. Very few moderately sized agglomerates were collected, while most of the particles were small fine spheres. Figure 8.25(b) shows an SEM photomicrograph of small partially coalesced particles formed from a 1.0 wt% jet and trapped around the edge of a Hastelloy disk. During the run, very few agglomerates were collected on the disk surface. Figure 8.26 shows the surface of a piece of sapphire tubing secured in the cell during a run with a jet feed of 0.2 wt% Na₂SO₄ flowing at 0.5 g/min. Very few fine micron size particles were captured. This relationship between jet concentration and apparent agglomeration rates will be discussed in Section 9.3.

A Hastelloy frit was employed as a collection device in a number of runs similar to those described above. The particles impinged upon the top surface of the frit and became trapped in the cracks. If the total particle mass and number were high, a filter cake developed on the surface of the frit (evenly dispersed). Figure 8.27(a) shows the top surface of a piece of filter cake formed during the precipitation of particles from a 3.0 wt% Na₂SO₄ jet flowing at 0.5 g/min. The weight of the filter cake, which easily broke off of the frit after the run, accounted for approximately 90% of the salt mass in the jet feed. Other solids, which were stuck on the frit or on the cell walls, were not weighted. The surface of the cake contained cracks, which allowed the SCW effluent to pass through it (see Figure 8.27(a)). Within the accuracy of the upstream pressure gauge [±50 psig (±3.5 bar)], no detectable pressure drop developed during the run. Figure 8.27(b)
Figure 8.24  SEM photomicrographs of Na$_2$SO$_4$ particles precipitated from a 3.0 wt% jet with the optical cell block temperature held at approximately 400°C; collected on bottom inner surface of cell (FR47, Jet feed: 0.5 g/min, 275-325°C; SCW flow: 10.2 g/min, 550°C; Pressure = 252 bar; Mixed stream temperature = 395°C).
Figure 8.25  SEM photomicrographs of Na$_2$SO$_4$ particles precipitated from a 1.0 wt% jet flowing at 0.5 g/min, (a) collected on a piece of sapphire tubing (FR15), (b) trapped around the edge of a Hastelloy disk (FR41). (Jet feed: 120-180°C; SCW flow: 10.2 g/min, 528°C; Pressure = 249 bar).
Figure 8.26  SEM photomicrographs of Na₂SO₄ particles precipitated from a 0.2 wt% jet flowing at 0.5 g/min; collected on a piece of sapphire tubing (FR22, Jet feed: 120-160°C; SCW flow: 10.2 g/min, 535°C; Pressure = 250 bar).
Figure 8.27 SEM photomicrographs of Na₂SO₄ particles precipitated from a 3.0 wt% jet flowing at 0.5 g/min; collected on a Hastelloy frit, (a) surface of filter cake, (b) edge of a piece of the filter cake (FR35, Jet feed: 115-140°C; SCW feed: 10.3 g/min, 560°C; Pressure = 250 bar).
shows the magnified view of an edge of the filter cake. The primary particles are between 1 and 3 μm long, and no large agglomerates are visible. This suggests that the majority of particles formed were less than 3 μm long, and that the large agglomerates collected on the sapphire tube piece and Hastelloy disk (see Figures 8.20 and 8.21) were a small fraction of the total particle concentration.

Figure 8.28 shows the particles formed from a 1.0 wt% jet flowing at 0.5 g/min. Again, a Hastelloy frit was used to collect the particles, but the total mass of the salt solution injected into the cell was kept low, in order to not form a cake on the frit surface. Most of the particles collected appear to be approximately between 1 and 3 μm long, with perhaps some smaller fines stuck to their surface.

One particle collection run was conducted at a subcritical pressure of 200 bar (FR42). The jet feed was a 1.0 wt% Na₂SO₄ solution flowing at 0.5 g/min, and the supercritical water feed was 10.3 g/min. Over 90% of the particles were collected on the Hastelloy disk secured in the cell, unlike similar runs at 250 bar, where disk collection efficiencies were less than 5%. Figure 8.29 shows the typical particles collected during the 200 bar run. The size distribution is wide, however, there are a significant number of large particles over 25 μm in length. The particles from two comparable runs at a pressure of 250 bar were shown in Figure 8.25. In those runs, very few large particles were collected on the sapphire tube piece or Hastelloy disk.

8.3.4 X-Ray Diffraction Analysis

Powder X-ray diffraction tests were performed on three salt samples from the particle collection runs, to test for crystal structure. Basic X-ray diffraction theory can be found in many physical chemistry textbooks and in a number of monographs, such as Glusker and Trueblood (1985). A short review of the theory was given in Section 6.3.2. In brief, a powder solid is bombarded with X-rays, and the scattered radiation is measured at various angles. Constructive interferences due to scattering off atoms in different crystal planes result in maximums in the scattering pattern, which are related to each other by the Bragg condition. Each crystal substance has its own specific spectra, which can be used as a fingerprint to identify structures. Any randomness or imperfections in the crystal structure will produce diffuse intensities in addition to the sharp Bragg reflections.
Figure 8.28  SEM photomicrographs of Na$_2$SO$_4$ particles precipitated from a 1.0 wt% jet flowing at 0.5 g/min; collected on a Hastelloy frit, (a) particles trapped in cracks of frit, (b) magnified view of particles (FR40, Jet feed: 115-125°C; SCW feed: 10.3 g/min, 545°C; Pressure = 251 bar).
Figure 8.29  SEM photomicrographs of Na$_2$SO$_4$ particles precipitated from a 1.0 wt% jet mixed with subcritical water at 200 bar; collected on a Hastelloy disk (FR42, Jet feed: 0.5 g/min, 110-130$^\circ$C; Pure Water feed: 10.3 g/min, 540$^\circ$C).
in the powder diffraction spectra.

Crystalline sodium chloride is known to exist only in a cubic structure. X-ray diffraction tests for NaCl were performed to determine if any significant imperfections existed in the lattice, since the solid was formed under harsh temperature and supersaturation conditions. Figure 8.30 shows the powder X-ray diffraction results for NaCl formed from a 3.0 wt% jet flowing at 1.0 g/min, in addition to the spectra of analytical grade NaCl purchased from Mallinckrodt. The spectra are virtually identical, with no noticeable peak shifting or broadening due to SCW precipitation conditions.

As discussed in Section 6.3.2, crystalline sodium sulfate has been reported to exist in five polymorphic structures. At temperatures above 241°C, the stable phase is hexagonal, which readily inverts to more stable phases, such as orthorhombic, during cooling. Figure 8.31 shows the powder X-ray diffraction spectra for Na₂SO₄ formed from a 3.0 wt% jet flowing at 1.0 g/min, in addition to the spectra for the analytical grade salt purchased from Mallinckrodt. The spectra are practically identical. Both samples were identified in a computer search as the stable, anhydrous, low-temperature, orthorhombic form of sodium sulfate. Therefore, if the precipitated solid was the high-temperature hexagonal form, no evidence of it remained after cooling.

8.4 Laser Extinction Measurements

The particle collection experiments described in Section 8.3 provided useful size and morphology data. During many of the runs, in-situ laser extinction measurements were performed to quantify the extent of solid formation. In addition, specific extinction experiments were conducted in which a single parameter, such as, jet flow rate, jet composition, system pressure, and SCW flow rate, were varied. These tests helped identify important variables affecting the shock crystallization of salts from supercritical water.
Figure 8.30  Powder X-ray diffraction spectra of NaCl salt samples, (a) analytical grade standard, (b) ground particles precipitated from SCW, (FR6, Jet Feed: 3.0 wt%, 1.0 g/min, 110-140°C; SCW feed: 10.2 g/min, 534°C; Pressure = 251 bar, see Table 8.3 for complete conditions).
Figure 8.31  Powder X-ray diffraction spectra of Na₂SO₄ salt samples, (a) analytical grade standard, (b) ground particles precipitated from SCW, (FR8, Jet Feed: 3.0 wt%, 1.0 g/min, 107-140°C; SCW feed: 10.2 g/min, 532°C; Pressure = 249 bar, see Table 8.3 for complete conditions).
8.4.1 General Definitions and Theory

The theory of light scattering and absorption has been fully described in a number of classic works (van de Hulst, 1957; and Kerker, 1969), and two recent books have discussed recent developments in the field (Bayvel and Jones, 1981; and Bohren and Huffman, 1983). Here, only a brief review of the theory for light extinction will be given, along with the use and limitations as applied to the present experimental program.

Extinction is the attenuation of light intensity due to scattering and absorption as it passes through a medium. In the shock crystallization experiments, the attenuation was caused by scattering from either small solid particles or liquid droplets. The extinction from a non-interacting, monodisperse, dilute suspension of particles can be described by a form of the Beer-Lambert law;

\[ T = I / I_o = \exp \left( - N C_{\text{ext}} l \right) \]  \hspace{1cm} (8.1)

where, \( T \) is the transmission, \( I \) and \( I_o \) are the intensities of the transmitted and incident laser beam, respectively, \( N \) is number of particles per unit volume, \( C_{\text{ext}} \) is extinction cross-sectional area, and \( l \) is the path length of the beam through the medium. The Beer-Lambert law is valid in systems were multiple scattering is negligible (low \( N \)). In systems where particle densities are high, multiple scattering will become significant and the transmittance will no longer be an exponential function of particle concentration. Van de Hulst (1957) has stated that multiple scattering must be accounted for if transmission levels are below around 75%. Other researchers have stated that useful size information can be obtained in systems with transmissions as low as 20% (Fenn, 1976).

The extinction cross-sectional area can be written as the sum of the scattering \( (C_{\text{sca}}) \) and absorption \( (C_{\text{abs}}) \) cross-sectional areas;

\[ C_{\text{ext}} = C_{\text{sca}} + C_{\text{abs}} \]  \hspace{1cm} (8.2)

All of the cross-sectional areas are functions of particle size, refractive indexes of the particle and medium, and the properties of the incident light (polarization and wavelength). Exact theory exists for the calculation of cross-sectional areas for a number
of simple shapes, such as, spheres and oriented cylinders. In our study, a computer program provided by Bohren and Huffman (1983) for light scattering calculations for spherical particles (Mie scattering equations) was used.

The scattering efficiency, $Q_{sca}$, is defined as the ratio between the scattering cross-sectional area and the geometric cross-sectional area. For a spherical particle,

$$Q_{sca} = \frac{C_{sca}}{\pi r_p^2} \quad \text{(8.3)}$$

where, $r_p$ is the radius of the particle. The absorption and extinction efficiencies are defined in a similar matter. As the diameter of a particle becomes much greater than the wavelength of the incident light, the extinction efficiency reaches an asymptotic value of 2. This results from the combined effects of refraction, reflection, and diffraction, and simplifies calculations for large particles. For particle sizes of the same order of magnitude as the wavelength of light, the extinction efficiency oscillates with particle size (van de Hulst, 1957).

Two parameters which influence light extinction by a particle are the refractive index and the dimensionless size, alpha. In its most general form, the refractive index of a material is expressed as a complex number;

$$m = n + n_i \, i \quad \text{(8.4)}$$

where $n$ and $n_i$ are the real and imaginary parts of the refractive index, respectively, and $i = \sqrt{-1}$. In this study, the scattering medium consists of inorganic salt particles or brine droplets in supercritical water, which are both nonabsorbing. The imaginary part of the refractive index is zero for nonabsorbing particles, and the laser extinction will be solely due to scattering ($Q_{ext} = Q_{sca}$). In Mie’s theory, the scattering from a sphere is governed by the ratio of the particle size to the wavelength of the light, found in the parameter alpha;

$$\alpha = \frac{\pi d_p}{\lambda} \quad \text{(8.5)}$$
where \( d_p \) is the diameter of the particle and \( \lambda \) is the wavelength of light in the medium.

In extinction measurements, it is very hard to totally eliminate scattered light from striking the detector. This is especially true if the particle diameter is much greater than the wavelength of light, in which case much of the scattered radiation is in the forward direction. Gumprecht and Sliepcevich (1953) proposed a correction factor, \( R_{\text{sca}} \), to account for the scattered light measured by the detector. \( R_{\text{sca}} \) is defined as the ratio of the apparent scattering coefficient to the total scattering coefficient. The equation for \( R_{\text{sca}} \) (developed from diffraction theory) is;

\[
R_{\text{sca}} = 0.5 \left[ 1 + (J_0(\alpha\theta))^2 + (J_1(\alpha\theta))^2 \right]
\] (8.6)

where \( J_0 \) and \( J_1 \) are Bessel functions of order zero and one, respectively, and theta, \( \theta \), is the half angle of the cone seen by the detector, which depends on the geometry of the detection system. In this study, \( \theta \) was approximately 0.02 radians (1.1 degrees).

Figure 8.32 shows the scattering efficiency, \( Q_{\text{sca}} \), and the forward scattering correction factor, \( R_{\text{sca}} \), as a function of particle diameter. \( Q_{\text{sca}} \) was calculated from Mie theory using the program of Bohren and Huffman (1983) with a light wavelength of 632.8 nm, a medium refractive index of 1.0 (water vapor), and a particle refractive index of 1.48 (sodium sulfate at 25°C). The scattering efficiency oscillates with particle diameter. The forward scattering correction factor, \( R_{\text{sca}} \), shown in Figure 8.32(b), was calculated using equation (8.6) with \( \lambda \) equal to 632.8 nm and \( \theta \) equal to 0.02 radians. \( R_{\text{sca}} \) becomes significant for particle diameters greater than about 5 microns.

Using the above modifications, the transmission for a monodisperse system of nonabsorbing, spherical particles of diameter, \( d_p \), is

\[
T = I / I_o = \exp \left[ - N Q_{\text{sca}} R_{\text{sca}} (\pi/4) d_p^2 l \right]
\] (8.7)

In the shock crystallization experiments, the particle number density per cm\(^3\), \( N \), can be related to the mass flow rate of salt in the jet feed. First, it is first assumed that all the salt crystallizes, which is a good approximation since both NaCl and Na\(_2\)SO\(_4\) have negligible solubilities in the supercritical water effluent. Second, it is assumed that an
Figure 8.32  Particle size dependence of functions used in transmission calculations, (a) scattering coefficient, (b) forward scattering correction factor.

$\lambda = 0.633 \text{ um}$

$n_p = 1.48$

$\theta = 0.02 \text{ radians}$

$\lambda = 0.633 \text{ um}$
average or characteristic particle size, \( <d_p> \), can be used to describe the solid particle size distribution which is, of course, not monodisperse. \( N \) is then given as,

\[
N = w_s \cdot \frac{1}{\rho_s} \cdot \frac{6}{\pi <d_p>^3} \cdot \frac{1}{V_f}
\]  

(8.8)

where \( w_s \) is the mass flow rate of salt, \( \rho_s \) is the density of the salt particles, and \( V_f \) is the volumetric flow rate of the mixed stream (cell effluent). Inserting equation (8.8) into equation (8.7) yields,

\[
\frac{I}{I_o} = \exp \left[ -\frac{3}{2} \frac{Q_{sca}}{\rho_s <d_p> V_f} \right] \cdot \left( \frac{2}{\rho_s <d_p> V_f} \right)
\]  

(8.9)

The turbidity is given as,

\[
\tau = -\frac{1}{l} \ln \left( \frac{I}{I_o} \right) = \left[ \frac{3}{2} \frac{Q_{sca}}{\rho_s <d_p> V_f} \right]
\]  

(8.10)

A measurement of the turbidity of a particle suspension can be used to estimate an average particle size, which will be a moment of the actual size distribution (Kerker, 1969). Since the \( Q_{sca} \) often oscillates with particle size, multiple solutions are possible. To help alleviate this problem, the extinction measurements were augmented with SEM analysis of collected particles.

The scattering efficiency is also a function of the degree of polydispersity in a system and the shape of the particles. As the size distribution broadens, the ripple structure of \( Q_{sca} \) disappears and the oscillations begin to decrease (Fenn, 1976; Bohren and Huffman, 1983). For irregular shaped particles, the maxima in the efficiency may also disappear due to random orientations (Fenn, 1976). Due to the uncertainties in \( Q_{sca} \), the average particle sizes calculated from turbidity measurements must be viewed with some caution.
8.4.2 Jets with Na$_2$SO$_4$ Particles

Concentration effects: High turbidity levels were frequently measured with sodium sulfate jets at supercritical pressures. Figure 8.33 shows a strip chart recording of the transmitted laser power during a shock crystallization experiment (FR31) with the nozzle tip located in the upper flow tube. The jet flow rate was 0.5 g/min with an exit temperature of approximately 125°C, while the SCW flow rate was 10.2 g/min. During the run, the pressure remained very constant at 250 bar, as shown in the strip chart trace of the pressure transducer output in Figure 8.33. Throughout the run, 2 ml. samples of Na$_2$SO$_4$ solutions of various concentrations were injected into the jet feed. Approximately two minutes were required for the salt solution to travel from the sample loop to the jet exit, during which time some dispersion occurred. This is evident in the transmission curves in Figure 8.33, which show a gradual rather than a sharp changes. The curves also show the magnitude of the laser power fluctuations.

The transmission was calculated by dividing the transmitted power by the incident baseline power (I/I$_o$). Figure 8.34 shows the transmission measured during FR31. A steady decrease in the transmitted power with increased salt concentration was observed. For the 2.0 wt% jet, the measure transmission was very low (approximately 1%). The raw transmission data are listed in Appendix 11.3.

An average particle size can calculated from the experimental transmission values by solving equation (8.10) either numerically or graphically. Figure 8.35 shows the graphical solution for a 0.4 wt% jet flowing at 0.5 g/min. This corresponds to a salt mass flow rate of 0.002 g/min. The experimental turbidity intersects the curve in two places, which represent two possible average particle sizes. Thus, either an average particle diameter of 0.25 or 1.3 μm could account for the measured transmission. Since the turbidity value only gives a single piece of data for each jet, it is impossible to distinguish between the multiple solutions, which were caused by the oscillatory nature of Q$_{scn}$. Another measurement, such as, the turbidity at a different wavelength, could be used to distinguish between the two diameter values (Kerker, 1969). Nonetheless, uncertainties in Q$_{scn}$ from particle size distribution and non-spherical shape effects would still persist.

A plot of turbidity as a function of jet concentration is linear, if the average
Figure 8.33  Strip chart showing measured laser power during shock crystallization experiments with Na$_2$SO$_4$ jets (FR31).
Figure 8.34 Laser transmission measurements as a function of Na$_2$SO$_4$ jet concentration (FR31, see Appendix 11.3 for complete run conditions and results).
Figure 8.35 Calculated turbidity as a function of particle diameter for a 0.4 wt% Na$_2$SO$_4$ jet flowing at 0.5 g/min, experimental value shown as horizontal line (one point from FR31).
particle size does not depend on jet concentration. The relationship between the salt mass flow rate, \( w_s \), and the jet mass flow rate, \( w_j \), is:

\[
w_s = w_j \left( \frac{\text{wt\% salt in jet}}{100} \right)
\]

(8.11)

Using this definition, equation (8.10) becomes,

\[
\tau = \left[ \frac{3 Q_{\text{sc}} R_{\text{sc}} (w_j/100)}{2 \rho_s <d_p> V_f} \right] \left( \text{wt\% salt in jet} \right)
\]

(8.12)

Figure 8.36 shows the results of FR31 plotted as turbidity versus the jet concentration in wt\%. The linear relationship of equation (8.14) is also plotted in the graph for various average particle diameters. Again, due to the oscillatory nature of \( Q_{\text{sc}} \), each line corresponds to two values of \( <d_p> \). The data shows a surprisingly linear correlation, which suggests a weak dependence of \( <d_p> \) on jet concentration. Although the lower concentration data show an upward bend, the corresponding change in \( <d_p> \) is small. For jets with concentrations greater than about 0.7 wt\%, multiple scattering may be significant, in which case the Beer-Lambert law is no longer valid.

