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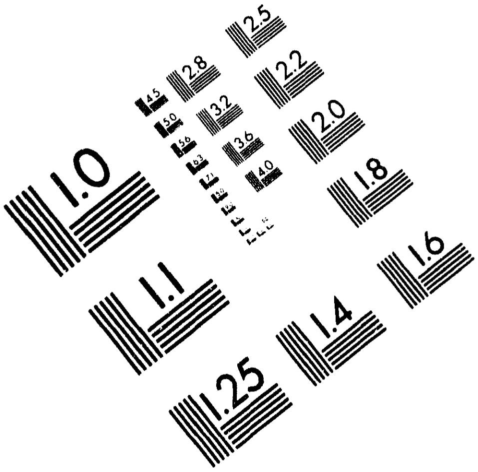

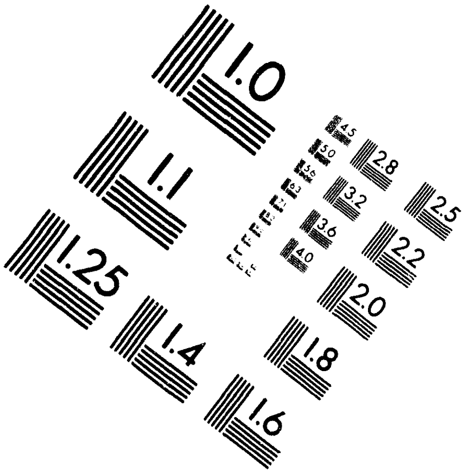

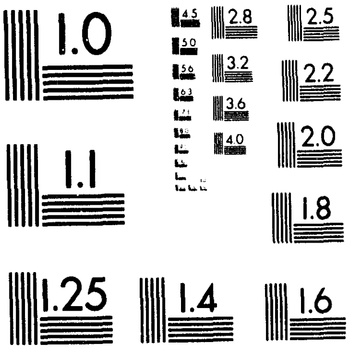

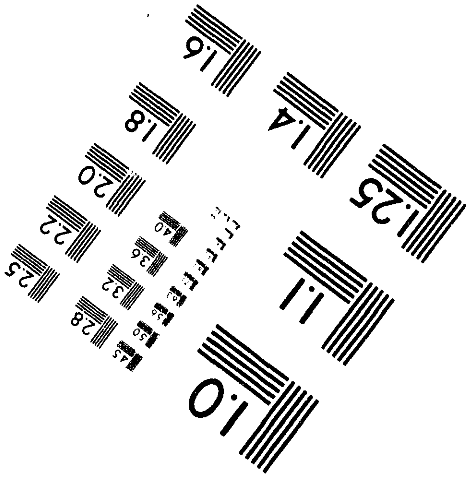

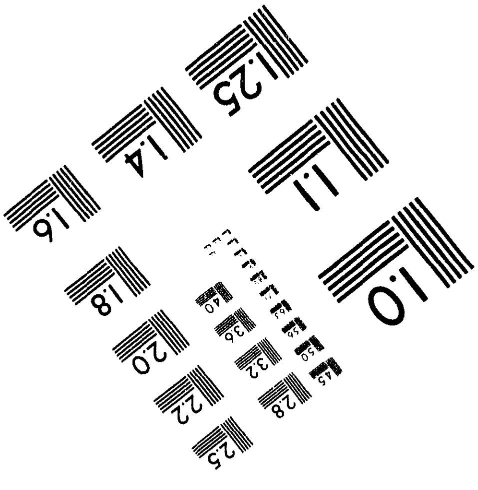

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EXPERIMENTAL TECHNIQUES TO DETERMINE SALT FORMATION AND DEPOSITION IN SUPERCRITICAL WATER OXIDATION REACTORS

Jennifer P. C. Chan, Costanzo A. LaJeunesse, and Steven F. Rice
Sandia National Laboratories
Livermore, California

ABSTRACT

Supercritical Water Oxidation (SCWO) is an emerging technology for destroying aqueous organic waste. Feed material, containing organic waste at concentrations typically less than 10 wt% in water, is pressurized and heated to conditions above water's critical point (374°C, 22.1 MPa) where the ability of water to dissolve hydrocarbons and other organic chemicals is greatly enhanced. An oxidizer, for example, air, oxygen, or hydrogen peroxide, is then added to the feed. Given adequate residence time and reaction temperature, the SCWO process rapidly produces innocuous combustion products. Organic carbon and nitrogen in the feed emerge as CO_2 and N_2; metals, heteroatoms, and halides appear in the effluent as inorganic salts and acids.