SEM photomicrographs from two Hastelloy frit particle collection runs with 3.0 and 0.5 wt\% Na\(_2\)SO\(_4\) jets are shown in Figure 8.37. The particle sizes appear similar, however, there does seem to be a significant number of fines collected during the 0.5 wt\% run. The degree of coalescence of particles on the frit surface is difficult to specify quantitatively. Consequently, a definite average particle size in solution can not be determined. The large agglomerates in Figures 8.20 and 8.25, which were preferentially collected on the sapphire tube pieces, must have only represented a small fraction of the total precipitated solids, since an average particle size of order 10 \( \mu \)m could not account for the levels of turbidity observed during the runs.

**Jet flow rate effects:** Turbidity measurements were made for series of Na\(_2\)SO\(_4\) solutions at two different jet flow rates (FR14). The results are plotted as a function of salt mass flow rate in Figure 8.38. The turbidity is multiplied by the total mixed volumetric flow
Figure 8.36  Measured laser turbidity as a function of Na$_2$SO$_4$ jet concentration (FR31); lines shown are theoretical values from eq. (8.12) for particle diameters shown.
Figure 8.37  SEM photomicrographs of Na₂SO₄ particles collected on a Hastelloy frit from jets with identical flow rates of 0.5 g/min, but different salt concentrations (FR35 & FR38; Jet feed: 110-140°C; SCW feed: 10.3 g/min, 560°C; Pressure = 250 bar, see Table 8.3 for complete run conditions).
Figure 8.38  Measured turbidity as a function of Na$_2$SO$_4$ mass flow rate (FR14, Jet feed: 110-170$^\circ$C; SCW feed: 10.2 g/min, 542$^\circ$C; Pressure = 250 bar, see Appendix 11.3 for complete run conditions and results).
rate, $V_t$, since this parameter also depends on the jet flow rate. As in FR31, the low concentration results show an upward bend. For the salt mass flow rates of 0.002 and 0.004 g/min, the measured turbidity was slightly higher for the 0.5 g/min jets.

The flow rate effect was further explored by injecting a series of solutions at a constant salt mass flow rate of 0.003 g/min. The jet flow rates were varied from 0.3 g/min to 1.5 g/min, with corresponding jet concentrations of 1.0 to 0.2 wt\%, respectively. The turbidities are shown in Figure 8.39. If there was no effect on the average particle size, the data should fall on a horizontal line, which is not the case. Because of oscillatory nature of $Q_{sa}$ and the unknown particle distribution effects on it, it is difficult to relate the turbidity change to a specific shift in particle size distribution.

To better determine the effect of jet flow rate and concentration, two particle collection runs were performed. The turbidity values from these flow runs, FR48 and FR49, are also plotted in Figure 8.39, while SEM photomicrographs from the runs are shown in Figure 8.40. There does not appear to be a significant difference in particle morphology or size collected during the runs, which seems to contradict the turbidity measurements. However, the particle sizes are in the range were $Q_{sa}$ is a strong function of $<d_p>$. Thus, small changes in the particle size distribution could have caused the significant changes in turbidity shown in Figure 8.39. In the future, experiments varying only jet flow rate, while keeping the concentration constant, should be performed to further explore this effect.

**Pressure effects:** A series of turbidity measurements were conducted where jet flow rate was held constant and the pressure and jet concentration were varied. Figure 8.41 shows the results. The turbidity is multiplied by total volumetric flow rate, $V_r$, to account for the change in the mixed stream specific volume with pressure. There was a minor pressure affect in the supercritical region, 230 and 300 bar, mostly likely only corresponding to a small shift in particle size distribution. Surprisingly, the measured turbidity for the 1.0 wt\% and 3.0 wt\% jets at 200 bar were zero. This dramatic change in the scattering properties of the precipitates as a function of pressure is consistent with the size range of the particles collected from a 3.0 wt\% jet at 200 bar (see Figure 8.29). In the run, most of the particles were captured (over 90\%) with the majority large
Figure 8.39  Effect of jet flow rate on laser turbidity. Na$_2$SO$_4$ jet concentrations varied to keep salt mass flow rate constant at 0.003 g/min (Jet feed: 110-150$^\circ$C; SCW feed: 10.2 g/min, 563$^\circ$C, Pressure = 249 bar).
Figure 8.40 SEM photomicrographs of Na₂SO₄ particles collected on a Hastelloy frit from jets with salt mass flow rates of 0.003 g/min (FR48 & FR49; Jet feed: 130-150°C; SCW feed: 10.2 g/min, 550°C; Pressure = 250 bar, see Table 8.3 for complete run conditions).
Figure 8.41  Effect of system pressure on laser turbidity (FR18, Jet feed: 120-180°C, 0.5 g/min; SCW feed: 10.2 g/min, 562°C; see Appendix 11.3 for complete run conditions and results).
agglomerates over 20 μm.

**Residence time effects:** The residence time of the precipitates in the cell was varied by changing the flow rate of the SCW feed. Turbidity measurements were performed during two particle collection runs with jets of 0.5 wt% Na₂SO₄ flowing at 0.3 g/min. The SCW flow rates in the runs, which were designated FR52 and FR53, were 14.6 g/min and 4.2 g/min, respectively. The residence times were estimated to be 7.7 sec for FR52 and 25 sec for FR53, using the density and flow rate of the mixed stream and the cell volume from the nozzle tip to the surface of the Hastelloy frit (≈25 cm³). As shown in Table 8.6, the measured transmission was significantly higher for FR53 (4.2 g/min SCW feed), which had a lower volumetric flow rate, Vᵣ, and therefore a higher concentration of precipitated particles, N. When the change in Vᵣ is considered (last column of Table 8.6), the difference in the extent of light scattering vanishes. This conclusion is further collaborated by the SEM photos shown in Figure 8.42. The particle size ranges for FR52 and FR53 were both between 1 to 3 μm. Since the effect of residence time on particle size or corrected turbidity was insignificant, the agglomeration rates during the runs must have been low. This will be further discussed in Section 9.3.3.

### 8.4.3 Jets with NaCl Particles

The turbidity measured during shock crystallization experiments with sodium chloride jets was always much less than that for sodium sulfate jets under identical run conditions, while also being frequently unsteady. Table 8.7 lists transmission results from NaCl runs with different jet concentrations at two jet flow rates. In four of the runs, the particles were collected and average sizes from SEM photomicrographs were estimated. Average particle sizes were also calculated from the experimental turbidity from equation (8.10). Since the majority of the NaCl particles had length scales over 5 μm, the scattering coefficient, Qₛₑₐ, was set to 2.0. Most of the calculated values are on the low side of the size ranges from the SEM photos. Figure 8.43 shows the calculated average particle sizes as a function of jet concentration. For both flow rates, there is a definite trend towards larger particles at higher concentrations. This is consistent with the SEM results presented in Section 8.3.2 (see Figures 8.13, 8.15, and 8.16) and listed in Table
Table 8.6  Effect of SCW flow rate on sodium sulfate precipitation.†

<table>
<thead>
<tr>
<th>Flow Run #</th>
<th>SCW flow (g/min)</th>
<th>Residence time (sec)</th>
<th>%T</th>
<th>Turbidity, $\tau$ (cm$^{-1}$)</th>
<th>$V_f$ (cm$^3$/min)</th>
<th>$\tau V_f$</th>
</tr>
</thead>
<tbody>
<tr>
<td>52</td>
<td>14.6</td>
<td>7.7</td>
<td>69.9</td>
<td>0.10</td>
<td>195</td>
<td>20</td>
</tr>
<tr>
<td>53</td>
<td>4.2</td>
<td>25</td>
<td>24.3</td>
<td>0.40</td>
<td>60</td>
<td>24</td>
</tr>
</tbody>
</table>

†  Pressure = 250 bar; Jet feed: 0.5 wt%, 0.3 g/min, 115-145°C; SCW feed: 550°C; (see Table 8.3 for complete conditions).
Figure 8.42  SEM photomicrographs of Na₂SO₄ particles collected on a Hastelloy frit, effect of SCW feed rate (FR52 & FR53; Jet feed: 0.5 wt%, 0.3 g/min, 115-145°C; SCW feed: 550°C; Pressure = 250 bar, see Table 8.3 for complete run conditions).
Table 8.7  Laser transmission measurements with NaCl jets.

<table>
<thead>
<tr>
<th>Flow Run #</th>
<th>flow (g/min)</th>
<th>concentration (wt%)</th>
<th>%T</th>
<th>Turbidity (cm⁻¹)</th>
<th>Particle size range (µm)</th>
<th>Calculated &lt;dₚ&gt; (µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>12</td>
<td>0.5</td>
<td>3.0</td>
<td>87</td>
<td>0.040</td>
<td>--</td>
<td>25</td>
</tr>
<tr>
<td>&quot;</td>
<td>&quot;</td>
<td>10.0</td>
<td>88</td>
<td>0.030</td>
<td>--</td>
<td>79</td>
</tr>
<tr>
<td>17</td>
<td>0.5</td>
<td>1.0</td>
<td>≈70</td>
<td>0.10</td>
<td>2 - 8</td>
<td>5.1</td>
</tr>
<tr>
<td>23</td>
<td>1.0</td>
<td>3.0</td>
<td>23</td>
<td>0.42</td>
<td>10 - 50</td>
<td>7.0</td>
</tr>
<tr>
<td>27</td>
<td>0.5</td>
<td>3.0</td>
<td>≈83</td>
<td>0.053</td>
<td>20 - 100</td>
<td>22</td>
</tr>
<tr>
<td>30</td>
<td>1.0</td>
<td>0.5</td>
<td>35</td>
<td>0.30</td>
<td>5 - 25</td>
<td>1.7</td>
</tr>
<tr>
<td>39</td>
<td>0.5</td>
<td>0.5</td>
<td>94</td>
<td>0.018</td>
<td>--</td>
<td>13</td>
</tr>
<tr>
<td>&quot;</td>
<td>&quot;</td>
<td>1.0</td>
<td>91</td>
<td>0.027</td>
<td>--</td>
<td>16</td>
</tr>
<tr>
<td>&quot;</td>
<td>&quot;</td>
<td>3.0</td>
<td>88</td>
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<tr>
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<td>&quot;</td>
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<td>89</td>
<td>0.027</td>
<td>--</td>
<td>87</td>
</tr>
</tbody>
</table>

* estimated from SEM photomicrographs
† from equation (8.12) with Qₑ = 2.0
‡ Pressure = 250 bar; Jet exit temperature = 100-150°C; SCW feed: 10.2 g/min, 550-565°C, (see Table 8.3 and Appendix 11.3 for exact run conditions).
Figure 8.43  Average particle diameters calculated from transmission measurements with NaCl jets. Data shown in Table 8.7, (Pressure = 250 bar; SCW feed: 10.2 g/min, 550°C; Jet feed: 110-150°C).
8.7. The calculated average particle sizes are also smaller for the 1.0 g/min jet, which may be a result of increased brine dispersion at the higher flow rate.

8.4.4 Mixed NaCl/Na₂SO₄ Solution Jets

Laser transmission measurements were performed on 1.0 wt% Na₂SO₄ jets with varying NaCl concentration. Figure 8.44 shows a sample of the strip chart recording of the laser power and pressure traces during the experiment. The first injection shown was from a solution of 1.0 wt% Na₂SO₄. As the sample exited the nozzle, a rapid drop in the laser power was observed. The next power trace shown in Figure 8.44 is a 1.0 wt% NaCl solution. The resulting decrease in laser power was unsteady and much lower than that observed for the pure Na₂SO₄ jet. The last two injections shown are solutions of salt mixtures. The resulting laser power decrease showed a peculiar pattern, supposedly caused by sample dilution. The middle steady transmitted power measurement corresponds to the actual sample concentration, while the initial and final spikes correspond to the diluted sample. The dilution was caused by dispersion as the sample traveled from the sample loop to the nozzle exit.

Figure 8.45 shows the measured transmission from the mixed solutions as a function of NaCl concentration. The middle region of the laser power traces were used to calculate the transmissions. The transmitted laser power increased with NaCl concentration in the jet. As discussed in section 4.4, sodium sulfate solubility in high temperature aqueous sodium chloride solutions increases with sodium chloride concentration, which would lead to a decreased rate of Na₂SO₄ precipitation and thus greater light transmission. These effects are further discussed in Section 8.6.3.

8.5 In-situ Particle Size Distributions

Salt particles in SCW are susceptible to coalescence and other effects related to their plastic/sticky behavior. Thus particle size and morphology interpretations of in situ conditions based on collected samples is potentially ambiguous. Tests were performed with a Malvern Series 2600c droplet and particle size analyzer to determine the feasibility of in situ size distribution measurements of particles precipitated in supercritical water.
Figure 8.44  Strip chart showing measured laser power during shock crystallization experiments with jets of various compositions (FR39).
Figure 8.45  Effect of NaCl concentration on laser transmission from 1.0 wt% Na₂SO₄ jets (FR39).
8.5.1 Description of Malvern Analyzer

The Malvern analyzer was loaned to us from the MIT Combustion Research Facility. The instrument uses the principles of laser diffraction to determine droplet or particle size distributions between 1 to 1800 µm in six ranges, which depend on the focal length of the lens employed. The instrument was first developed in the 1970's by Switchenbank and co-workers, and later by Felton and Brown, all at the University of Sheffield (Switchenbank et al., 1977; Felton, 1978, 1979; Felton and Brown, 1980; Brown and Felton, 1985).

The principle of operation is shown in Figure 8.46(a). Parallel, monochromatic light from a low power He/Ne laser is passed through a medium containing a dispersed condensed phase. The scattered light at angles between 0 and 11 degrees in the forward direction is focused on to a multi-array detector. Because of the properties of the Fourier transform focal lens, the scattered light pattern does not depend on the position of the particle in the light path. The detector consists of 31 semicircular, silicone photodiodes (shown in Figure 8.46(b)). If the particles are spherical and multiple scattering is negligible, then the theory of Fraunhofer diffraction can be used to iteratively compute the distinct size distribution responsible for the measured energy pattern. Felton (1978) found that multiple scattering effects are minimal for transmissions above 50%, and reasonable size distributions can be estimated for much lower values. Calculation refinements are available to account for multiple scattering effects (Hirleman, 1988; Ulrich and Stepanski, 1989). The instrument also estimates the total particle concentration, by measuring the unscattered light energy focussed at the center of the detector.

Figure 8.47 shows a schematic of the Malvern analyzer configured around the optical cell. The instrument consisted of a transmitter, receiver, and a 286 personal computer (not shown). Two height adjustment stands were constructed from 1.27 cm thick aluminum plates to secure the units to the optical table. The transmitter originally produced a beam with a diameter of 8 mm, which was too wide to enable sufficient scattering angles to be measured through the windows in the optical cell. Thus, a 2 mm beam expander and spacial filter was purchased from Malvern Instruments Inc. (Southborough, MA).
Figure 8.46  Laser diffraction measurement with the Malvern analyzer.
Figure 8.47  Schematic of experimental setup for in-situ tests using Malvern particle size distribution analyzer.
A 100 mm focal lens was used in our experiments, which provided a detectable particle size range of 1.9 to 181 μm. The lens was situated approximately 12 inches from the center of the optical cell, which was well within the 13.5 inch cutoff distance specified by the manufacturer.

A particle standard of soda-lime glass spheres (1 to 30 μm) was used to verify that the instrument was setup and operating properly. New sapphire windows were required for beam alignment. The glass beads were suspended in water in the optical cell by a stirrer. The laser diffraction size distribution was slightly higher than the optical microscopy size distribution provided by the manufacturer, with average diameters (volume basis) of 19.5 and 18.5 μm, respectively. The difference may have been a result of agglomeration, and was considered negligible.

8.5.2 Measured Size Distributions

The first series of experiments were performed at a pressure of 250 bar, with the coned nozzle tip situated in the upper flow tube. The jet flow rate was 0.5 g/min with an exit temperature of 180-220°C. The supercritical water flow rate was 10.2 g/min with an inlet temperature of 565°C. Five salt solution samples were tested. For each run, a background power measurement was first taken. A 2 ml. volume of the sample was then injected into the jet feed, and the size analysis was performed approximately 1 minute after the injection. For each analysis, the 1000 power scans were measured. The scans themselves typically required a total of approximately 40 seconds, while the size distribution regression required an additional 5 to 10 seconds.

During the run, density fluctuations in the cell caused steering of the laser beam. The deflected beam would then strike the inner photo diode rings on the detector. In the regression, the data collected by the inner five detector rings was not used. Thus, some of the scattering information in the large particle size range (approximately 50 to 180 μm) was lost. The density gradients most likely also effected the measurements of the outer detector rings too, since the incident beam and the scattered rays were also deflected. Because of these difficulties, the distributions presented below should be used for qualitative comparison and rough quantitative estimates only. In the future, methods of lowering heat losses from the window ports and thus density gradients in the cell, should

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explored before additional laser diffraction tests are performed.

Figure 8.48 shows the size distribution results from the first Malvern test run. The distributions for the Na$_2$SO$_4$ jets were all below about 5 µm, and were slightly shifted to higher sizes for the more concentrated jets (see Figure 8.48(a-c)). The distributions also show a rapid fall-off at the low end, which mostly likely was caused by high-angle cutoff (vignetting) of the scattered light by the window retainers in the cell. Samples above 1.0 wt% Na$_2$SO$_4$ could not be tested, because the transmission was too low.

Two size distributions from jets of 1.0 and 3.0 wt% NaCl are shown in Figures 8.48(d) and 8.48(e), respectively. The range of sizes detected were consistent with the particle collection and laser transmission experiments. The jagged appearance of the distributions and the abrupt size cutoff at about 25 µm may have been caused by laser beam steering.

A second run was performed to test the effect of pressure and al:$\_$. mixtures on the distributions. The nozzle used in the run had its tip situated high in the upper flow tube, which provided more time for the two streams to mix before passing through the laser beam. It was hoped that this would reduce the power fluctuations during the tests, which was not the case. The first three distributions shown in Figures 8.49(a-c) were obtained from injections made at 250 bar. Both pure salt distributions are similar to those obtained in the first run. The mixed NaCl/Na$_2$SO$_4$ solution produced a bimodal size distribution with peaks at around 4 and 20 µm. The light transmission level for the mixed jet was also generally lower than that for the pure Na$_2$SO$_4$ jets. Again, the size distributions may have been cutoff at the extremes, due to vignetting and the power fluctuations.

The final samples were injected at a system pressure of 200 bar. For both a 0.4 and 2.0 wt% Na$_2$SO$_4$ jet, the transmission was approximately 100%, and no size distribution could be obtained. For NaCl jets of 2.0 and 10.0 wt%, the transmission was also high, around 95%. The distributions for these samples are shown in Figures 8.49(d-e). Both show a shift to the larger sizes as compared to the 250 bar results for NaCl.
Figure 8.48  In-situ particle size distributions measured with Malvern Analyzer for various jet compositions (frequency % by volume, %T is percent transmission).
Figure 8.49  In-situ particle size distributions measured with Malvern Analyzer for various jet compositions and system pressures (frequency % by volume).
8.6 Proposed Precipitation Mechanisms

The precipitation mechanisms proposed in this section were developed in part from the phase behavior of the model salt-water systems (reviewed in Chapter 4), the isobaric phase equilibrium experiments (described in Chapter 6), and the shock crystallization results of this chapter. As a first approximation, salt-water phase relationships can be used to devise possible mechanisms for solid salt formation during the SCWO of a waste stream containing dissolved salts. In the actual SCWO process, components such as gases and organic wastes form a significant percentage of the reactor medium. The mechanisms of solid salt formation in these more complicated systems may also depend on their specific phase relationships.

8.6.1 NaCl Precipitation

The NaCl-H₂O isobaric phase diagrams at 200 and 250 bar are shown superimposed on one another in Figure 8.50. The diagrams were constructed using compiled data from Bischoff and Pitzer (1989) and Linke (1958), and predictions from Pitzer and Pabalan (1986). The concentration axis is linear with an expanded lower section. Also shown in the figure is a schematic of the path taken by a 3.0 wt% NaCl jet, as it is simultaneously heated and diluted by rapid mixing with a hot supercritical water stream. The final dilution factor is twenty. A possible mechanism for shock crystallization in this system is that a highly concentrated aqueous brine serves as a precursor to solid NaCl precipitation. At both pressures, the vapor-liquid region extends over a wide concentration range. This is more apparent in Figure 8.51, which shows the isobaric phase diagrams with a logarithmic concentration axis.

Once the heated jet enters the vapor-liquid region, a disperse concentrated liquid phase will form. The liquid droplets will become more concentrated in salt as the solution gets hotter, while the volume of the liquid phase will diminish due to its increasing salt composition. Once the three-phase temperature is reached, the liquid brine will become unstable, and a phase transformation from vapor-liquid to vapor-solid will occur. At 200 and 250 bar, the three-phase co-existence temperatures are 420 and 450°C, respectively. Table 8.8 summarizes the shock crystallization results for the sodium chloride experiments. The mechanism derived from the phase behavior of the NaCl-H₂O
Figure 8.50 Schematic of heated jet path shown on the temperature-composition NaCl-H$_2$O phase diagram (linear concentration scale).
Figure 8.51  Schematic of heated jet path shown on the temperature-composition NaCl-H₂O phase diagram (logarithmic concentration scale).
Table 8.8 Summary of NaCl shock crystallization results.

<table>
<thead>
<tr>
<th>NaCl at 250 bar</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Jet appearance</strong></td>
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<tr>
<td><strong>Particle collection characteristics</strong></td>
</tr>
<tr>
<td><strong>Laser transmission</strong></td>
</tr>
<tr>
<td><strong>Malvern size distributions</strong></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>NaCl at 200 bar</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Jet appearance</strong></td>
</tr>
<tr>
<td><strong>Particle collection characteristics</strong></td>
</tr>
<tr>
<td><strong>Laser transmission</strong></td>
</tr>
<tr>
<td><strong>Malvern size distributions</strong></td>
</tr>
</tbody>
</table>
system provides a possible explanation for experimental findings. At both pressures, two-phase flow containing liquid droplets was observed. Unstable solid growth from disperse liquid droplets is a possible cause of the amorphous morphology and relatively large size of the NaCl solids. The particles also appeared quite porous with many hollow inner regions, which would be expected if the concentrated brine droplets (up to 50 wt% salt) underwent rapid transformation to pure solid salt and dilute vapor.

Both the size of the photographed liquid droplets and the dimensions of the collected particles increased significantly as operating pressure was lowered from 250 to 200 bar in separate runs. This change was possibly caused by the distinct difference in the shapes of the vapor-liquid regions at 200 and 250 bar (see Figure 8.51). At the subcritical pressure of 200 bar, the vapor and liquid region starts at a point on the boiling curve of pure water (0 wt% NaCl), while at the supercritical pressure of 250 bar the region begins at a point on the binary critical locus (approximately 0.9 wt% NaCl). Therefore, the 200 bar vapor-liquid region is much flatter than the 250 bar region, which may have caused more rapid formation and coalescence of the liquid-phase in the jet. Also, the vapor-liquid region and the three-phase point at 200 bar occur at lower temperatures, which provided less time for the liquid-phase in the jet to disperse.

8.6.2 Na₂SO₄ Precipitation

The 200 and 250 bar Na₂SO₄-H₂O phase diagrams are shown superimposed on top of one another in Figure 8.52. A section of the saturation curve and a schematic of the path taken by a heated 3.0 wt% jet are also plotted. The 250 bar salt solubility curve decreases continuously with increased temperature, and does not intersect the saturation or three-phase line (below which a small, two-phase (V-L) region exists). Therefore, at 250 bar, solid precipitation most likely occurs directly from the homogeneous fluid without first forming a concentrated liquid brine. The precipitation commences once the solubility curve is crossed and continues as the jet is heated to the final mixed temperature.

A summary of the shock crystallization results for sodium sulfate is listed in Table 8.9. At 250 bar, the appearance of the jet, the size of the collected primary particles, and the transmission results are all consistent with the mechanism of homogeneous nucleation.
Figure 8.52  Schematic of heated jet path shown on the temperature-composition $\text{Na}_2\text{SO}_4 - \text{H}_2\text{O}$ phase diagram.
Table 8.9 Summary of Na$_2$SO$_4$ shock crystallization results.

<table>
<thead>
<tr>
<th>Na$_2$SO$_4$ at 250 bar</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Jet appearance</strong></td>
</tr>
<tr>
<td><strong>Particle collection characteristics</strong></td>
</tr>
<tr>
<td><strong>Laser transmission</strong></td>
</tr>
<tr>
<td><strong>Malvern size distribution</strong></td>
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</tbody>
</table>

<table>
<thead>
<tr>
<th>Na$_2$SO$_4$ at 200 bar</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Jet appearance</strong></td>
</tr>
<tr>
<td><strong>Particle collection characteristics</strong></td>
</tr>
<tr>
<td><strong>Laser transmission</strong></td>
</tr>
<tr>
<td><strong>Malvern size distribution</strong></td>
</tr>
</tbody>
</table>

Table 8.10 Summary of mixed solution shock crystallization results.

Mixed NaCl/Na$_2$SO$_4$ Solutions at 250 bar

| **Jet appearance** | 3/3%: clear, more similar to NaCl than Na$_2$SO$_4$ jets |
|--------------------|
| **Particle collection characteristics** | solid caked on bottom cell walls, no loose particles collected |
| **Laser transmission** | transmission decreased as NaCl jet concentration increased |
| **Malvern size distribution** | bimodal distribution of small (< 5 μm) and large (> 15 μm) particles |
and rapid growth.

Below 221 bar, a two- (V-L), and three-phase (V-L-S) region exists in the Na₂SO₄-H₂O system. The 200 bar solubility curve shown in Figure 8.52 intersects the saturation line at approximately, 365°C and 1.0 wt% Na₂SO₄. Although some precipitation of fines could occur as the jet approaches the three-phase temperature, most of the solid will form during the phase transformation from the 1.0 wt% liquid brine to pure solid and a dilute vapor solution. This hypothesis is supported by the large sizes of the sodium sulfate solids collected at 200 bar (see Figure 8.29) and the zero turbidity observed for sodium sulfate jets at 200 bar (see Figures 1.12 and 8.41).

8.6.3 Mixed NaCl/Na₂SO₄ Solution Precipitation

The results of the shock crystallization experiments with mixed salt solutions of NaCl and Na₂SO₄ are summarized in Table 8.10. Many of the findings can be explained using the 250 bar ternary system phase diagram (Figure 4.15). Schematics of the paths of three different heated jets are shown in Figure 8.53 in the upper-portion of the 250 bar phase diagram. Four levels of mixing of the jet and the SCW feed are shown. The initial locations of the jets are all in the homogeneous, liquid phase region (150°C diagram). With the addition of 3.7% of the SCW feed, the jets are partially diluted and heated to approximately 370°C. At this temperature, Na₂SO₄ precipitation should occur from jet c, and perhaps from jet b, which is very close to the qualitatively drawn phase boundary. The amount of precipitation from jet c would also be greater than that from jet b, given the positions of the jets in the S₈-L region. No Na₂SO₄ precipitation would be expected from jet a, even at temperatures up to the fully mixed value of 515°C, since the only solid phase is NaCl, however, a liquid brine phase concentrated in Na₂SO₄ would be formed. This complicated effect of NaCl concentration on Na₂SO₄ precipitation was observed during the transmission measurements. In the SCWO process, micron-size, homogeneously nucleated, sodium sulfate particles are undesirable, since they could become entrained in the reactor effluent and clog filters or downstream heat-exchanger lines. In the future, flow experiments including an air stream should be performed to extend the mixed salt solution results to actual SCWO reactor compositions.

The existence of concentrated brines at temperatures of 515°C and above in the
Pressure = 250 bar

Jet Feed: 0.5 g/min  150 °C
  a: 1.0 wt% Na₂SO₄ & 3.0 wt% NaCl
  b: 3.0 wt% Na₂SO₄ & 3.0 wt% NaCl
  c: 3.0 wt% Na₂SO₄ & 1.0 wt% NaCl

SCW Feed: 10.0 g/min  550 °C

W = H₂O
A = NaCl
B = Na₂SO₄

V = vapor phase
L = liquid phase
S = solid phase
----- tie line

Figure 8.53  Composition of three different jets at various levels of mixing shown on the upper portion of the model ternary system phase diagram at 250 bar.
ternary system could explain the difficulty encountered in collecting particles during the mixed solution jet runs. Any solids which were precipitated may have redissolved in a liquid phase, which collected at the bottom of the cell. In addition, for some mixed solution compositions, only liquid brine droplets may have been formed with no solid precipitation.

8.7 Future Research Directions

In the actual SCWO process, there is usually an additional feed of air or oxygen to the reactor. This could significantly shift the phase boundaries in the model salt-water systems, which would in turn affect the precipitation mechanisms and particle sizes. The effect of gas composition can be explored in the experimental flow system by adding an air compressor, which would mix a gas stream with the SCW stream before the feed heater. A gas/liquid separator could also be added downstream of the optical cell.

The creation of salts by in-situ neutralization of acidic oxidation products is another important source of solids in the SCWO process. Oxidation-neutralization experiments should be performed to determine the sizes of solids formed by this mechanism. Model waste compounds with chlorine and sulfur heteroatoms need to be selected, preferably ones with known oxidation kinetics. The jet feed could be an aqueous solution of an organic compound and NaOH, while either O₂ or H₂O₂ could be added to the SCW feed. The precipitated solids could be collected on a Hastelloy frit, while laser transmission or other light scattering measurements are performed.
Chapter 9.
Modeling of Shock Crystallization

The rapid or shock-like precipitation of salts from supercritical water is complex as it involves multi-component, multi-phase thermodynamics; extreme temperature, density, viscosity, and composition gradients; non-linear nucleation and growth kinetics; and heat, mass, and momentum transfer. At this time, the development of a rigorous model for shock crystallization is not possible, since many (or most) of the required rate parameters are unknown. As a start, the total problem was dissected and only certain individual steps were examined. Section 9.1 describes numerical modeling of a laminar pure water jet issuing into a coaxially flowing supercritical water stream. Estimates of homogeneous nucleation and diffusion-limited growth rates are presented in Section 9.2, while particle growth by agglomeration is discussed in Section 9.3. Finally, future modeling directions are recommended in Section 9.4.

9.1 Numerical Simulations of Laminar Jets

The prediction of velocity and temperature profiles in the experimental jets is desirable to help characterize the rates of mixing and the location of possible phase transformations. As an initial step towards reaching this goal, laminar pure water jets were simulated. For a pure water jet at 250 bar, the transport properties, such as density and viscosity vary greatly with temperature, but the fluid remains in a single phase region (see Figure 2.3).

The transport rates in heated jets are characterized by the Reynolds and Grashof numbers, which are typically evaluated at the exit conditions. For a circular jet, the characteristic length is the nozzle diameter, \( d_{\text{noz}} \). The Reynolds number is given as,

\[
\text{Re} = \frac{u_0 d_{\text{noz}}}{v_0} \quad (9.1)
\]
where \( u_o \) is the jet velocity, \( v_o \) is the kinematic viscosity of the jet fluid evaluated at the jet exit temperature. The Reynolds number characterizes the importance of inertial forces relative to viscous forces in the jet. In a system with density gradients, the Grashof number is used to evaluate the importance of buoyancy forces relative to the viscous forces. The Grashof number is defined as,

\[
Gr = \frac{g (\rho_o - \rho_\infty) L^3}{\rho_o v_o^2}\tag{9.2}
\]

where \( g \) is the gravitational constant (980 \( \text{cm/s}^2 \)), \( \rho_o \) is the density of the ambient fluid, \( \rho_o \) is the exit density of the jet fluid, and \( L \) is a characteristic length. Although the nozzle diameter is often used to evaluate \( Gr \) for vertical jets (Chen and Rodi, 1980), a length scale in the axial direction is more appropriate for jets directed downward, since the gravitational force acts in the direction of flow. Another common dimensionless number used to evaluate buoyant jet flow is the Froude number, which is defined as \( Re^2/Gr \). Thus, the Froude number is the ratio of the inertial to buoyancy forces in a jet,

\[
Fr = \frac{\rho_o u_o^2 d_{noz}^2}{g L^3 (\rho_o - \rho_\infty)}\tag{9.3}
\]

A jet with a \( Fr \) number close to zero is greatly influenced by buoyancy forces, and is referred to as a plume.

Table 9.1 lists the exit properties of a typical water jet used in our studies of shock crystallization with the nozzle tip at the center of the cell. In addition, the properties of the supercritical water stream that would mix with the jet are listed as well. The Reynolds number for either stream is below the critical value for turbulent flow, which is typically stated as 300 (Streeeter, 1961; Chen and Rodi, 1980). The Froude number is very low \((10^2 \text{ to } 10^3)\), which signifies that buoyancy or gravitational forces will be important in determining the mixing rates.
Table 9.1  Typical jet and SCW stream properties.

<p>| | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Nozzle diameter (cm)</td>
<td>0.084</td>
</tr>
<tr>
<td>Inner cell diameter (cm)</td>
<td>2.54</td>
</tr>
<tr>
<td>Pressure (bar)</td>
<td>250</td>
</tr>
<tr>
<td><strong>Jet:</strong></td>
<td></td>
</tr>
<tr>
<td>flow (g/min)</td>
<td>0.50</td>
</tr>
<tr>
<td>temperature (°C)</td>
<td>150</td>
</tr>
<tr>
<td>density (g/cm³)</td>
<td>0.930</td>
</tr>
<tr>
<td>viscosity (g/cm·s)</td>
<td>1.89 x 10⁻³</td>
</tr>
<tr>
<td>velocity (cm/s)</td>
<td>1.61</td>
</tr>
<tr>
<td>Re</td>
<td>67</td>
</tr>
<tr>
<td><strong>SCW:</strong></td>
<td></td>
</tr>
<tr>
<td>flow (g/min)</td>
<td>10.2</td>
</tr>
<tr>
<td>temperature (°C)</td>
<td>550</td>
</tr>
<tr>
<td>density (g/cm³)</td>
<td>0.0786</td>
</tr>
<tr>
<td>viscosity (g/cm·s)</td>
<td>3.25 x 10⁻⁴</td>
</tr>
<tr>
<td>velocity (cm/s)</td>
<td>0.43</td>
</tr>
<tr>
<td>Re</td>
<td>260</td>
</tr>
<tr>
<td><strong>Grashof #,</strong></td>
<td></td>
</tr>
<tr>
<td>with L = d_{boz}</td>
<td>1.3 x 10⁵</td>
</tr>
<tr>
<td>with L = 1 cm</td>
<td>2.2 x 10⁸</td>
</tr>
<tr>
<td><strong>Froude #,</strong></td>
<td></td>
</tr>
<tr>
<td>with L = d_{boz}</td>
<td>3.4 x 10⁻²</td>
</tr>
<tr>
<td>with L = 1 cm</td>
<td>2.0 x 10⁻⁵</td>
</tr>
</tbody>
</table>
9.1.1 Finite Difference Code

A numerical code was written to simulate an axisymmetric jet issuing into an infinite stationary or moving medium. The jet was assumed to be fully expanded with the pressure of the jet equal to the pressure of the surrounding medium. This is a good approximation for a jet emerging from a tube (Hornbeck, 1973). The axisymmetric free jet is illustrated in Figure 9.1. The subscript p denotes the primary (jet) stream, while the subscript s denotes the secondary (SCW) stream. Due to the rough edge caused by weld at the nozzle exit and the close proximity of the inner thermocouple to the exit (see Figure 8.5), the initial nozzle profile was assumed to be flat.

The conversation equations and the boundary conditions for a axisymmetric, laminar free jet are listed in Table 9.2. Since there is a primary flow direction (axially), the standard boundary layer approximations were used (Anderson et al., 1984), with the transverse momentum equation neglected and the diffusion terms for heat and momentum transfer in the axial direction set to zero. Additionally, the enthalpy representation of the heat equation was used. Initially, the energy equation was solved with temperature as the conserved variable, but convergence problems were encountered due to the spike in heat capacity (see Figure 2.4(f)). The mean heat capacity, \(<c_p>\), was used to convert the conduction term back to a temperature driving force. \(<c_p>\) is defined as, \(H_{ref}/T-T_{ref}\). The enthalpy derivative in the conduction term, \(\partial H/\partial r\), is approximated by \((H_{k+1} - H_{k-1})/2\Delta r\), which can be written as, \((T_{k+1} - T_{ref})<c_p> + H_{ref} - (T_{k-1} - T_{ref})<c_p> - H_{ref} \)/ \(2\Delta r\), or \(<c_p>(T_{k+1} - T_{k-1})/2\Delta r\). For property evaluation, the enthalpies at each point were converted to temperature using a table look-up routine (Press et al., 1986). The table was constructed with data from the HGK EOS for pure water (Haar et al., 1984).