The oxidation of organic material containing heteroatoms, such as sulfur or phosphorous, forms acid anions. In the presence of metal ions, salts are formed and precipitate out of the supercritical fluid. In a tubular configured reactor, these salts agglomerate, adhere to the reactor wall, and eventually interfere in the processing of the organic component by causing a flow restriction in the reactor leading to an increase in pressure. This rapid precipitation is due to an extreme drop in salt solubility that occurs as the feed stream becomes supercritical.

To design a system that can accommodate the formation of these salts, it is important to understand the deposition process quantitatively. A phenomenological model is developed in this paper to predict the time that reactor pressure begins to rise as a function of the fluid axial temperature profile and effective solubility curve. The experimental techniques used to generate effective solubility curves for one salt of interest, Na_2SO_4, are described, and data is generated for comparison. Good correlation between the model and experiment is shown.

An operational technique is also discussed that allows the deposited salt to be redissolved in a single phase and removed from the affected portion of the reactor. This technique is demonstrated experimentally for a 0.5 wt% Na_2SO_4 solution.

INTRODUCTION

Sandia National Laboratories, California, SNL/CA, has been advancing the development of SCWO technology for the treatment of hazardous waste since 1987, beginning with the design and construction of a small volume, optically accessible reactor to understand the initiation of flames in a supercritical water medium [1, 2]. SNL/CA then developed two larger bench-scale tubular SCWO reactors, that are modular in construction and have ten to fifty gallons per day capacity. SNL/CA has destroyed simulated Hanford tank waste, and surrogate industrial waste consisting of pesticides, oil, and solvents. We have also conducted feasibility tests on obsolete military smokes, dyes, and pyrotechnics [3-6]. Recently, a secondary explosive, ammonium picrate, was also successfully tested with high destruction efficiency. Detailed experimental results from the destruction of ammonium picrate will appear in a subsequent paper.

SCWO is conceptually simple. Aqueous waste, typically ranging from 1-10 wt% oxidizable material, is pressurized and heated to conditions above the critical point of water (374°C, 22.1 MPa) where it can function as a fuel in an oxidation reaction. An oxidizer is added either to the cold feed or to a preheated feed. The elevated temperature of the mix is maintained primarily by the excess heat of reaction, and, given adequate reaction time, the waste-fuel is converted to innocuous materials.

Early patents on this process were issued to Modell [7] and Dickenson [8] for the concept of SCWO and the application of

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SCWO to the destruction of aqueous organic wastes in the early 80's. In addition to work at SNL/CA, SCWO has undergone rapid development by a number of scientists and engineers, primarily within the United States. The interested reader is referred to the review article by Tester, et. al. [9].

Despite this rapid development, salt deposition and subsequent flow system fouling remain important technical issues surrounding the practical applicability of SCWO to the destruction of toxic chemicals and other hazardous materials. Salts found in the flow system of a supercritical water reactor originate from several sources. Oxidation of organic material containing heteroatoms, such as sulfur and phosphorous, form acid anions. Due to concerns associated with the corrosive nature of acidic flows, many operational schemes involve neutralizing these acids with a base such as sodium hydroxide. In the presence of metal ions, salts are formed which precipitate out of the supercritical fluid and adhere to the reactor wall. Often, as in the case of the water soluble dyes we have tested, the metal ions are present in the chemical composition of the original organic to be oxidized.

Deposited salt leads to an increase in pressure in the reactor. To design a system that can accommodate the formation of these salts, it is important to understand the deposition process quantitatively. This paper describes a phenomenological model to predict the time that a pressure rise develops in the flow system as a result of a constriction of the flow path. This model describes the time it takes for a plug to form in terms of fluid temperature profiles and effective solubility curves. The experimental techniques used to generate solubility curves for one salt of interest, Na_2SO_4, are described and data is presented for comparison. Good correlation between the model and experiment is shown.