The implicit difference representation of Hornbeck (1973) was adapted to solve the conservation equations. An upwind formula was used for the axial derivatives, while a central difference formula was used for the radial derivatives. This allowed a marching solution in the axial direction starting at \(r=0\). At each step, a tridiagonal coefficient matrix was solved for the axial and enthalpy profiles. The corresponding water properties at each point were then updated using a table of temperature versus density, viscosity, and thermal conductivity created with the HGK EOS. Finally, the radial velocity profile was calculated from the continuity equation. This procedure was continued until the velocity
Figure 9.1  Schematic of initial boundary conditions used in the axisymmetric free jet simulations.
Table 9.2  Conservation equations for the finite difference simulation of a steady-state, axisymmetric free jet (with standard boundary layer approximations).

continuity:

\[ \frac{\partial (\rho u)}{\partial z} + \frac{1}{r} \frac{\partial (\rho rv)}{\partial r} = 0 \]

momentum in the axial direction (with \( \partial P/\partial z = 0 \)):

\[ \rho \left( u \frac{\partial u}{\partial z} + v \frac{\partial u}{\partial r} \right) = \frac{1}{r} \frac{\partial}{\partial r} \left( \mu r \frac{\partial u}{\partial r} \right) + g (\rho - \rho_s) \]

energy (neglecting axial conduction):

\[ \rho \left( u \frac{\partial H}{\partial z} + v \frac{\partial H}{\partial r} \right) = \frac{1}{r} \frac{\partial}{\partial r} \left( \frac{k}{<c_p>} r \frac{\partial H}{\partial r} \right) \]

properties at 250 bar (from HGK EOS):

\[ \rho = f(T) \quad \mu = f(T) \quad k = f(T) \]

where, \( z = \) axial coordinate \quad \( r = \) radial coordinate \quad \( u = \) axial velocity

\( v = \) radial velocity \quad \( T = \) temperature \quad \( H = \) enthalpy

\(<c_p> = \) mean heat capacity = \( (H-H_{ref})/(T-T_{ref}) \)

\( \rho, \mu = \) fluid density and viscosity, respectively

\( k = \) fluid thermal conductivity

\( g = \) gravitational constant

\( \rho_s = \) density of secondary stream or medium

Boundary Conditions

\begin{align*}
 u(r,0) &= u_p & H(r,0) &= H_p & \text{for } & r \leq a \\
 u(r,0) &= u_s & H(r,0) &= H_s & \text{for } & r > a \\
 u(\infty, z) &= u_s & H(\infty, z) &= H_s \\
 \frac{\partial u}{\partial r}(0, z) &= 0 & \frac{\partial H}{\partial r}(0, z) &= 0 & v(0, z) &= 0
\end{align*}
and enthalpy values converged, at which time another axial step was taken. The iteration was required since the water properties were a strong function of temperature.

The finite difference grid was set wide enough to assure that the radial properties reached the secondary stream values far away from the jet centerline. Since the flow was axisymmetric, only half of the jet was simulated. To assure that the code was converging, the temperature and velocity profiles were checked as a function of radial and axial step sizes.

9.1.2 Fluid Dynamics Analysis Package (FIDAP)

A finite element simulation program from Fluid Dynamics International, Inc. (Evanston, IL) was also used to model pure water jets. The code, called FIDAP, was run on the MIT Cray X-MP to check our finite difference predictions. It also allowed the actual cell geometry to be easily modeled.

The conservation equations solved by FIDAP for an axisymmetric, laminar jet are listed in Table 9.3. The program solves the complete Navier-Stokes equations, and uses a temperature explicit energy equation. As in the finite difference solution, convergence problems due to the heat capacity spike near the critical temperature were encountered. To obtain convergence, enthalpies were specified as the temperature boundary conditions, and the heat capacity was set to one. Also, the properties were listed in the input file as a function of enthalpy (30 sets of points). To recast the driving force in the conduction term back to temperature, the conductivity was divided by the mean heat capacity, $<c_p>$. After the simulation, the enthalpy profiles from FIDAP were converted to temperature, using the table look-up routine developed for the finite difference simulation.

The FIDAP grid was set wide enough to assure that the secondary stream properties existed around the jet. The outer boundary properties were set equal to the secondary stream initial values. The FIDAP input files used in the jet simulations are listed in Appendix 11.4. The symmetry (or centerline) axis was specified by setting the radial velocity component to zero, while leaving the axial velocity component free (i.e. not specified).
Table 9.3  Conservation equations used in FIDAP for the finite element simulation of a steady-state, axisymmetric free jet (newtonian fluid).

continuity:

$$\frac{\partial (\rho u)}{\partial z} + \frac{1}{r} \frac{\partial (\rho rv)}{\partial r} = 0$$

momentum in the axial and radial directions:

$$\rho \left( u \frac{\partial u}{\partial z} + v \frac{\partial u}{\partial r} \right) = \frac{1}{r} \frac{\partial}{\partial r} \left[ \mu r \frac{\partial u}{\partial r} \right] - \frac{\partial P}{\partial z} + \mu \frac{\partial^2 u}{\partial z^2} + g (\rho - \rho_s)$$

$$\rho \left( u \frac{\partial v}{\partial z} + v \frac{\partial v}{\partial r} \right) = \frac{\partial}{\partial r} \left[ \frac{1}{r} \frac{\partial}{\partial r} (\mu rv) \right] - \frac{\partial P}{\partial z} + \mu \frac{\partial^2 v}{\partial z^2}$$

energy:

$$\rho c_p^\star \left( u \frac{\partial H}{\partial z} + v \frac{\partial H}{\partial r} \right) - \frac{1}{r} \frac{\partial}{\partial r} \left( k^\star r \frac{\partial H}{\partial r} \right) + \frac{\partial}{\partial z} \left( k^\star \frac{\partial H}{\partial z} \right)$$

density:

$$\rho = \rho_s \left[ 1 - \beta_\text{H} \left( H - H_s \right) \right]$$

properties:

$$c_p^\star = 1.0 \quad k^\star = k/c_p^\star = f(H) \quad \mu = f(H) \quad \beta_\text{H} = f(H)$$

where,  
$$z = \text{axial coordinate} \quad r = \text{radial coordinate}$$
$$u = \text{axial velocity} \quad v = \text{radial velocity}$$
$$\rho, \mu = \text{fluid density and viscosity, respectively}$$
$$k = \text{fluid thermal conductivity}$$
$$<c_p> = \text{mean heat capacity} = (H-H_s)/(T-T_s)$$
$$H_s \text{ and } T_s = \text{enthalpy and temperature of secondary stream}$$
9.1.3 Free Jet Predictions

Before the actual water properties were incorporated into the jet simulations, a
constant property jet was modeled to verify the numerical codes. The results of the
simulation are discussed in Appendix 11.4. The velocity and temperature profiles
predicted by FIDAP and the finite difference code were in good agreement.

The first pure water jet modeled had the properties listed in Table 9.1. In the
simulation, the buoyancy force was not considered. The predicted centerline axial
velocity and temperature profiles are shown in Figure 9.2. The temperature profiles from
FIDAP and the finite difference code are nearly identical, while there is a significant
difference in the axial velocity decay curves. This most likely is due to the more exact
momentum formulation used in FIDAP, which solved the full Navier-Stokes equations.

As a result of the large driving force at the exit of the jet, the centerline
temperature rapidly rises. Near 380°C, the temperature rise slows, due to the nonlinear
enthalpy dependence on temperature (see Figure 2.4(e)). At higher temperatures, the
driving force decreases, and the temperature rise is slower. Figure 9.3 shows the radial
temperature profiles for five axial locations. The initial condition is given at z/d_{noz} = 0.0.
Again, the predicted profiles show good agreement. Figure 9.4 shows the predicted axial
velocity radial profiles. The finite difference profiles show the same trend as the FIDAP
profiles, but they are offset at the centerline.

In the actual jet experiments, the flow is downward in the vertical direction, thus,
buoyancy forces should be important. Also, the jet is confined, and the secondary SCW
stream is finite. The effect of these modifications to the simulations are discussed in the
following section.

9.1.4 Gravity and Confined Geometry Effects

The laminar, free jet simulation described above was modified to include the
buoyancy force. The resulting velocity and temperature profiles showed distinct changes.
The centerline velocity of the jet increased as it exited the nozzle, as shown in Figure
9.5(b). This is not surprising, since the density of the jet fluid is approximately a factor
of 12 greater than the secondary SCW stream density.

The predicted centerline temperature profiles for the buoyant jet are shown in
Figure 9.2  Centerline velocity and temperature profiles for a laminar free jet issuing into a coaxially flowing supercritical water stream (buoyancy force neglected). FIDAP - Fluid Dynamics Analysis Package developed by FDI Inc., (Evanston, IL)
Figure 9.3  Temperature profiles for a laminar free jet issuing into a coaxially flowing supercritical water stream (buoyancy force neglected).
FIDAP - Fluid Dynamics Analysis Package
FD - finite difference
Figure 9.4  Axial velocity profiles for a laminar free jet issuing into a coaxially flowing supercritical water stream (buoyancy force neglected).
Figure 9.5  Centerline velocity and temperature profiles for a laminar free jet issuing into a coaxially flowing supercritical water stream (buoyancy force included).
Figure 9.5(a). Judging by the centerline temperature profile of the non-buoyant jet (Figure 9.2(a)), there does not appear to be a great effect of buoyancy. However, the radial temperature profiles are much narrower for the buoyant jet shown in Figure 9.6. The shape of the temperature profiles can be explain by examining the controlling terms in the energy conservation equation. Since the jet is increasing in velocity, the entrainment of the surrounding fluid will also increase. This causes the radial velocity to increase and the radial temperature profiles to narrow. Along the centerline the radial velocity is zero, and the jet heating is primarily a result of radial conduction.

The axial velocity radial profiles for the buoyant jet are shown in Figure 9.7. As with the temperature, the radial profiles are much narrower than the non-buoyant jet case. An interesting difference between the finite difference predicted radial profiles and the FIDAP profiles can be seen if the velocity axis is expanded, as shown in Figure 9.8. The more exact formulation of FIDAP predicts a decrease in the secondary stream velocity near the jet axis. This is caused by entrainment of SCW by the accelerating dense jet. Although significant, the predicted entrainment rate is not high enough to produce a recirculation zone ($u/u_{\text{prim}} < 0.0$)

To more closely match the actual jet experiments, the cell geometry was modeled with FIDAP (see Appendix 11.4 for input file and simulation grid). At the walls, the axial and radial velocities were set to zero. For simplification, the wall temperature was set equal to the inlet secondary stream temperature. The predicted confined jet centerline profiles are compared to the free jet centerline profiles in Figure 9.9. The temperature profile is slightly changed, while the velocity profile is effected to a greater extent. This is expected, since the SCW steam is no longer infinite, which causes the entrainment rate is be somewhat restricted. Figure 9.10 shows the radial profiles at an axial distance of $z/d_{\text{noz}} = 40$. Because the wall is at a radial distance of $r/a=30$, the effect of confinement is small.

In the optical cell, a dimensionless axial distance of $z/d_{\text{noz}} = 40$ corresponds to an actual distance of 3.4 cm, which is approximately at the effluent exit. The mixed temperature thermocouple was located at a distance of $z/d_{\text{noz}} = 25$, and in all of the experiments with the jet exit near the center of the cell, the measured mixed stream temperature was very close to the macroscopic fully mixed value, within 5°C (see Table
Figure 9.6  Temperature profiles for a laminar free jet issuing into a coaxially flowing supercritical water stream (buoyancy force included).
Figure 9.7  Axial velocity profiles for a laminar free jet issuing into a coaxially flowing supercritical water stream (buoyancy force included).
Figure 9.8  Expanded axial velocity profiles for a laminar free jet issuing into a coaxially flowing supercritical water stream (buoyancy force included).
Figure 9.9  Comparison of predicted centerline profiles for a free and a confined jet.
Figure 9.10  Comparison of predicted radial profiles at $z/d_{roz}=40$ (a) temperature, (b) dimensionless axial velocity.
8.2). For a 0.5 g/min jet, the mixed temperature was measured as 512°C, which is much lower than the predicted centerline temperature of approximately 340°C at z/d_{noz} = 40. Therefore, it can be concluded that the supercritical water jets contained some degree of turbulence. Turbulent transport rates would increase the mixing and entrainment, and allow the jet to fully mix with the SCW stream before exiting the cell. Turbulent free jet correlations and models do exist (Beer and Chigier, 1983), but their use is limited for modeling this system, due to the nonlinear property variations for water.

9.2 Nucleation and Growth at High Supersaturation

Salt formation in the supercritical oxidation process can be described as a shock crystallization mechanism. Salts enter the reactor dissolved in a warm liquid waste stream, and undergo a shock crystallization when the stream mixes with the supercritical reactor medium. During the mixing process, rapid heating occurs by direct contact and from the exothermic reaction enthalpy liberated as the oxidation proceeds. At this point, the salt solubility has fallen by orders of magnitudes, leading to high supersaturation values, which cause rapid nucleation and growth of solid salt particles. There is essentially no information available on the high temperature and high supersaturation rates of nucleation and growth of salt particles in supercritical water.

The relative supersaturation is defined as,

\[ \phi = \frac{(C - C_{eq})}{C_{eq}} \]  \hspace{1cm} (9.4)

where C is the solute concentration, and C_{eq} is the equilibrium concentration or solubility of the solute at bulk conditions. In order to calculate the maximum obtainable supersaturation in the SCWO process, C is taken as the inlet salt concentration. For a 3.0 wt% NaCl jet and a reactor solubility of 0.02 wt% (at 550°C and 250 bars), the relative supersaturation is about 150. On a molarity scale, the relative supersaturation is about 1900. This increase is due to the low density (0.0786 g/cm³) of water at the bulk conditions of 550°C and 250 bars. Both of these supersaturation values are orders of magnitude higher than typical values encountered in industrial crystallization processes.
involving aqueous solutions (Chiang and Donohue, 1987). This is true even if a dilution factor of 10 is included to account for the mixing of the waste stream with the supercritical water in the reactor.

Although no studies exist on precipitating salts by rapidly mixing a liquid stream with supercritical water, some researchers have precipitated solutes by rapid expansion of supercritical solutions (RESS) through a nozzle. The RESS process has recently been reviewed by Tom and Debenedetti (1991). The solvent expansion causes a large decrease in solute solubility, and leads to supersaturation ratios of the same order of magnitude (or even higher) than those obtained in the flow experiments.

Debenedetti and co-workers at Princeton used this method to study the crystallization of naphthalene and other organics from supercritical carbon dioxide (Mohamed et al., 1989a,b). The particle size distributions of the crystals were found to be more narrow than those obtained in conventional crystallization processes, where temperature gradients cause non-uniform nucleation and growth rates in the solvent. Typical naphthalene particles sizes ranged from 4 to 150 µm, and were highly dependent on pre- and post- expansion temperature and initial solute concentration. Tom and Debenedetti (1991) studied the precipitation of biocompatible polymers from supercritical CO₂. The particle sizes ranged from 2 to 40 µm, and had spherical, needle, and irregular morphologies. The shock crystallization of salts in supercritical water is an isobaric process with extreme temperature gradients, which may lead to particle size distributions wider than those formed in the RESS process.

Debenedetti (1990) has modeled the RESS process using the theory of homogeneous nucleation. He used the Peng-Robinson equation of state to account for the non-ideal thermodynamics, and considered three different jet temperature-pressure expansion paths. The predicted nucleation rates were surprisingly flat due to the competing expansion effects of increased supersaturation and lowered temperatures. Since nucleation rates were very dependent on the unknown solute-solvent interfacial tension, quantitative predictions could not be made.

A group at Pacific Northwest Laboratories (Richland, WA) have also used the expansion technique to study precipitation from supercritical fluids (Matson et al., 1986 and 1987). Some of the systems examined included, SiO₂-H₂O, GeO₂-H₂O, and polymer-
small chain hydrocarbons. Supposedly, the particles were formed by homogeneous nucleation from the fluid phase.

In the SiO₂-H₂O experiments, the size of the silica particles was a function of initial solute concentration, which ranged from 500 to 3000 ppm at pre-expansion conditions of 470°C and 600 bars. The higher initial concentrations resulted in larger, slightly agglomerated particles (=1 μm). The particles were collected on a plate inside a vacuum chamber, which was held at a pressure below 0.01 bars (Matson et al., 1986). By substituting dilute electrolyte solutions (10⁻³ to 10⁻⁴ M KI or NaCl) for the distilled water, the expansion produced ultrafine silica particles (<< 0.1 μm), which were highly agglomerated. X-ray fluorescence tests revealed that these powders were homogeneous mixtures of SiO₂ and salt. Although the supersaturation ratios obtained in these silica precipitation studies were most likely two to three orders of magnitudes higher than those encountered in SCWO, the effect of initial solute concentration and impurities on particle sizes may be the same.

The classical theory of nucleation and growth of solutes from aqueous solutions at low supersaturation is well established (Strickland-Constable, 1968, and Ohara and Reid, 1973). At high supersaturations, much less in known, but homogeneous nucleation and mass transfer limited growth should prevail, which was found to be the case in experiments conducted by Nielsen (1969). He studied precipitation of barium and lead salts in water at room temperature. High supersaturation ratios were established by rapid mixing of two stable solutions. For example, mixing of barium chloride and sodium sulfate solutions will precipitate out barium sulfate, which has a very low solubility in room temperature water. Using the mixing technique, Nielsen was able to obtain relative supersaturation values between 60 and 1500 (on a molarity scale), comparable to those encountered in supercritical water.

Neither experimental nor theoretical work on the high temperature and pressure nucleation and growth kinetics of salts in supercritical water has been reported in the literature. For NaCl, studies on crystallization from aqueous solutions have focused on temperatures below 75°C and low values of supersaturation (Rumford and Bain, 1960, Rodriguez-Clemente, 1975). Studies of crystal growth of minerals at hydrothermal conditions (high temperatures and extreme pressures) have been reviewed by Laudise

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(1962). One study reported that large NaCl crystals (>2mm) were easily formed from water at a temperature of 370°C and 1347 bars (1330 atm.), but no rate data were provided.

9.2.1 Homogeneous Nucleation

Nucleation and growth rates, in addition to growth mechanisms, are highly dependent on temperature and supersaturation. As in the RESS process and the precipitation of sparingly soluble salts, such as BaSO₄, the shock crystallization of salts from supercritical water may also be initiated by homogeneous nucleation.

The classical theory of homogeneous nucleation begins by calculating the free energy required to form a cluster of molecules from a fluid phase. Both the energy from the phase change due to condensation and the energy required to form the surface of the cluster is considered (Nielsen, 1964). By minimizing the free energy change, an equation for the critical radius results,

$$r^* = \frac{2 \sigma v_s}{k_B T \ln S}$$

(9.5)

where $\sigma$ is the interfacial tension, $v_s$ is the molecular volume of the solute, $k_B$ is the Boltzmann's constant, and $S$ is the supersaturation ratio, $C/C_{eq}$. Clusters with sizes greater than $r^*$ are stable, and will tend to grow. One of the most questionable assumptions used in the theory is the application of bulk thermodynamic properties, such as the interfacial tension, to small molecular clusters.

In the shock crystallization experiments with sodium sulfate, many fine particles were formed, possibly due to homogeneous nucleation. The nucleation most likely occurred near a temperature of 385°C, since the sodium sulfate solubility at 250 bar falls to very low values as the critical temperature of water (374°C) is passed. Equation (9.5) can be used to estimate critical cluster sizes at 385°C for various interfacial tensions. The molecular volume of Na₂SO₄ was estimated as $9.4 \times 10^{-23}$ cm (from the macroscopic density). Figure 9.11 shows the predicted $r^*$ values. At high supersaturation values, the critical radius curves are fairly flat. Also, the effect of the interfacial tension is less at high supersaturations.
Figure 9.11  Critical radius predicted by classical theory of homogeneous nucleation at conditions relevant to precipitation from supercritical water.
The classical theory of homogeneous nucleation also provides an estimate of the rate of formation of new particles,

\[ J = A_N \exp \left[ -\frac{16 \pi \sigma^2}{3 k_B^3 T^3 \ln^2(\phi + 1)} \right] \]  

(9.6)

where, \( J \) is the nucleation rate in particles/cm\(^3\)s (Davey, 1982). A typical value for the pre-exponential factor, \( A_N \), for precipitation of sparingly soluble salts from aqueous solution is \( 10^{30} \) (Nielsen, 1964). For high supersaturation, the exponential term in equation (9.6) will approach one, and extreme levels of nucleation and many fine sub-micron particles will result.

Figure 9.12 shows the predicted nucleation rates as a function of supersaturation ratio using equation (9.6). The calculations were performed at a temperature of 385°C with an equilibrium solubility of 1 ppm. The effect of the supersaturation ratio on the nucleation rate is highly dependent on the value of interfacial surface energy or tension between the molecular cluster and the solvent. The difficulty of obtaining a value of this interfacial tension by direct measurement is a major problem with the homogeneous nucleation theory.

### 9.2.2 Diffusion Limited Growth

If homogeneous nucleation occurs, many sub-micron particles should be formed. These particles could grow by condensation of additional molecules from the fluid phase to the solid phase, or by collision and coagulation with other particles. Many models for crystal growth exist (Ohara and Reid, 1973). Due to the large number of unknown parameters in most of these models, a semi-empirical approach is frequently used. The semi-empirical models typically have a power-law form,

\[ R = k_+ \phi^a \]  

(9.7)

where \( \phi \) is the relative supersaturation, \( k_+ \) is the rate constant, and \( a \) is the order of the growth (Garside, 1984). Both \( k_+ \) and \( a \) are determined experimentally. With the extreme temperatures and levels of supersaturation encountered during the shock crystallization
Figure 9.12  Homogeneous nucleation rate predictions of classical theory as applied to the shock crystallization of $\text{Na}_2\text{SO}_4$ ($A_N = 10^{30} \text{ cm}^{-3} \text{ s}^{-1}$, $T = 385^\circ \text{C}$, $C_{eq} = 1 \text{ ppm}, v_s = 9.4 \times 10^{-23} \text{ cm}^3$)
of salts, the growth rate may be limited by mass transfer. For this case, the rate is a linear function of supersaturation, and \( k_s \) is equivalent to a mass transfer coefficient and is correlated with the dimensionless Reynolds and Schmidt numbers (Ohara and Reid, 1973).

For bulk diffusion limited growth, the linear growth rate of a crystal can be written as,

\[
\frac{dr}{dt} = \frac{v_s D_s (C - C_{eq})}{r} \tag{9.8}
\]

where \( t \) is the time, \( D_s \) is the diffusion coefficient of the solute, and \( C \) and \( C_{eq} \) are the solute concentration and equilibrium solubility, respectively, in units of molecules/cm\(^3\). Nielsen (1964) developed an analytical solution to the diffusion growth equation. He first defined the extent of reaction, \( \alpha_{rx} \), as,

\[
\alpha_{rx} = \frac{C_o - C}{C_o - C_{eq}} \tag{9.9}
\]

where \( C_o \) is the initial solute concentration. Nielsen then proposed the following relationship between \( \alpha_{rx} \) and \( r \);

\[
r(t) = r_i \alpha_{rx}^{1/3} \tag{9.10}
\]

where \( r_i \) is the final particle radius \((t=\infty)\). This equation should be valid for particles with morphologies close to spherical. Nielsen then inserted \( \alpha_{rx} \) and \( r(t) \) into equation (9.8) and integrated from \( \alpha_{rx}=0 \) to \( \alpha_{rx}=1 \). He obtained,

\[
t = \frac{r_i^2}{3 v_s D_s (C - C_{eq})} \left[ \frac{1}{2} \ln \frac{1 - \alpha}{(1 - \alpha^{1/3})^3} - \sqrt{3} \tan^{-1} \frac{\sqrt{3}}{1 + 2 \alpha^{1/3}} \right] \tag{9.11}
\]

This equation can be used to plot the extent of reaction (or particle size) as a function of time, provided that the final particle radius, solute diffusion coefficient, and the initial and equilibrium solute concentrations are known. The final particle diameter in many of the sodium sulfate shock crystallization experiments was approximately 1.0 \( \mu \)m.

An estimate of the diffusion coefficient of a solute, \( D_s \), in supercritical water can
be obtained from the pure water self-diffusion coefficient, \( D_w \). Lamb et al. (1981) measured the self-diffusion coefficient of supercritical water as a function of density and temperature. The data were regressed with a semi-empirical equation. Figure 9.13 shows the predicted water self-diffusion coefficient as a function of temperature at a pressure of 250 bar. For a temperature of 385°C, the water self-diffusion coefficient is approximately \( 1.0 \times 10^{-3} \text{ cm}^2/\text{s} \).

For sodium sulfate, the equilibrium solute concentration was estimated as 1 ppm, which corresponds to \( 1.3 \times 10^{15} \) molecules/cm\(^3\) at a temperature of 385°C (water density of 0.315 g/cm\(^3\)). The initial solute concentration was taken as \( 1.7 \times 10^{19} \) molecules/cm\(^3\), which corresponds to a 3.0 wt% and 150°C jet, diluted by 240% to account for mixing with pure SCW as the jet is heated to 385°C. The growth temperature was chosen as 385°C, to provide a conservative estimate of the growth rate, since the diffusion coefficient increases with temperature.

The predicted particle-time growth curve is shown in Figure 9.14. Although this is a rough estimate, the plot does show that diffusion-limited growth is consistent with the final primary particle sizes collected during the sodium sulfate shock crystallization experiments. Rapid growth could explain the relatively large size of the collected sodium sulfate particles, since homogeneous nucleation predicts initial clusters of size much less than 1 \( \mu \text{m} \).

### 9.3 Growth by Agglomeration

Agglomeration following inter-particle collisions may also be an important mechanism effecting the final size and morphology of solids formed in the supercritical water oxidation process. Some of the sodium sulfate particles collected during the shock crystallization experiments appeared to be partially coalesced aggregates (see Figure 8.20 and 8.25(a)). Also, clusters of sodium chloride particles were frequently gathered, but the aggregates may have formed on the collection device and not in the supercritical water medium (see Figure 8.14). A numerical model was developed to estimate collision rates and final aggregate sizes of salt particles formed during the shock crystallization experiments.
Figure 9.13  Self-diffusion coefficient of water at 250 bar.
Figure 9.14  Time required to reach a final particle diameter of 1 micron assuming diffusion-limited growth.
9.3.1 Definitions and Theory

Salt particles can also grow by collision followed by agglomeration and/or coagulation with other particles. In this case, particle size will increase during growth, but total particle concentration will decrease. Growth by agglomeration or coagulation is proportional to the collision frequency, \( N_{ij}^* \), defined as the number of collisions occurring per unit time per unit volume between particles of volume \( v_i \) and \( v_j \),

\[
N_{ij}^* = \beta_{ij}(v_i, v_j)n_i n_j
\]  

(9.12)

where, \( \beta \) is the collision frequency function, \( n \) is the particle concentration, and the subscripts \( i \) and \( j \) denote particles of volume \( v_i \) or \( v_j \) (Friedlander, 1977). The collision frequency function depends on particle size, fluid properties, and collision mechanism. Possible mechanisms include, Brownian motion, laminar shear, differential sedimentation, and turbulent acceleration and shear.

For Brownian motion in the continuum regime (particle sizes much greater than the mean free path of the gas molecules), the collision frequency function can be estimated as,

\[
\beta_{ij} = 2\pi (D_i + D_j) (d_i + d_j)
\]  

(9.13)

where \( D_i \) is the particle diffusion coefficient, and \( d_i \) is the particle diameter. The Stokes-Einstein equation can be used to estimate \( D_i \),

\[
D_i = \frac{k_B T C_{sc}}{3\pi \mu d_i}
\]  

(9.14)

where \( C_{sc} \) is the slip correction factor and \( \mu \) is the fluid viscosity (Flagan and Seinfeld, 1988).

The collision frequency function for particles in a laminar flow field is,

\[
\beta_{ij} = \frac{1}{6} (d_i + d_j)^3 \frac{du}{dy}
\]  

(9.15)
where $\frac{du}{dy}$ is the average velocity gradient (Friedlander, 1977).

Particles of different diameters can also collide as a result of unequal settling velocities, with the large particles over taking and hitting the smaller particles. The collision frequency function for differential sedimentation is,

$$\beta_{ij} = \eta \frac{\pi}{4} (d_i + d_j)^2 |v_i - v_j|$$  \hspace{1cm} (9.16)

where $\eta$ is the capture efficiency, and $v_i$ is the terminal settling velocity of a particle with a diameter of $d_i$ (Friedlander, 1977; Reist, 1984). The terminal settling velocity is given as,

$$v_i = \frac{d_i^2 (\rho_p - \rho) g C_{sc}}{18 \mu}$$  \hspace{1cm} (9.17)

where $\rho_p$ is the density of the particle, $g$ is the gravitational constant, and $\rho$ and $\mu$ are the density and viscosity of the medium, respectively. The capture efficiency accounts for small particles being swept out of the flow path of larger ones. It can be estimated as,

$$\eta = \left( \frac{d_s}{d_L} \right)^2 - \left( \frac{d_s}{d_L} \right)^4$$  \hspace{1cm} (9.18)

where $d_L$ is the diameter of the larger particle and $d_s$ is the diameter of the smaller particle (Reist, 1984).

Once the collision frequencies are known, a particle balance is used to keep track of the size distribution of a system of particles as a function of time. This requires the solution of many differential equations, one for each cluster size. For a cluster of $k$ primary particles, the differential equation is,

$$\frac{dn_k}{dt} = \frac{1}{2} \sum_{j=1}^{k-1} \beta_{jk-j} n_j n_{k-j} - \sum_{j=1}^{k-1} \beta_{jk} n_j n_k$$  \hspace{1cm} (9.19)

$k = 1,2,3,\ldots,k_{\text{max}}$
where \( n_i \) is the concentration of clusters with \( i \) primary particles. The first term accounts for the creation of \( k \) clusters by collisions between clusters of size \( j \) and \( k-j \), while the second term accounts for the loss of \( k \) clusters by collision with clusters of any size. \( k_{\text{max}} \) is the maximum cluster size considered in the numerical solution, and it must be chosen high enough to assure negligible loss of particle mass by cluster size cut-off.

9.3.2 Collision Frequencies in SCW

The collision mechanisms described above were used to estimate collision frequencies of salt particles in a supercritical water medium. The calculations were performed at the typical mixed stream conditions of 550°C and 250 bar. Since many salt particles, such as sodium sulfate, tend to be "sticky" at the bulk SCWO reactor conditions, the collision efficiency was assumed to be one. The particle density was taken as 2.5 g/cm\(^3\), while the water density and viscosity were calculated with the HGK EOS (Haar et al., 1984). Because of the uncertainty of the velocity profiles in the optical cell, it is difficult to estimate an average velocity gradient required to calculate the collision frequency function for laminar shear. For the calculations which follow, a mean centerline velocity of 5.0 cm/s and a jet radius of 1 cm were assumed, which results in an average velocity gradient of 5.0 s\(^{-1}\).

The relative importance of the various collision mechanisms will depend on the size of the colliding particles. Figure 9.15 shows the predicted collision frequencies for a 0.1 μm particle interacting with particles of diameter between 0.01 and 1.0 μm. For all the sizes, a Brownian motion mechanism dominates. The collision frequency function for differential sedimentation is zero for particles of equal diameter (0.1 μm in Figure 9.15), since both particles will settle with identical velocities.

Figures 9.16 and 9.17 show similar plots for a particle of 1.0 and 10.0 μm diameter, respectively. For the 1.0 μm particle, collision with large particles (>5μm) by the mechanisms of laminar shear and differential sedimentation are comparable to Brownian motion effects, while for a 10.0 μm particle, shear and sedimentation are the dominant mechanisms.
Figure 9.15  Comparison of coagulation mechanisms for particles of 0.1 um diameter interacting with other particles in SCW (T=550°C, P=250 bar).
Figure 9.16  Comparison of coagulation mechanisms for particles of 1.0 um diameter interacting with other particles in SCW (550°C, 250 bar).
Figure 9.17  Comparison of coagulation mechanisms for particles of 10.0 um diameter interacting with other particles in SCW (550°C, 250 bar).
9.3.3 Predicted Agglomeration Rates

The collision frequencies predicted above were used to estimate final aggregate sizes formed during the shock crystallization of sodium sulfate. As discussed in Section 8.3.3, fairly large aggregates were collected during experiments with jets of 3.0 wt% Na₂SO₄. The primary particle size was approximately 1.0 μm, while the aggregates reached sizes of about 10 μm (see Figure 8.20). Also, the primary particles appeared to be only partially coalesced, therefore the actual density of the aggregates is less than the salt density. This was accounted for with a packing factor, which was assumed to be 0.52 (square cubic packing).

The agglomeration calculations were performed for a monodisperse system of spheres with diameters of 1 μm. The initial particle concentration, N₀, was calculated by assuming all the salt in the jet feed crystallized. Thus, for a 3.0 wt% jet flowing at 0.5 g/min, the salt mass flow rate is 0.015 g/min. For salt spheres of 5.24x10⁻¹³ cm³ volume (1.0 μm diameter) with a density 2.5 g/cm³, the particle flow rate is 1.15x10⁻¹⁰ min⁻¹. If the SCW stream is flowing at 10.2 g/min and the mixed stream conditions are 550°C and 250 bar at a density of 0.0786 g/cm³, the total volumetric flow rate (including the jet flow) will be 136 cm³/min. This gives an initial particle concentration of 8.4x10⁷ cm⁻³.

The maximum cluster size considered in the calculations was 70 particles. The corresponding 70 ordinary differential equations were integrated with the program LSODE (Hindmarsh, 1983). The predicted aggregate cluster size distributions at two times are shown in Figure 9.18. The times of 5 s and 10 s correspond to typical fluid residence times for experiments with the nozzle tip near the center of the cell and in the upper flow tube, respectively. In both cases, the predicted contributions of laminar shear and differential sedimentation are small. The maximum cluster sizes are fairly small (less than 20 particles), and could not account for the large aggregates collected in the sodium sulfate experiments. Hence, the simulation results support the hypothesis that the large aggregates formed near the jet exit where enhanced particle concentrations and shear rates existed. It is difficult to account for these factors in the agglomeration calculations, since the actual mixing rates in the jet are unknown.

Similar agglomeration calculations were performed to qualitatively examine the effect of initial jet concentration on final cluster size distribution. Initial jet
Figure 9.18  Prediction of final size distribution of aggregates formed during the shock crystallization of a 3.0 wt% Na₂SO₄ jet.
concentrations from 0.3 to 10.0 wt% were simulated. Again, the system of particles at
time zero was assumed be monodisperse spheres with diameters of 1.0 μm. Figure 9.19
shows the cluster size distributions after a time of 15 s. As expected, the collision rates
are very concentration dependent, with a maximum cluster size of about 7 for a 0.3 wt% 
jet and over 50 for a 10.0 wt% jet. This trend is consistent with the size of the sodium 
sulfate aggregates collected on sapphire tube pieces for jets of varying initial 
concentrations.

9.4 Recommendations for Future Modeling

From the laminar jet numerical simulation, it was concluded that some degree of 
turbulence exists is the experimental jets. Turbulence models could be incorporated in 
the simulation to enhance the mixing rates. Since turbulence models require experiment 
data to fit the empirical parameters, there use is limited. The thermodynamic properties 
of specific salt-water systems must also eventually be added to the simulation to allow 
for the prediction of phase nucleation. This will complicate the fluid dynamics, since 
two-phase, vapor-liquid flow will result for some systems, such as, NaCl-H₂O. Also, the 
nucleation kinetics of condensed phases in SCW water have not been quantitatively 
characterized.

Bulk agglomeration calculations should be modified to account for possible 
intensified collision frequencies near the jet exit. This would require estimating the 
temperature and flow profiles in the jet. Also, once the degree of turbulence in the jet 
is estimated, turbulent collision mechanisms can be considered (see for example, Levich, 
1962).
Figure 9.19  Effect of initial jet sodium sulfate concentration on predicted cluster size distribution after a residence time of 15 sec.
Chapter 10.
Conclusions and Recommendations

10.1 Conclusions

1. **Experimental Apparatus.** An apparatus for gathering high temperature and pressure equilibria and precipitation data in salt-water systems was designed, constructed, and tested.

2. **NaCl thermodynamic modeling.** Conventional thermodynamic approaches have been applied to the NaCl-H$_2$O at extreme conditions. In their present form, these approaches do not satisfactorily describe the very non-ideal nature of the system in the temperature, pressure, and composition ranges tested.

3. **Isobaric phase equilibria experiments.** A method for observing phase transformations and locating phase boundaries under isobaric conditions was developed and tested on the NaCl-H$_2$O and Na$_2$SO$_4$-H$_2$O systems at 250 bar. The method not only provides direct observation of phase changes and location of phase boundaries by visual means, it can also be used to verify interpolated data from traditional isothermal experiments which use sampling techniques.

4. **NaCl solubility in sub- and supercritical water.** The solubility of sodium chloride in water vapor was determined in a continuous flow apparatus at supercritical temperatures ranging from 450 to 550 ºC and sub- and supercritical pressures varying from 100 to 250 bar. Measured sodium chloride concentrations ranged from 0.9 to 101 ppm (by weight). Hydrolysis of the solid NaCl was found as a possible explanation for some of the reported discrepancies in the literature. The hydrolysis of sodium chloride to form sodium hydroxide and hydrochloric acid becomes significant at temperatures above 500ºC.

5. **Na$_2$SO$_4$ solubility in SCW.** Experiments 500ºC and 250 bar were performed. Measured sodium sulfate concentrations were about 0.9 ppm ± 0.2 ppm, and exhibited unsteady behavior. Although only an estimate of Na$_2$SO$_4$ solubility could be obtained, this value was over two orders of magnitude lower than that for sodium chloride at identical conditions.

6. **NaCl and Na$_2$SO$_4$ precipitation at 250 bar.** The phase behavior in the sodium chloride-water and sodium sulfate-water systems has a profound effect on the morphology and size of the precipitated solids. Results indicate that sodium
chloride solutions first pass through a vapor-liquid equilibrium state before solid salt is formed, and that sodium sulfate solutions nucleate solids directly from a homogeneous fluid phase. The sodium sulfate solids appeared much finer and also more aggregated than the sodium chloride solids. The diameter of the primary sodium sulfate particles were typically between 1 and 3 microns, while some aggregates reached diameters up to about 20 microns. Sodium chloride solids had many hollow inner regions with a size range of 5 to 25 μm for a 0.5 wt% jet and 20 to 100 μm for a 10.0 wt% jet.