An operational strategy is also discussed that allows the deposited salt to be redissolved and removed from the affected portion of the reactor. This technique is demonstrated experimentally for a 0.5 wt% Na_2SO_4 solution.

DYE TREATMENT TESTS

The need to develop a quantitative understanding of the deposition process originated during a feasibility study to destroy obsolete munitions for the U. S. Army. The chemical composition of the munitions included organic dyes, inorganic salts, metallic salts, and heavy metals. The open air burning of these munitions produces toxic gases and destruction using incineration met with limited success due to the high inorganic content of the feeds. A more detailed discussion of the problems associated with disposal can be found in the experimental study conducted on these compounds [4]. Consequently, the military is investigating alternative technologies, including SCWO, to destroy the obsolete munitions inventory.

Difficulties processing $Na_2(C_{16}H_{10}N_2O_7S_2)$, Acid Orange 10, are representative of the operational problems encountered in destroying water soluble dyes using SCWO. This dye was destroyed using the flow reactor shown schematically in Figure 1. The reactor has a maximum operating temperature of 650°C and a maximum operating pressure of 51.0 MPa (7500 psi). Flowrate can be varied from about 1.5 ml/s (ambient condition feed, 25°C) to 0.2 ml/s. The feed and oxidizer heater sections are two parallel lengths of tubing heated by a series of tube furnaces with combined power of 4500 W on each line. These furnaces are individually controlled with process controllers. The reactor section is heated with six 375 W cable heaters which are used to maintain isothermal conditions along the reactor. The high-temperature portions of the system are made of 9/16" (1.43 cm) OD - 3/16" (0.477 cm) ID Inconel 625 tubing with Inconel 625 high-pressure fittings as unions. The temperature of the feed, oxidizer, and reacting fluid is measured with Inconel 600 sheathed Type-K thermocouples located directly in the fluid. The reaction is quenched with two simple counterflow heat exchangers.

The reactor is approximately 750 cm long, with two 90° turns at 260 and 300 cm. Thermocouples are located in the flow approximately every 60 cm at unions joining individual sections of the tubing. Pressure transducers are placed at three locations. PT1 is at the inlet to the reactor before any heaters. PT2 is located 140 cm into the reactor in the initial heat-up section. PT3 is located at the end of the system just before the pressure letdown regulator (c. f. , Figure 1). The readings of these transducers are recorded continuously throughout a test such that the development of a plug or constriction due to salt deposition can be detected as a pressure differential from one transducer to the next. PT2, at 140 cm, was located directly after the position of the plug formation in the experiments.

Testing was done by one of two different methods. The principal difference between the two methods is that in the first, the ingredients are preheated separately, prior to mixing, while in the second, all reactants are combined and then heated. When using the second method, the oxidant heater section was not used and was disconnected from the reactor portion of the system. Some dye pyrolysis and charring occurred using the first method, producing products that adhered to the reactor wall and could not be removed except by mechanical honing. As a result, most of the testing was done using the second method.

When operating with the second method, most processing tests were terminated due to plugging within the flow reactor. White salt deposits formed in the preheat section of the reactor and resulted in complete plugging. Figure 2 shows the pressure evolution of the system with time during a typical test. Subsequent analysis of the white powder that was removed from the reactor after cooldown indicated it was anhydrous sodium sulfate that was precipitated homogeneously from the fluid as it was heated. Collection of the sodium sulfate involves disassembly and destruction of a section of the reactor and consequently was not done for the bulk of the experiment in the study.

Although all dyes were destroyed in excess of 99.5%, based on total organic carbon analysis, tests generally concluded with a shut down of the reactor due to overpressurization.

Sulfur in the organic dyes oxidized under SCWO conditions to form sulfate ion. Because these dyes are principally sodium salts of organic acids, the sulfate is balanced by the sodium counter ion forming sodium sulfate and by H^+ forming sulfuric acid. In general, the Na^+ content of the dyes is insufficient to balance the sulfate product completely and as a result the effluents are acidic. Some sulfate remains in the reactor as Na_2SO_4 and the rest emerges in the effluent as H_2SO_4. Analysis of the effluent by specific ion electrode indicated that approximately 97% of the sodium in the feed remained in the reactor.