7. **NaCl and Na₂SO₄ precipitation at 200 bar.** For NaCl, the subcritical pressure caused a dramatic increase in particle size, most likely due to a phase boundary shift in the NaCl-H₂O system. For Na₂SO₄, the precipitation mechanism changed with pressure, and particle size range increased to between 2 and 50 μm.

8. **Mixed NaCl/Na₂SO₄ solution precipitation at 250 bar.** The increased solubility of Na₂SO₄ in NaCl brines causes less fine particle nucleation, and favors liquid brine formation.

9. **Shock crystallization modeling.** Diffusion limited growth was shown to be a possible explanation for the micron size of the sodium sulfate precipitates. Agglomeration calculations showed that primary particle collisions in the bulk SCW medium could not account for the large Na₂SO₄ aggregates, which most likely formed near the jet exit.

10.2 **Recommendations**

1. The isobaric technique for locating phase boundaries and characterizing phase equilibria should be used to study other common salts, such as, KCl, K₂SO₄, and Na₂CO₃ in supercritical water. This information is required to develop precipitation mechanisms for these salts in the SCWO process.

2. Additional solubility data for Na₂SO₄ should be obtained using an autoclave operated in a batch mode. The data should then be regressed with a solvation model, for use in predicting supersaturation values required to model shock crystallization.

3. The effect of other components, such as organics or gases, on the phase behavior and precipitation mechanisms in the model salt-water system should be explored, since these components make up a significant percentage of the actual SCWO reactor contents.
4. The creation of salts by in-situ neutralization of acidic oxidation products is another important source of solids in the SCWO process. Oxidation/neutralization experiments should be performed to determine the sizes of solids formed by this mechanism. Model waste compounds with chlorine and sulfur heteroatoms should be selected, preferably ones with known oxidation kinetics. The jet feed could be an aqueous solution of an organic compound and NaOH, while either O₂ or H₂O₂ could be added to the SCW feed. The precipitated solids could be collected on a Hastelloy frit, while laser transmission or other light scattering measurements are performed.

5. Additional shock crystallization experiments should be performed to determine the effect of nozzle diameter on NaCl and Na₂SO₄ particle sizes and morphologies. Laser drilling can be used to obtain very small diameters (<100 μm). This information is required for proper extension of the results to systems of larger scale.

6. Experiments using a low-angle light scattering instrument to measure in-situ particle size distribution were hindered by laser power fluctuations. Before additional tests are conducted, modifications to the experimental apparatus are necessary to decrease the temperature gradients in the optical cell, especially from the window ports. Small heaters could be attached to the window retainers and controlled with a thermocouple in contact with the window surface.

7. The nucleation and growth calculations should be extended to estimate the effects of concentration and temperature gradients at the jet exit. These gradients can be approximated from transport modeling. Numerical simulations of a laminar jet exhibited very slow mixing rates, thus some degree of buoyancy driven turbulence must be considered.
Chapter 11.
Appendices

11.1 Notation

\( a \) activity
\( A_N \) pre-exponential constant for nucleation rate
\( A_\lambda \) Debye-Huckel parameter
\( C \) species concentration
\( d_p \) particle diameter
\( \langle d_p \rangle \) average particle diameter
\( d_i \) diameter of cluster of size \( i \)
\( d_{noz} \) nozzle diameter
\( D \) diffusion coefficient
\( f \) pure component fugacity
\( \hat{f} \) mixture fugacity
\( g \) gravitational constant (980 cm/s\(^2\))
\( I \) ionic strength (Chapter 5)
\( I \) light intensity (Chapter 8)
\( k_{12} \) binary interaction parameter (PREOS)
\( k_B \) Boltzmann’s constant
\( K \) equilibrium constant
\( l \) light path length through medium
\( L \) characteristic length scale
\( m \) molality
\( n \) hydration number
\( n_i \) concentration of clusters of size \( i \) (Chapter 9)
\( n_i \) moles of component \( i \) (Chapter 5)
\( N \) particle concentration (#/cm\(^3\))
\( N^* \) collision frequency (#/cm\(^3\)s)
\( P \) pressure
\( Q_{sca} \) scattering efficiency
\( r_p \) \hspace{1cm} \text{particle radius} \\
\( r^* \) \hspace{1cm} \text{critical cluster radius} \\
\( R \) \hspace{1cm} \text{universal gas constant} \\
\( R_{\text{sca}} \) \hspace{1cm} \text{scattering correction factor} \\
\( S \) \hspace{1cm} \text{supersaturation} = \frac{C}{C_{eq}} \\
\( t \) \hspace{1cm} \text{time} \\
\( T \) \hspace{1cm} \text{temperature} \\
\( T \) \hspace{1cm} \text{transmission} \ (I/I_0) \\
\( u_e \) \hspace{1cm} \text{jet exit axial velocity} \\
\( V_f \) \hspace{1cm} \text{volumetric flow rate} \\
\( x \) \hspace{1cm} \text{mole fraction in condensed phase} \\
\( y \) \hspace{1cm} \text{mole fraction in gas or fluid phase} \\
\( w \) \hspace{1cm} \text{mass flow rate} \\

\text{Greek letters} \\
\( \alpha \) \hspace{1cm} \text{dimensionless size parameter} \\
\( \alpha_{\text{Rx}} \) \hspace{1cm} \text{extent of reaction} \\
\( \beta \) \hspace{1cm} \text{collision frequency function} \\
\( \Gamma \) \hspace{1cm} \text{reduced activity coefficient} \\
\( \gamma \) \hspace{1cm} \text{activity coefficient} \\
\( \eta \) \hspace{1cm} \text{capture efficiency} \\
\( \theta \) \hspace{1cm} \text{half-angle of seen by detector} \\
\( \lambda \) \hspace{1cm} \text{light wavelength in medium} \\
\( \mu \) \hspace{1cm} \text{chemical potential or fluid viscosity} \\
\( \nu \) \hspace{1cm} \text{kinematic viscosity} \\
\( \nu_s \) \hspace{1cm} \text{molecular volume of solute} \\
\( \rho \) \hspace{1cm} \text{density} \\
\( \sigma \) \hspace{1cm} \text{interfacial tension} \\
\( \tau \) \hspace{1cm} \text{turbidity} \\
\( \phi \) \hspace{1cm} \text{relative supersaturation} \\
\( \Phi \) \hspace{1cm} \text{fugacity coefficient}
11.2 Shock Crystallization Run Procedure

previous day:

1: Clean out cell - flush with water
2: Assemble cell and particle collection piece inside (weigh first) - usually can leave window holders, plugs and bottom flow port in place, but tighten all retainers. With cell upright in vise, place rubber plug over bottom flow port, and fill cell with distilled water. Insert top flow port; the o-ring may have to be replaced if it was deformed when the flow port was removed. Use squirt bottle to top off cell with water and plug top flow port. Set cell on its side on bench top.
3: Attach two 316SS straps to cell, and insert first set of six strip heaters with two on the bottom face (see Figure 11.1).
4: Insert thermocouple into thermowell in the bottom face of the cell.
5: Flush out feed lines of the apparatus to remove air (SCW heater and nozzle feed). Flush out back pressure regulator and inline filter.
6: Place cell on the apparatus stand.
7: Hook-up the down stream cooling heat exchanger, the nozzle assembly, and the inlet SCW line to the cell (use anti-seize lubricant on the glands).
8: Hook-up nozzle feed line.
9: Fill all reservoirs.
10: Secure LEXAN shields to frame.
11: Pressure test the cell. To pressurize, run the SSI pump at 2.5 g/min and the Milton Roy pump at 10 g/min. Before building up pressure, flush out the system for around 10 min. Check for leaks, if none lower pressure.
12: Place 2nd set of strip heaters on cell, check both sets for shorts using multimeter; also momentarily turn on cell heaters to test for short.
13: Attach glass plates to window port retainers.
14: Place TC into thermowell in top face of cell.
15: Wrap heating tape and insulation around SCW feed line and top high pressure cross.
16: Carefully connect nozzle cooling lines.
17: Place insulation around cell. Four inches on sides and top. Stuff pieces of insulation around bottom high pressure cross.
18: Connect all TC’s to indicators.
19: Set up analytic tools (lights, laser, camera etc...)
Figure 11.1  Schematic of cell setup for shock crystallization experiments (cell is shown on its side, before it is placed on stand).
when ready to begin run:
20: Plug in heaters and turn on circuit breaker.
21: Turn on ventilation fan and heat exchanger cooling water.
22: Secure LEXAN shields to frame.
23: Pressurize cell.
24: Set desired initial jet and scw feed rates. Flow pure water during heating.
25: Take initial cold system flow rate measurement.
26: Start timer and turn on heaters. Typical variac settings to begin are 30% for the SCW feed heater, 20% for the heating tape, and 35% for the cell strip heaters.
27: Check flow rate and heat-up rate every 30-40 minutes. Do not heat-up at a rate much greater than 1.5 °C/min, since this could cause window breakage.
28: When near desired temperature, turn on nozzle cooling.
29: When steady state conditions are reached, switch jet feed to salt solution or fill sample loop and inject salt solution into jet feed.

shut down:
1: Shut off nozzle cooling and close down jet feed pump (close SSI pump ball valve, bleed down pressure in pump line slowly using drain valve and shut off pump).
2: Take steady state temperature readings if desired.
3: Shut off all heaters and switch off the SCW feed heater circuit breaker.
4: Close down SCW (Milton Roy) feed pump.
5: Slowly lower pressure in system. Close micro-metering valve, open the back pressure regulator. Use micro-metering valve to slowly lower pressure making sure the inner cell temperature does not fall below 500 °C.
6: Flush system with Nitrogen. Use SCW feed line by connecting N₂ gas tank (pressure regulated to 40 psig) to drain line. It will usually take approximately 5 minutes for the nitrogen to push the water out of the system.
7: After flushing with N₂ at a somewhat high flow rate for around 10 min, lower the flow to 100-200 cc/min and leave overnight. Move SCW feed tank to floor or close valve to assure no water enters the cell.
8: Shut off the heat exchanger cooling water, the strip chart recorder, lights etc...
9: Loosen insulation around cell, and make sure the ventilation fan remains on during cooling.
10: When cell is cool, first disconnect nozzle feed line. Flush out line with N₂ to remove any remaining water. Remove cell from stand and open to collect particles.
11.3 Shock Crystallization Run Sheets

Only the run sheets for experiments with multiple sample injections involving laser
transmission measurements, Malvern size distribution analysis, or photo and video documentation
are included. The particle collection runs were summarized in Table 8.3. The run sheets are
presented in the following order:

FR10  Video recording of jets, nozzle tip in view of window (#3).
FR11  Video recording of jets, nozzle tip at flow tube (#4a).
FR12  Extinction measurements, concentration effects.
FR14  Na$_2$SO$_4$ extinction measurements, flow rate and concentration effects.
FR18  Na$_2$SO$_4$ extinction measurements, pressure effects.
FR20  35 mm photos of jets at 250 bar, 50 mm lens.
FR29  Na$_2$SO$_4$ extinction measurements, flow rate and concentration effects.
FR31  Na$_2$SO$_4$ extinction measurements, concentration effects.
FR39  Mixed solution extinction measurements.
FR43  Malvern test, nozzle in flow tube (#4B).
FR44  Malvern test, nozzle at top of flow tube (#1B).
FR46  35 mm photos of jets at 200 and 250 bar, stereomicroscope.
FR50  35 mm photos of jets at 200, 230, and 250 bar; 50 mm lens.
Shock Crystallization of Sodium Chloride and Sodium Sulfate

Flow Run #10 4/29/91

Analytic Method(s) Video recording, 50 mm lens with a 14 mm spacer.

<table>
<thead>
<tr>
<th>Nozzle</th>
<th>Type</th>
<th>#3, coned tip</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Position</td>
<td>tip at top of window</td>
</tr>
</tbody>
</table>

| Pressure       |          | 248-251 bar |

| Jet Feed       | Flowrate | 0.5 g/min |
|                | Exit Temp. | 100-110 C |
|                | Delivery   | Sample Loop (1 ml) |

| SCW Feed       | Flowrate | 10.2 g/min |
|                | Inlet Temp. | 554 C |

| Mixed Stream   | Exit Temp. | 545 C |

| Cell Block     | Top Temp.  | 604 C |
|                | Bot. Temp. | 600 C |

| Nozzle Cooling | Type      | distilled water |
|               | Flowrate  | 2.9 cc/min @STP |

Summary of Video Recorded Jets

<table>
<thead>
<tr>
<th>Video Time (hr:min)</th>
<th>Jet Feed</th>
</tr>
</thead>
<tbody>
<tr>
<td>8:06</td>
<td>3.0 wt% NaCl</td>
</tr>
<tr>
<td>8:26</td>
<td>3.0 wt% Na2SO4</td>
</tr>
<tr>
<td>9:36</td>
<td>1.5 wt% NaCl &amp; 1.5 wt% Na2SO4</td>
</tr>
<tr>
<td>9:52</td>
<td>10.0 wt% NaCl</td>
</tr>
<tr>
<td>9:58</td>
<td>10.0 wt% NaCl</td>
</tr>
<tr>
<td>10:28</td>
<td>20.0 wt% NaCl</td>
</tr>
<tr>
<td>10:51</td>
<td>10.0 wt% Na2SO4</td>
</tr>
<tr>
<td>11:08</td>
<td>5.0 wt% NaCl &amp; 5.0 wt% Na2SO4</td>
</tr>
</tbody>
</table>
Shock Crystallization and Neutralization

**Flow Run #11**  
5/25/91

**Analytic Method(s)**  
Video recording, 50 mm lense with a 14 mm spacer.

**Nozzle**

<table>
<thead>
<tr>
<th>Type</th>
<th>#4A, coned tip</th>
</tr>
</thead>
<tbody>
<tr>
<td>Position</td>
<td>tip in flow tube</td>
</tr>
</tbody>
</table>

**Pressure**

|                | 248-251 bar |

**Jet Feed**

<table>
<thead>
<tr>
<th>Flowrate</th>
<th>0.5 g/min</th>
</tr>
</thead>
<tbody>
<tr>
<td>Exit Temp.</td>
<td>125-145 C</td>
</tr>
<tr>
<td>Delivery</td>
<td>Sample Loop (1 ml)</td>
</tr>
</tbody>
</table>

**SCW Feed**

<table>
<thead>
<tr>
<th>Flowrate</th>
<th>10.2 g/min</th>
</tr>
</thead>
<tbody>
<tr>
<td>Inlet Temp.</td>
<td>545 C</td>
</tr>
</tbody>
</table>

**Mixed Stream**

| Exit Temp. | 555 C |

**Cell Block**

| Top Temp.   | 601 C |
|            |       |
| Bot. Temp.  | 601 C |

**Nozzle Cooling**

<table>
<thead>
<tr>
<th>Type</th>
<th>distilled water</th>
</tr>
</thead>
<tbody>
<tr>
<td>Flowrate</td>
<td>2.8 cc/min @STP</td>
</tr>
</tbody>
</table>

**Notes**

After SCW feed switched to 0.1 wt% NaOH solution, effluent from cell had an H2S odor. A high level of corrosion occured during the run, most likely due to the NaOH feed. Solid salts were brown colored.

**Summary of Video Recorded Jets**

<table>
<thead>
<tr>
<th>Video Time (hr:min)</th>
<th>SCW Feed</th>
<th>Jet Feed</th>
</tr>
</thead>
<tbody>
<tr>
<td>6:08</td>
<td>pure H2O</td>
<td>3.0 wt% NaCl</td>
</tr>
<tr>
<td>6:22</td>
<td></td>
<td>0.5 wt% Na2SO4</td>
</tr>
<tr>
<td>6:33</td>
<td></td>
<td>3.0 wt% Na2SO4</td>
</tr>
<tr>
<td>7:00</td>
<td></td>
<td>3.0 wt% NaCl &amp; 3.0 wt% Na2SO4</td>
</tr>
<tr>
<td>7:18</td>
<td></td>
<td>10.0 wt% NaCl</td>
</tr>
<tr>
<td>8:25</td>
<td>0.1 wt% NaOH</td>
<td>1.85 wt% HCl</td>
</tr>
<tr>
<td>8:35</td>
<td></td>
<td>2.50 wt% H2SO4</td>
</tr>
<tr>
<td>8:42</td>
<td></td>
<td>3.64 wt% HCl</td>
</tr>
</tbody>
</table>
Shock Crystallization of Sodium Chloride and Sodium Sulfate
Flow Run #12 5/29/91

Analytic Method(s)  Extinction Measurements

** Nozzle **
<table>
<thead>
<tr>
<th>Type</th>
<th>#4B, coned tip</th>
</tr>
</thead>
<tbody>
<tr>
<td>Position</td>
<td>at flow tube</td>
</tr>
</tbody>
</table>

** Pressure **

| 250-253 bar |

** Jet Feed **
| Flowrate  | 0.5 g/min |
| Exit Temp. | ** TC failure ** |
| Delivery  | Sample Loop (1 ml) |

** SCW Feed **
| Flowrate | 10.2 g/min |
| Inlet Temp. | 554 C |

** Mixed Stream **
| Exit Temp. | 560 C |

** Cell Block **
| Top Temp.  | 602 C |
| Bot. Temp. | 602 C |

** Nozzle Cooling **
| Type       | distilled water |
| Flowrate   | 2.6 cc/min @ STP |

Summary of Extinction Measurements

<table>
<thead>
<tr>
<th>Jet Compo. wt%</th>
<th>Salt</th>
<th>Laser Power (uW)</th>
<th>%T</th>
<th>Abs -ln(L/Lo)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Initial</td>
<td>Trans\</td>
<td>Ambient-</td>
</tr>
<tr>
<td>0.05</td>
<td>Na₂SO₄</td>
<td>6.27</td>
<td>5.97</td>
<td>0.045</td>
</tr>
<tr>
<td>0.03</td>
<td>&quot;</td>
<td>6.32</td>
<td>6.10</td>
<td>0.047</td>
</tr>
<tr>
<td>0.3</td>
<td>&quot;</td>
<td>6.36</td>
<td>3.40</td>
<td>0.048</td>
</tr>
<tr>
<td>0.1</td>
<td>&quot;</td>
<td>6.43</td>
<td>5.62</td>
<td>0.049</td>
</tr>
<tr>
<td>1.0</td>
<td>&quot;</td>
<td>6.47</td>
<td>0.55</td>
<td>0.051</td>
</tr>
<tr>
<td>0.5</td>
<td>&quot;</td>
<td>6.49</td>
<td>1.66</td>
<td>0.053</td>
</tr>
<tr>
<td>3.0</td>
<td>&quot;</td>
<td>6.53</td>
<td>0.15</td>
<td>0.054</td>
</tr>
<tr>
<td>0.5</td>
<td>&quot;</td>
<td>6.38</td>
<td>1.83</td>
<td>0.056</td>
</tr>
<tr>
<td>3.0</td>
<td>NaCl</td>
<td>6.2</td>
<td>5.4</td>
<td>0.057</td>
</tr>
<tr>
<td>10.0</td>
<td>&quot;</td>
<td>6.5</td>
<td>5.7</td>
<td>0.058</td>
</tr>
<tr>
<td>3/3</td>
<td>Mixed</td>
<td>6.7</td>
<td>4.4</td>
<td>0.060</td>
</tr>
<tr>
<td>0.3</td>
<td>Na₂SO₄</td>
<td>7.18</td>
<td>2.72</td>
<td>0.062</td>
</tr>
<tr>
<td>0.1</td>
<td>&quot;</td>
<td>7.01</td>
<td>5.31</td>
<td>0.063</td>
</tr>
<tr>
<td>0.03</td>
<td>&quot;</td>
<td>6.97</td>
<td>6.62</td>
<td>0.065</td>
</tr>
<tr>
<td>1.0</td>
<td>&quot;</td>
<td>6.93</td>
<td>0.56</td>
<td>0.066</td>
</tr>
</tbody>
</table>

~ ambient power estimated from later runs
\^ extinction was unsteady for NaCl runs and mixed salt run (average %T given).
Shock Crystallization of Sodium Sulfate - Effect of Jet Flowrate

Flow Run #14  
6/8/91

**Analytic Method(s)**

- Extinction Measurements

**Nozzle**

- Type: #2B, flat tip
- Position: in flow tube

**Pressure**

- 249-251 bar

**Jet Feed**

- Delivery: Sample Loop (2 & 5 ml)

**SCW Feed**

- Flowrate: 10.2 g/min

**Cell Block**

- Top Temp.: 602 C
- Bot. Temp.: 602 C

**Nozzle Cooling**

- Type: distilled water
- Flowrate: 2.9 cc/min @STP

<table>
<thead>
<tr>
<th>Jet Flow (g/min)</th>
<th>Jet Temp. (°C)</th>
<th>SCW Temp. (°C)</th>
<th>Mixed T (°C)</th>
<th>SV (g/cc)</th>
<th>Vf (cc/min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5</td>
<td>120-180</td>
<td>541</td>
<td>560</td>
<td>13.01</td>
<td>139.2</td>
</tr>
<tr>
<td>1.0</td>
<td>110-150</td>
<td>543</td>
<td>553</td>
<td>12.80</td>
<td>143.4</td>
</tr>
</tbody>
</table>

### Summary of Extinction Measurements

<table>
<thead>
<tr>
<th>Jet Flowrate (g/min)</th>
<th>Jet Compo. wt% Na₂SO₄</th>
<th>Laser Power (uW)</th>
<th>%T</th>
<th>Abs -Ir. (l/l₀)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5</td>
<td>0.6</td>
<td>6.79</td>
<td>1.75</td>
<td>0.045</td>
</tr>
<tr>
<td>0.5</td>
<td>0.1</td>
<td>6.75</td>
<td>6.06</td>
<td>0.047</td>
</tr>
<tr>
<td>0.5</td>
<td>0.4</td>
<td>6.71</td>
<td>2.97</td>
<td>0.048</td>
</tr>
<tr>
<td>0.5</td>
<td>0.03</td>
<td>6.66</td>
<td>6.52</td>
<td>0.049</td>
</tr>
<tr>
<td>0.5</td>
<td>0.05</td>
<td>6.93</td>
<td>6.65</td>
<td>0.051</td>
</tr>
<tr>
<td>0.5</td>
<td>0.2</td>
<td>6.83</td>
<td>5.08</td>
<td>0.053</td>
</tr>
<tr>
<td>0.5</td>
<td>0.8</td>
<td>6.76</td>
<td>0.95</td>
<td>0.054</td>
</tr>
<tr>
<td>0.5</td>
<td>2.0</td>
<td>6.61</td>
<td>0.12</td>
<td>0.056</td>
</tr>
<tr>
<td>1.0</td>
<td>0.03</td>
<td>6.48</td>
<td>6.22</td>
<td>0.057</td>
</tr>
<tr>
<td>1.0</td>
<td>0.1</td>
<td>6.41</td>
<td>4.90</td>
<td>0.058</td>
</tr>
<tr>
<td>1.0</td>
<td>0.4</td>
<td>6.36</td>
<td>1.13</td>
<td>0.060</td>
</tr>
<tr>
<td>1.0</td>
<td>0.4</td>
<td>5.92</td>
<td>1.05</td>
<td>0.062</td>
</tr>
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<td>1.0</td>
<td>0.05</td>
<td>5.70</td>
<td>5.10</td>
<td>0.063</td>
</tr>
<tr>
<td>1.0</td>
<td>0.2</td>
<td>5.59</td>
<td>2.78</td>
<td>0.065</td>
</tr>
<tr>
<td>1.0</td>
<td>0.1</td>
<td>5.43</td>
<td>4.15</td>
<td>0.066</td>
</tr>
<tr>
<td>1.0</td>
<td>0.6</td>
<td>5.28</td>
<td>0.36</td>
<td>0.066</td>
</tr>
<tr>
<td>1.0</td>
<td>0.8</td>
<td>5.12</td>
<td>0.15</td>
<td>0.066</td>
</tr>
</tbody>
</table>

*ambient power estimated*
Shock Crystallization of Sodium Sulfate - Pressure Effects
Flow Run #18  
6/19/91

**Analytic Method(s)**

<table>
<thead>
<tr>
<th>Nozzle</th>
<th>Type</th>
<th>#2B, flat tip</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Position</td>
<td>in flow tube</td>
</tr>
</tbody>
</table>

**Jet Feed**

<table>
<thead>
<tr>
<th>Flowrate</th>
<th>0.5 g/min</th>
</tr>
</thead>
<tbody>
<tr>
<td>Delivery</td>
<td>Sample Loop (2 ml)</td>
</tr>
</tbody>
</table>

**SCW Feed**

<table>
<thead>
<tr>
<th>Flowrate</th>
<th>10.2 g/min</th>
</tr>
</thead>
</table>

**Cell Block**

| Top Temp. | 602 C |
| Bot. Temp. | 601 C |

**Nozzle Cooling**

| Type | distilled water |
| Flowrate | 2.9 cc/min @STP |

<table>
<thead>
<tr>
<th>Pressure (bar)</th>
<th>Jet Temp. (C)</th>
<th>SCW feed Temp (C)</th>
<th>Mixed Temp (C)</th>
<th>S. Vol. (cm3/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>229</td>
<td>120-190</td>
<td>556</td>
<td>563</td>
<td>14.5</td>
</tr>
<tr>
<td>297</td>
<td>125-195</td>
<td>566</td>
<td>567</td>
<td>10.7</td>
</tr>
<tr>
<td>228</td>
<td>120-170</td>
<td>564</td>
<td>564</td>
<td>14.6</td>
</tr>
<tr>
<td>200</td>
<td>102-120</td>
<td>557</td>
<td>554</td>
<td>16.7</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Pressure (bar)</th>
<th>Jet Compo. wt% Na2SO4</th>
<th>Laser Power (uW)</th>
<th>%T</th>
<th>Abs (-ln(I/I_0))</th>
</tr>
</thead>
<tbody>
<tr>
<td>229</td>
<td>0.1</td>
<td>6.84</td>
<td>6.32</td>
<td>0.040</td>
</tr>
<tr>
<td>*</td>
<td>0.6</td>
<td>6.86</td>
<td>2.50</td>
<td>0.042</td>
</tr>
<tr>
<td>*</td>
<td>0.3</td>
<td>6.87</td>
<td>4.52</td>
<td>0.044</td>
</tr>
<tr>
<td>*</td>
<td>1.0</td>
<td>6.88</td>
<td>1.28</td>
<td>0.046</td>
</tr>
<tr>
<td>297</td>
<td>0.1</td>
<td>6.98</td>
<td>6.34</td>
<td>0.048</td>
</tr>
<tr>
<td>*</td>
<td>0.6</td>
<td>6.99</td>
<td>2.28</td>
<td>0.050</td>
</tr>
<tr>
<td>*</td>
<td>0.3</td>
<td>6.98</td>
<td>4.51</td>
<td>0.052</td>
</tr>
<tr>
<td>*</td>
<td>1.0</td>
<td>6.97</td>
<td>0.73</td>
<td>0.054</td>
</tr>
<tr>
<td>228</td>
<td>1.0</td>
<td>6.88</td>
<td>1.45</td>
<td>0.056</td>
</tr>
<tr>
<td>200</td>
<td>1.0</td>
<td>6.65</td>
<td>6.65</td>
<td>0.058</td>
</tr>
<tr>
<td>*</td>
<td>3.0</td>
<td>6.65</td>
<td>6.65</td>
<td>0.060</td>
</tr>
</tbody>
</table>
Shock Crystallization of Sodium Chloride and Sodium Sulfate

Flow Run #20 6/29/91

Analytic Method(s) 35 mm photos (135 mm lens w/ 87 mm spacer).

Nozzle
- Type: #3, coned tip
- Position: tip at top of window

Pressure
- 250 bar

Jet Feed
- Flowrate: 0.5 g/min
- Exit Temp.: 115-165 C
- Delivery: Sample Loop (2 ml)

SCW Feed
- Flowrate: 10.2 g/min
- Inlet Temp.: 562 C

Mixed Stream
- Exit Temp.: 540 C

Cell Block
- Top Temp.: 600 C
- Bot. Temp.: 602 C

Nozzle Cooling
- Type: distilled water
- Flowrate: 3.2 cc/min @STP

Notes
- Used a 1/500 sec. shutter speed with ILFORD HP5 plus 400 B/W film.

Summary of Photoed Jets

<table>
<thead>
<tr>
<th>Run Time (hr:min)</th>
<th>Jet Feed</th>
</tr>
</thead>
<tbody>
<tr>
<td>8:06</td>
<td>3.0 wt% NaCl</td>
</tr>
<tr>
<td>8:26</td>
<td>3.0 wt% Na2SO4</td>
</tr>
<tr>
<td>9:58</td>
<td>10.0 wt% NaCl</td>
</tr>
<tr>
<td>11:08</td>
<td>3.0 wt% NaCl &amp; 3.0 wt% Na2SO4</td>
</tr>
</tbody>
</table>
Shock Crystallization of Sodium Sulfate - Effect of Jet Flowrate

Flow Run #29 7/25/91

Analytic Method(s)  Extinction Measurements

**Nozzle**
- Type: #4, coned tip
- Position: in flow tube

**Pressure**
- 249 bar

**Jet Feed**
- Delivery: Sample Loop (2 & 5 ml)
- Salt Flow: 0.003 g Na₂SO₄/min

**SCW Feed**
- Flowrate: 10.2 g/min

**Cell Block**
- Top Temp.: 600 C
- Bot. Temp.: 600 C

**Nozzle Cooling**
- Type: distilled water

<table>
<thead>
<tr>
<th>Jet Flow (g/min)</th>
<th>Jet Temp. (C)</th>
<th>SCW Temp. (C)</th>
<th>Mixed T (C)</th>
<th>Mixed V (cm³/g)</th>
<th>Noz CW (cc/min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.3</td>
<td>135-180</td>
<td>560</td>
<td>568.5</td>
<td>13.32</td>
<td>3.8</td>
</tr>
<tr>
<td>0.5</td>
<td>120-140</td>
<td>565</td>
<td>565</td>
<td>13.22</td>
<td>2.3</td>
</tr>
<tr>
<td>0.7</td>
<td>120-135</td>
<td>565</td>
<td>563</td>
<td>13.16</td>
<td>2.0</td>
</tr>
<tr>
<td>1.0</td>
<td>110-130</td>
<td>564</td>
<td>558</td>
<td>13.01</td>
<td>1.8</td>
</tr>
<tr>
<td>1.5</td>
<td>110-130</td>
<td>568</td>
<td>551</td>
<td>12.81</td>
<td>1.5</td>
</tr>
</tbody>
</table>

Summary of Extinction Measurements (constant salt flow)

<table>
<thead>
<tr>
<th>Jet Flowrate (g/min)</th>
<th>Jet Compo. wt% Na₂SO₄</th>
<th>Laser Power (μW)</th>
<th>%T</th>
<th>Abs -ln(l/lo)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5</td>
<td>0.6</td>
<td>5.94</td>
<td>2.10</td>
<td>0.030</td>
</tr>
<tr>
<td>0.7</td>
<td>0.43</td>
<td>6.01</td>
<td>2.35</td>
<td>0.033</td>
</tr>
<tr>
<td>0.3</td>
<td>1.0</td>
<td>6.10</td>
<td>1.82</td>
<td>0.036</td>
</tr>
<tr>
<td>1.0</td>
<td>0.3</td>
<td>6.04</td>
<td>2.57</td>
<td>0.039</td>
</tr>
<tr>
<td>1.5</td>
<td>0.2</td>
<td>6.00</td>
<td>2.73</td>
<td>0.042</td>
</tr>
<tr>
<td>0.5</td>
<td>0.6</td>
<td>6.05</td>
<td>2.09</td>
<td>0.045</td>
</tr>
<tr>
<td>1.0</td>
<td>0.3</td>
<td>5.95</td>
<td>2.49</td>
<td>0.048</td>
</tr>
</tbody>
</table>

Note: sample loop of 5 ml used for last four injections
Shock Crystallization of Sodium Sulfate

Flow Run #31 8/3/91

Analytic Method(s)  Extinction Measurements

<table>
<thead>
<tr>
<th>Nozzle</th>
<th>Type</th>
<th>#4B, coned tip</th>
</tr>
</thead>
<tbody>
<tr>
<td>Position</td>
<td>in flow tube</td>
<td></td>
</tr>
</tbody>
</table>

Pressure

<p>| | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>249.5 bar</td>
<td></td>
</tr>
</tbody>
</table>

Jet Feed

<p>| | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Flowrate</td>
<td>0.5 g/min</td>
</tr>
<tr>
<td>Exit Temp.</td>
<td>115-135 C</td>
</tr>
<tr>
<td>Delivery</td>
<td>Sample Loop (2 ml)</td>
</tr>
</tbody>
</table>

SCW Feed

<p>| | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Flowrate</td>
<td>10.2 g/min</td>
</tr>
<tr>
<td>Inlet Temp.</td>
<td>562 C</td>
</tr>
</tbody>
</table>

Mixed Stream

<p>| | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Exit Temp.</td>
<td>565 C</td>
</tr>
</tbody>
</table>

Cell Block

<p>| | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Top Temp.</td>
<td>600 C</td>
</tr>
<tr>
<td>Bot. Temp.</td>
<td>600 C</td>
</tr>
</tbody>
</table>

Nozzle Cooling

<p>| | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Type</td>
<td>distilled water</td>
</tr>
<tr>
<td>Flowrate</td>
<td>2.4 cc/min @STP</td>
</tr>
</tbody>
</table>

Summary of Extinction Measurements

<table>
<thead>
<tr>
<th>Jet Compo.</th>
<th>Laser Power (uW)</th>
<th>%T</th>
<th>Abs -ln(I/I₀)</th>
</tr>
</thead>
<tbody>
<tr>
<td>wt% Na₂SO₄</td>
<td>Initial</td>
<td>Trans</td>
<td>Ambient</td>
</tr>
<tr>
<td>0.8</td>
<td>5.64</td>
<td>1.22</td>
<td>0.030</td>
</tr>
<tr>
<td>0.2</td>
<td>5.65</td>
<td>4.68</td>
<td>0.032</td>
</tr>
<tr>
<td>1.5</td>
<td>5.66</td>
<td>0.23</td>
<td>0.034</td>
</tr>
<tr>
<td>0.6</td>
<td>5.67</td>
<td>2.04</td>
<td>0.036</td>
</tr>
<tr>
<td>0.1</td>
<td>5.65</td>
<td>5.28</td>
<td>0.038</td>
</tr>
<tr>
<td>1.0</td>
<td>5.63</td>
<td>0.70</td>
<td>0.040</td>
</tr>
<tr>
<td>0.4</td>
<td>5.58</td>
<td>3.23</td>
<td>0.041</td>
</tr>
<tr>
<td>0.05</td>
<td>5.55</td>
<td>5.39</td>
<td>0.043</td>
</tr>
<tr>
<td>2.0</td>
<td>5.52</td>
<td>0.11</td>
<td>0.045</td>
</tr>
<tr>
<td>0.6</td>
<td>5.47</td>
<td>1.93</td>
<td>0.047</td>
</tr>
<tr>
<td>0.1</td>
<td>5.41</td>
<td>5.03</td>
<td>0.049</td>
</tr>
<tr>
<td>1.5</td>
<td>5.35</td>
<td>0.22</td>
<td>0.051</td>
</tr>
</tbody>
</table>
Shock Crystallization - Laser Extinction Mixed Jets
Flow Run #39 5/16/92

Analytic Method(s) - Extinction Measurements

Nozzle
- Type: #4, coned tip
- Position: in flow tube

Pressure
- 250 bar

Jet Feed
- Flowrate: 0.5 g/min
- Exit Temp.: 110-150 C
- Delivery: Sample Loop (2 ml)

SCW Feed
- Flowrate: 10.0 g/min
- Inlet Temp.: 559 C

Mixed Stream
- Exit Temp.: 565 C

Cell Block
- Top Temp.: 595 C
- Bot. Temp.: 595 C

Nozzle Cooling
- Type: distilled water
- Flowrate: 1.7 cc/min @ STP

Summary of Extinction Measurements

<table>
<thead>
<tr>
<th>Jet Composition (wt%)</th>
<th>Laser Power (uW)</th>
<th>%T</th>
<th>Abs</th>
<th>Note</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na₂SO₄ : NaCl</td>
<td>Initial</td>
<td>Trans</td>
<td>Ambient</td>
<td></td>
</tr>
<tr>
<td>1.0 0.0</td>
<td>11.36</td>
<td>0.83</td>
<td>0.031</td>
<td>7.0</td>
</tr>
<tr>
<td>0.0 1.0</td>
<td>11.25</td>
<td>7.84</td>
<td>0.032</td>
<td>69.6</td>
</tr>
<tr>
<td>1.0 1.0</td>
<td>11.50</td>
<td>9.56</td>
<td>0.033</td>
<td>83.1</td>
</tr>
<tr>
<td>1.0 0.33</td>
<td>11.25</td>
<td>0.68</td>
<td>0.034</td>
<td>5.8</td>
</tr>
<tr>
<td>1.0 3.0</td>
<td>11.30</td>
<td>10.33</td>
<td>0.035</td>
<td>91.4</td>
</tr>
<tr>
<td>1.0 0.66</td>
<td>11.30</td>
<td>8.82</td>
<td>0.035</td>
<td>78.0</td>
</tr>
<tr>
<td>1.0 0.33</td>
<td>11.38</td>
<td>0.55</td>
<td>0.037</td>
<td>4.5</td>
</tr>
<tr>
<td>0.0 0.5</td>
<td>11.26</td>
<td>10.63</td>
<td>0.038</td>
<td>94.4</td>
</tr>
<tr>
<td>0.0 3.0</td>
<td>10.57</td>
<td>9.27</td>
<td>0.039</td>
<td>87.7</td>
</tr>
<tr>
<td>0.0 1.0</td>
<td>10.00</td>
<td>9.07</td>
<td>0.040</td>
<td>90.7</td>
</tr>
<tr>
<td>0.0 10.0</td>
<td>9.42</td>
<td>8.60</td>
<td>0.041</td>
<td>91.3</td>
</tr>
</tbody>
</table>