MODEL DESCRIPTION

To understand and quantify the deposition process, the following model is proposed and illustrated in Figure 3. Consider a small element of volume $A\Delta x$ within the tubular reactor, where A is the cross-sectional area. Assume that the solubility or salt concentration in the water, C, is a function of the fluid temperature, T, at a given pressure. Assume, further, that salt not dissolved in the water precipitates as an anhydrous solid, as indicated by analytical results of the deposit from the dye test, and that deposition and adherence to the reactor wall occurs at the place of precipitation. From the principle of conservation of mass, over an interval of time Δt,

$$\rho\, V_s(x,\Delta t) = [C(T)_x - C(T)_{x+\Delta x}]\, \dot{m}\, \Delta t, \tag{1}$$

where ρ is the density of the salt, V_s is the volume of the salt deposited within the volume $A\Delta x$, and C is the solubility of the salt of interest in wt% in pressurized water; $\dot{m}$ is the mass flowrate of fluid through the volume $A\Delta x$. The change in mass flowrate is small due to salt deposition and is neglected in equation (1).

V_s is equal to $A_s(x,t)\Delta x$, where $A_s(x,t)$ is the developing salt cross-sectional area, and increases monotonically in time as salt precipitates out of the single phase fluid medium. Note that based on the assumptions above, the salt is deposited where it comes out of solution and is not swept along in the flow. Substituting for V_s in equation (1), letting Δx approach zero, integrating forward in time, and rearranging, gives the developing deposition profile of the salt as a function of spatial and temporal locations:

$$A_s(x,t) = -\frac{\dot{m}\, t}{\rho}\frac{dC}{dx}. \tag{2}$$

Equation (2) indicates that A_s will increase with time until eventually reaching the cross-sectional area of the tube. The time that this occurs is defined as the "plugging" time, t_p. Presumably this will cause a rapid rise in pressure necessitating a shutdown of the reactor.

As described by equation (1) the concentration, C, is only a function of fluid temperature. It is experimentally obtained by varying the fluid temperature and measuring salt effluent concentration.

The concentration gradient, however, and the plugging time t_p, depend directly on heat transfer rate. This can be seen by setting A_s equal to the cross-sectional area of the tube and fixing $\dot{m}$. Then, for variable concentration gradient,

$$t_p \propto 1/\frac{dC}{dx}. \tag{3}$$

Concentration is a function of fluid temperature, and the fluid temperature is a function of reactor distance, x. Hence,

$$\frac{dC}{dx} = \frac{dC}{dT}\frac{dT}{dx}, \tag{4}$$

such that t_p for a particular salt system, is inversely proportional to the fluid temperature gradient:

$$t_p \propto 1/\frac{dT}{dx}. \tag{5}$$

In other words, as the heat transfer rate is increased, the time to plugging is reduced. This is verified experimentally in the next section.

MODEL EVALUATION

The concentration gradient is obtained by determining the solubility as a function of temperature and combining the solubility information with the temperature profile of the fluid as a function of position within the reactor.

The solubility of Na_2SO_4 has been studied in this temperature and pressure region by others [10, 11, 12]. However, at low solubility (< 0.1 wt%), there is scatter in the concentration as a function of temperature. To eliminate this source of uncertainty and to illustrate the generation of an effective solubility curve, the solubility of sodium sulfate at 250 bar was determined using the experimental apparatus shown in Figure 1. The experimental procedure is as follows: 1) A solution of Na_2SO_4 in deionized water is prepared at a concentration of 0.5 wt% and introduced into the pressurized reactor; 2) the solution is heated to a known temperature in the feed heater and reactor line only; 3) the effluent is rapidly cooled and analyzed for Na^+ ions by a specific ion electrode; 4) temperature is incremented and sample collection is repeated. The last 600 cm of the 750 cm reactor can be controlled to be isothermal within several °C after an initial heat up section.