Note 1: steady scattering of laser power
Note 2: scattered laser power unsteady, minimum %T given
Note 3: laser power showed an initial and final minimum (second %T) - see strip chart
Shock Crystallization - Malvern Test - Effect of Jet Concentration

Flow Run #43  7/18/92

Analytic Method(s)  Malvern Particle Size Analyzer

Nozzle
- Type: #4B, coned tip
- Position: in flow tube

Pressure
- 250 bar

Jet Feed
- Flowrate: 0.5 g/min
- Exit Temp.: 180-210 °C
- Delivery: Sample Loop (2 ml)

SCW Feed
- Flowrate: 10.2 g/min
- Inlet Temp.: 568 °C

Mixed Stream
- Exit Temp.: 565 °C

Cell Block
- Top Temp.: 588 °C
- Bot. Temp.: 585 °C

Nozzle Cooling
- Type: distilled water
- Flowrate: 1.0 cc/min @ STP

Summary of Malvern Measurements

<table>
<thead>
<tr>
<th>Jet Composition (wt%)</th>
<th>%OBS OBS=1-I/lo</th>
<th>D(4,3)</th>
<th>%T 100-%OBS</th>
<th>ABS -ln(T)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na₂SO₄</td>
<td>NaCl</td>
<td>0.2</td>
<td>1.0</td>
<td>2.7</td>
</tr>
<tr>
<td>0.5</td>
<td></td>
<td>68.4</td>
<td>2.5</td>
<td>31.6</td>
</tr>
<tr>
<td>1.0</td>
<td></td>
<td>4.9</td>
<td>13.2</td>
<td>95.1</td>
</tr>
<tr>
<td>1.0</td>
<td></td>
<td>91.4</td>
<td>2.0</td>
<td>8.6</td>
</tr>
<tr>
<td>3.0</td>
<td></td>
<td>3.5</td>
<td>14.3</td>
<td>86.5</td>
</tr>
</tbody>
</table>

Note 1: average diameter calculated with Malvern using kidlat 5,0
Note 2: 2 mm beam expander on Malvern laser (2 mW)

Malvern laser power fluctuated during the run due to beam steering caused by density gradients in the solution. For each analysis 1000 power scans were averaged and a background measurement was taken approximately one minute before salt injection. Due to the fluctuations, the five inner rings were disabled in the calculations. Most of the analyses showed adequate fit of the size distribution to the laser power measurements.
Shock Crystallization - Malvern Test - Pressure and Mixed Jet Effects

Flow Run #44  7/23/92

Analytic Method(s)  Malvern Particle Size Analyzer

Nozzle
Type  #1, flat tip
Position  top of flow tube

Jet Feed
Flowrate  0.5 g/min
Exit Temp.  120-180 C
Delivery  Sample Loop (2 ml)

SCW Feed
Flowrate  10.2 g/min
Inlet Temp.  550 C

Mixed Stream
Exit Temp.  568 C

Cell Block
Top Temp.  584 C
Bot. Temp.  585 C

Nozzle Cooling
Type  distilled water
Flowrate  0.6 cc/min @ STP

Summary of Malvern Measurements

<table>
<thead>
<tr>
<th>Jet Composition (wt%)</th>
<th>Pressure (bar)</th>
<th>%OBS</th>
<th>D(4,3)</th>
<th>%T 100-%OBS</th>
<th>ABS -ln(T)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na₂SO₄</td>
<td>NaCl</td>
<td>250</td>
<td>OBS=1-l/lo</td>
<td>2.7</td>
<td>60.4</td>
</tr>
<tr>
<td>0.4</td>
<td>2.0</td>
<td>4.3</td>
<td>12.7</td>
<td>95.7</td>
<td>0.04</td>
</tr>
<tr>
<td>0.5</td>
<td>1.0</td>
<td>20.0</td>
<td>9.7</td>
<td>80.0</td>
<td>0.22</td>
</tr>
<tr>
<td>0.4</td>
<td>2.0</td>
<td>5.2</td>
<td>16.3</td>
<td>94.8</td>
<td>0.05</td>
</tr>
<tr>
<td>2.0</td>
<td>10.0</td>
<td>0.0</td>
<td></td>
<td>100.0</td>
<td>0.00</td>
</tr>
<tr>
<td>200</td>
<td>200</td>
<td>3.4</td>
<td>17.6</td>
<td>96.6</td>
<td>0.03</td>
</tr>
</tbody>
</table>

(1) size distribution was binodal and appeared as a combination of the pure salt runs
(2) Obscuration was too low to perform size analysis

Malvern laser power fluctuated during the run due to beam steering caused by density gradients in the solution. For each analysis 1000 power scans were averaged and a background measurement was taken approximately one minute before salt injection. The five inner rings were disabled in the calculations to lessen the effects of the power fluctuations. The analyses showed a worst fit than Flow Run 43, and thus the sizes should be used for trends only. This could be due to window deterioration from corrosion.
Shock Crystallization - Stereomicroscope Photos
Flow Run #46  8/19/92

Analytic Method(s)  35 mm photos with stereomicroscope for magnification

Nozzle

<table>
<thead>
<tr>
<th>Type</th>
<th>#3, coned tip</th>
</tr>
</thead>
<tbody>
<tr>
<td>Position</td>
<td>tip at top of window</td>
</tr>
</tbody>
</table>

Pressure

<table>
<thead>
<tr>
<th></th>
<th>200 &amp; 250 bar</th>
</tr>
</thead>
</table>

Jet Feed

<table>
<thead>
<tr>
<th>Flowrate</th>
<th>0.5 g/min (unless noted)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Exit Temp.</td>
<td>115-140 C</td>
</tr>
<tr>
<td>Delivery</td>
<td>Sample Loop (2 ml)</td>
</tr>
</tbody>
</table>

SCW Feed

<table>
<thead>
<tr>
<th>Flowrate</th>
<th>10.2 g/min</th>
</tr>
</thead>
<tbody>
<tr>
<td>Inlet Temp.</td>
<td>545 C</td>
</tr>
</tbody>
</table>

Mixed Stream

<table>
<thead>
<tr>
<th>Exit Temp.</th>
<th>520 C</th>
</tr>
</thead>
</table>

Cell Block

<table>
<thead>
<tr>
<th>Top Temp.</th>
<th>585 C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bot. Temp.</td>
<td>586 C</td>
</tr>
</tbody>
</table>

Nozzle Cooling

<table>
<thead>
<tr>
<th>Type</th>
<th>distilled water</th>
</tr>
</thead>
<tbody>
<tr>
<td>Flowrate</td>
<td>1.6 cc/min @STP</td>
</tr>
</tbody>
</table>

Notes

Used a 1/250 sec. shutter speed with B/W film
Roll 1: Kodak TMAX 400, 36 exposures
Roll 2: Ilford HF5 plus 400, 36 exposures
Lighting: "Fiber-Light" High Intensity Illuminator, 200 W
During injection of 10% SS solution, solid salt piled up from the bottom of cell and was visible through the window port

Summary of Jet Photos

<table>
<thead>
<tr>
<th>Pressure (bar)</th>
<th>Jet Feed</th>
</tr>
</thead>
<tbody>
<tr>
<td>250</td>
<td>Pure H2O (0.25 - 2.0 g/min)</td>
</tr>
<tr>
<td></td>
<td>10.0 wt% NaCl</td>
</tr>
<tr>
<td></td>
<td>3.0 wt% NaCl &amp; 1.0 wt% Na2SO4</td>
</tr>
<tr>
<td></td>
<td>0.67 wt% NaCl &amp; 1.0 wt% Na2SO4</td>
</tr>
<tr>
<td></td>
<td>1.0 wt% Na2SO4</td>
</tr>
<tr>
<td>200</td>
<td>Pure H2O</td>
</tr>
<tr>
<td></td>
<td>10.0 wt% Na2SO4</td>
</tr>
</tbody>
</table>
Shock Crystallization - 35mm Camera Photos

Flow Run #50  9/5/92

Analytic Method(s) 35 mm photos - 50 mm lens with 21 mm teleconverter

Nozzle

<table>
<thead>
<tr>
<th>Type</th>
<th>#3, coned tip</th>
</tr>
</thead>
<tbody>
<tr>
<td>Position</td>
<td>tip at top of window</td>
</tr>
</tbody>
</table>

Pressure  200 - 250 bar

Jet Feed

| Flowrate | 0.25 g/min (unless noted) |
| Exit Temp. | 130-180 C |
| Delivery | Sample Loop (1 ml) |

SCW Feed

| Flowrate | 10.2 g/min |
| Inlet Temp. | 542 - 551 C |

Mixed Stream

| Exit Temp. | 516 - 536 C |

Cell Block

| Top Temp. | 588 C |
| Bot. Temp. | 582 C |

Nozzle Cooling

| Type | distilled water |
| Flowrate | 2.1 cc/min @STP |

Notes

Used a 1/500 sec. shutter speed with B/W film

Roll 1 & 2: Ilford HP5 plus 400, 36 exposures

Lighting: 60 W light bulb

Summary of Jet Photos

<table>
<thead>
<tr>
<th>Pressure (bar)</th>
<th>Jet Feed</th>
</tr>
</thead>
<tbody>
<tr>
<td>250</td>
<td>Pure H₂O</td>
</tr>
<tr>
<td>*</td>
<td>1.0 wt% Na₂SO₄</td>
</tr>
<tr>
<td>*</td>
<td>5.0 wt% Na₂SO₄</td>
</tr>
<tr>
<td>*</td>
<td>10.0 wt% NaCl</td>
</tr>
<tr>
<td>*</td>
<td>3.33 wt% NaCl &amp; 5.0 wt% Na₂SO₄</td>
</tr>
<tr>
<td>10.0 wt% Na₂SO₄</td>
<td></td>
</tr>
<tr>
<td>230</td>
<td>Pure H₂O</td>
</tr>
<tr>
<td>*</td>
<td>5.0 wt% Na₂SO₄</td>
</tr>
<tr>
<td>*</td>
<td>10.0 wt% NaCl</td>
</tr>
<tr>
<td>200</td>
<td>Pure H₂O (0.25 &amp; 0.5 g/min)</td>
</tr>
<tr>
<td>*</td>
<td>5.0 wt% Na₂SO₄</td>
</tr>
<tr>
<td>*</td>
<td>10.0 wt% NaCl</td>
</tr>
</tbody>
</table>
11.4 FIDAP Input Files

This appendix lists the input files used in the laminar jet simulations described in Sections 9.1.3 and 9.1.4. The Fluid Dynamics Analysis Package, FIDAP, developed by Fluid Dynamics International (Evanston, IL) was run on the MIT Cray X-MP. The program documentation should be consulted for an explanation of the files. In addition to the input files, schematics of the finite element grids and a comparison of the constant property free jet predicts of FIDAP and the finite difference code are also given. The included files and figures are described below.

**HF1.IN**  Table 11.1  Input file to simulate a constant property free jet (Re=200). Results only presented here.

**Figure 11.2**  Schematic of simulation grid for free jet.

**Figure 11.3**  Predicted centerline profiles.

**Figure 11.4**  Predicted radial profiles.

**LJ1.IN**  Table 11.2  Input file to simulate a water free jet issuing into a supercritical water stream with buoyancy force neglected (same geometry as HF1.IN). Results presented in Section 9.1.3.

**LJ2.IN**  Table 11.3  Input file to simulate a water free jet issuing into a supercritical water stream with buoyancy force included (same geometry as HF1.IN). Results presented in Section 9.1.4.

**LJ3a.IN**  Table 11.4  Input for confined jet with actual cell geometry. Results presented in Section 9.1.4.

**Figure 11.5**  Schematic of simulation grid for confined jet.
Table 11.1  FIDAP input file for simulation of a constant property laminar free jet issuing into a coaxially flowing stream (Re=200).

FILE: HF1.IN

*title
2-D axi-symmetric heated free jet
constant properties
*fimesh(2-d,imax=3,jmax=5)
expi
  / 1 2 3
  1 0 61
expj
  / 1 2 3 4 5
  1 0 9 0 31
parameter
  / units = cm
  radius  1.0
  width   20.0
  length  300.0
  / units = cm/s
  uprim   1.0
  usec    0.2
  / units = C
  tprim   150.0
  tsec    550.0
point(cartesian)
  /# i  j  k   x    y
  1 1 1 1 0  0
  2 1 3 1 0  radius
  3 1 5 1 0  width
  4 3 5 1 length width
  5 3 3 1 length radius
  6 3 1 1 length 0
line
  1 2 1.0  3
  6 5 1.0  3
  2 3 5.0  3
  5 4 5.0  3
  1 6 5.0  3
  2 5 5.0  3
  3 4 5.0  3
surface
  1 4
bcnode(ux)
  1 2 uprim
  2 3 usec
  3 4 usec
bcnode(uy)
  1 2 0.0
  2 3 0.0
  1 6 0.0
bcnode(temperature)
  1 2 tprim
  2 3 tsec
  3 4 tsec
area
  1 4
elements(quadrilateral,nodes=9,all)
end
*FIPREP
problem(steady, nonlinear, newtonian,
Boundary Conditions

line

1 - 2  \quad U = U_p  \
      \quad H = H_p  \
      \quad V = 0.0

2 - 3  \quad U = U_s  \
      \quad H = H_s  \
      \quad V = 0.0

3 - 4  \quad U = U_s  \
      \quad H = H_s

1 - 6  \quad V = 0.0

radius = 0.042 cm
width = 1.5
length = 10.1

Figure 11.2  Schematic of FIDAP simulation grid for free jet.
Figure 11.3  Comparison of constant property laminar free jet codes: centerline velocity and temperature profiles (Re = 200).  FiDAP - Fluid Dynamics Analysis Package (FDI, Inc., Evanston, IL).
Figure 11.4  Comparison of constant property laminar free jet codes: radial velocity and temperature profiles (Re = 200). Computer models described in Section 9.1.1 and 9.1.2.
Table 11.2  FIDAP input file for simulation of a laminar free jet issuing into a coaxially flowing supercritical water stream (buoyancy force neglected).

**FILE: LJ1.IN**

*title
2-D axi-symmetric heated free jet -
enthalpy formulation, 250 bar
*fimesh(2-d,imax=3,jmax=5)
expi
/ 1 2 3
   1 0 31
expj
/ 1 2 3 4 5
   1 0 11 0 21
parameter
/ units = cm
radius 0.042
width 1.5
length 10.1
/ units = cm/s
uprim 1.61
usec 0.43
/ units = J/g (enthalpy used for T)
hprim 647.8
hsec 3336.5
point(cartesian)
#/ i j k x   y
  1 1 1 1 0 0
  2 1 3 1 0 radius
  3 1 5 1 0 width
  4 3 5 1 length width
  5 3 3 1 length radius
  6 3 1 1 length 0
line
1 2 1.0 3
6 5 1.0 3
2 3 5.0 3
1 4 5.0 3
5 4 5.0 3
1 6 5.0 3
2 5 5.0 3
3 4 5.0 3
surface
1 4
bcnode(ux)
1 2 uprim
2 3 usec
3 4 usec
bcnode(uy)
1 2 0.0
2 3 0.0
1 6 0.0
bcnode(temperature)
1 2 hprim
2 3 hsec
3 4 hsec
area
1 4
elements(quadrilateral,nodes=9,all).
end

*FIPREP
Table 11.3 FIDAP input file for simulation of a laminar free jet issuing into a coaxially flowing supercritical water stream (buoyancy force included).

FILE: LJ2.IN

*title
2-D axi-symmetric heated free jet -
with buoyancy, 250 bar
*fimesh(2-d,imax=3,jmax=5)
expi
/ 1 2 3
 1 0 41
expj
/ 1 2 3 4 5
 1 0 15 0 51

parameter
/ units = cm
radius 0.042
width 1.5
length 10.1
/ units = cm/s
uprim 1.61
usec 0.43
/ units = J/g (enthalpy used for T)
hprim 647.8
hsec 3336.5

point(cartesian)
/# i j k x y
1 1 1 1 0 0
2 1 3 1 0 radius
3 1 5 1 0 width
4 3 5 1 length width
5 3 3 1 length radius
6 3 1 1 length 0

line
1 2 1.0 3
6 5 1.0 3
2 3 5.0 3
5 4 5.0 3
1 6 5.0 3
2 5 5.0 3
3 4 5.0 3

surface
1 4

bcsnode(ux)
1 2 uprim
2 3 usec
3 4 usec

bcsnode(uy)
1 2 0.0
2 3 0.0
1 6 0.0

bcsnode(temperature)
1 2 hprim
2 3 hsec
3 4 hsec

area
1 4

elements(quadrilateral,nodes=9,all)
end
*FIPREP
Table 11.4  FIDAP input file for simulation of a laminar confined jet issuing into a coaxially flowing supercritical water stream (buoyancy force included).

FILE: LJ3a.IN

*title
2-D axi-symmetric heated confined jet
- with buoyancy, 250 bar
*fimesh(2-d,imax=7,jmax=7)
expi
/ 1 2 3 4 5 6 7
 1 0 15 0 25 0 35
expj
/ 1 2 3 4 5
 1 0 11 0 31
parameter
/ units = cm
rad 0.042
wid1 0.45
wid2 1.27
len1 2.4
len2 3.7
len3 7.0
/ units = cm/s
uprim 1.61
usec 0.43
/ units = J/g (enthalpy used for T)
hprim 647.8
hsec 3336.5
point(cartesian)
/# i j k x y
1 1 1 1 0.0 0.0
2 1 3 1 0.0 rad
3 1 5 1 0.0 wid2
4 3 5 1 len1 wid2
5 3 3 1 len1 rad
6 3 1 1 len1 0.0
7 5 5 1 len2 wid1
8 5 3 1 len2 rad
9 5 1 1 len2 0.0
10 7 5 1 len3 wid1
11 7 3 1 len3 rad
12 7 1 1 len3 0.0
line
1 2 1.0 3
9 8 1.0 3
6 5 1.0 3
12 11 1.0 3
2 3 4.0 3 4.0 0.5
5 4 4.0 3 4.0 0.5
8 7 4.0 3 4.0 0.5
11 10 4.0 3 4.0 0.5
1 6 4.0 3
2 5 4.0 3
3 4 4.0 3
6 9 1.0 3
5 8 1.0 3
4 7 1.0 3
9 12 1.0 3
8 11 1.0 3
7 10 1.0 3

surface
1 4
6 7
9 10
bcnode(ux)
1 2 uprim
2 3 usec
3 4 0.0
4 7 0.0
7 10 0.0
bcnode(uy)
1 2 0.0
2 3 0.0
1 12 0.0
3 4 0.0
4 7 0.0
7 10 0.0
bcnode(temperature)
1 2 hprim
2 3 hsec
3 4 hsec
4 7 hsec
7 10 hsec
area
1 4
6 7
9 10
elements(quadrilateral, nodes=9, all)
end
*FIPREP

(remainder of file same as LJ2.IN)
Figure 11.5 Schematic of FIDAP simulation grid for confined jet in actual cell geometry.
Chapter 12.

References


Valyashko, V.M., "The phase diagram for a Type II system consisting of one volatile component and two nonvolatile ones", Geokhimiya, no.10, 1236-1243, in Russian, (1971b), abstract only translated in Geochemistry International, 8, 797, (1971b).