The results are converted to an Na_2SO_4 concentration curve as a function of temperature at 250 bar in Figure 4. The experimental data in the figure is well represented by the equation

$$T = 326.6 - 15.55 \log(C), \tag{6}$$

indicating the rapid drop in salt solubility as a function of temperature.

Data were generated for comparison with the deposition model. The procedure that was followed is similar to the procedure used to generate the effective solubility curve except that no intervention was done until a pressure excursion of 70 bar is experienced from the baseline pressure of 250 bar. This was defined as the plugging time. The fluid temperature profile is controlled by adjusting the set points at the individual section along the reactor to control the heat flux. Two different fluid temperature profiles were used (gradual and steep) and flowrate was varied at three different values, 0.6, 1.2, and 1.5 ml/s.

The experimentally measured fluid temperatures are shown in Figure 5 for the "gradual" and "steep" profiles, respectively. Temperature as a function of reactor distance is approximated by the following equations,

$$T = -321.8 + 272.7 \log(x) \tag{7}$$

and,

$$T = -127.8 + 232.4 \log(x). \qquad (8)$$

Equations (7) or (8) are combined with equation (6) and substituted into equation (2) to give the developing salt deposition profile. A_s, in equation (2), is set equal to the cross-sectional area of the tube, and then solved for the time to "plugging", t_p, to generate the comparison shown in Table 1. Flowrates were first varied from 0.6 to 1.5 ml/s with the "gradual" temperature profile superimposed on the fluid. The first two tests were identical to examine experimental reproducibility. In the final test, the temperature was changed to the "steep" profile and t_p was again compared to the model. Identical tests have a variation in experimental plugging time of about 10%. Agreement is good (within 20%) except at the highest flowrate (test 4). This may indicate that at high flowrates some of the precipitating salt is not deposited at the point of precipitation, but carried downstream where it adheres to the wall. Hence, A_s does not increase as quickly and plugging time is increased as indicated by the data at 1.5 ml/s. Comparing test 1 with test 5, t_p is significantly reduced when the steep temperature profile is impressed on the fluid.

DESIGN IMPLICATIONS

The effective solubility curve (c. f., Figure 4) suggests an operational scheme to prevent a plug from forming and eventually choking the flow. By reducing the temperature of the portion of the reactor between 360°C and 400°C to 360°C the solubility is increased by three orders of magnitude. By reducing the temperature to 320°C Armellini shows that the solubility is increased to 20 wt% at 250 bar [13]. The affected portion of the reactor can be reduced by less than 100°C and the accumulated salt redissolved and removed from the reactor. By knowing the location and time profile of the deposit, the affected portion can be isolated by valves and a pure water feed can be substituted for the reagent feed which is diverted to a parallel tube for continuous processing. The salt is then redissolved and removed as a brine stream.

This rinsing technique is illustrated in the results from a test shown in Figures 6 and 7. During this test, the reactor furnaces were turned off when the upstream pressure reached 34 MPa (about 42 minutes). The flow of Na_2SO_4 solution was then switched to pure water. The heat was also turned off at 42 minutes and the temperatures rapidly dropped to below 380°C at 48 minutes. Upstream pressure began to decrease at 48 minutes after all thermocouples had fallen below 380°C. The temperature of the thermocouples in the last 350 cm of the reactor are shown as a function of time in Figure 7. When the pressure differential had decayed to zero, the furnaces were turned on. At 52 minutes, the Na_2SO_4 flow was reestablished. At 95 minutes, upstream pressure again began to rise. This time, the Na_2SO_4 was changed to pure water but the furnaces were left on - note that in Figure 7 the temperature does not decay at this time. The pressure differential continues to grow until shutdown is initiated. Apparently, the plug could not be cleared without reducing temperature, consistent with the description of the salt deposition process presented in this paper.

Table 1. Comparison between model and experimental data at 250 bar.

Test No	Flowrate (g/s)	Temperature profile	t_p measured (Minutes)	t_p calculated (Minutes)
1	0.6	gradual	48	49.1
2	0.6	gradual	41	49.1
3	1.2	gradual	23	24.5
4	1.5	gradual	37	19.6
5	0.6	steep	28	23.0

The techniques presented here can be used to quantify salt deposition in SCWO tubular reactors. By knowing the chemical composition of the organic waste to be destroyed, the wt% loading of the developing salts can be calculated. An effective solubility curve can be generated from a limited number of experiments for the salt group(s) of interest. The fluid temperature profile can either be modeled, or as in this paper, measured experimentally. Finally, the salt deposition profile as a function of spatial and temporal variables can be determined from equation (2). The affected portion of the reactor can then be cleared as demonstrated. A parallel tube can continue to process organic waste while the salt is being removed as a brine stream in the first tube, or the organic stream can be switched to a pure water stream to quickly remove the salt build-up.

ACKNOWLEDGMENTS

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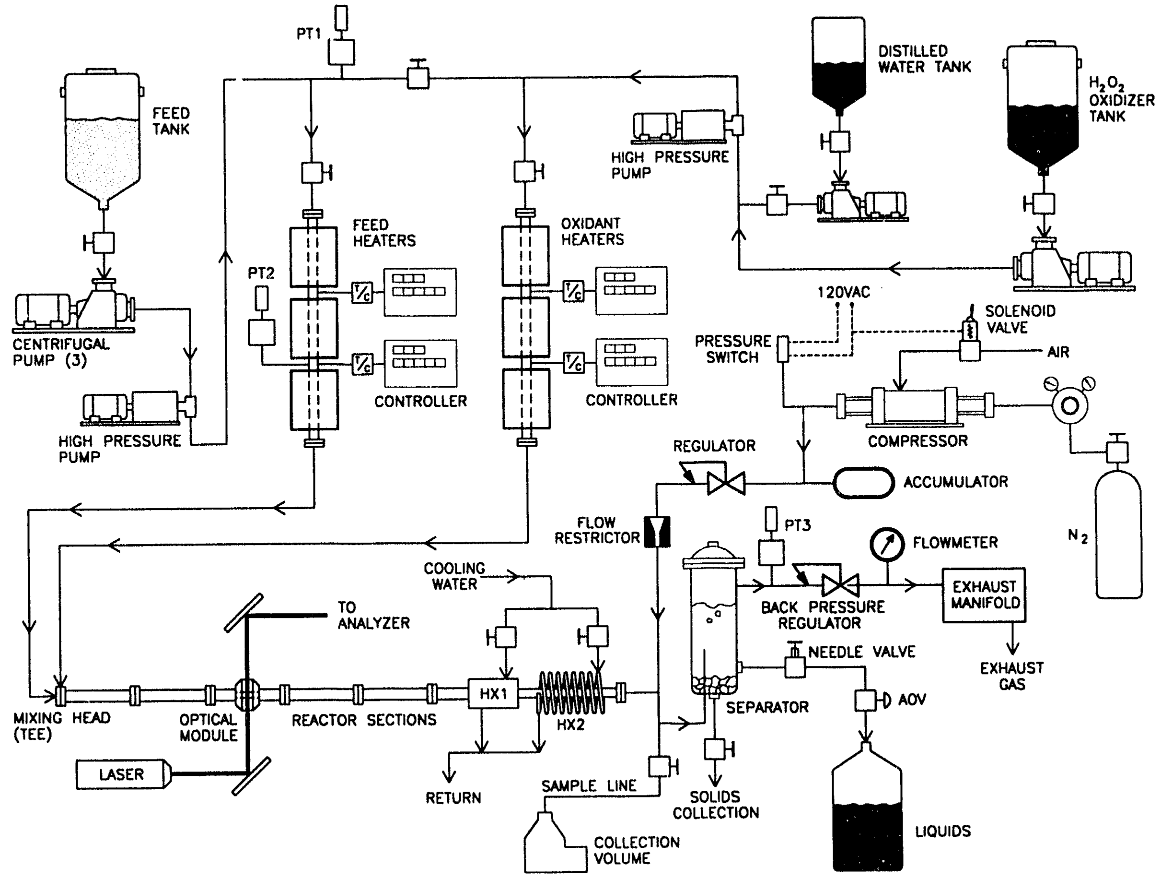

Figure 1. Schematic diagram of flow reactor. The overall system is composed of five main subsystems or modules: Pumping and Pressurization, Heating, Reactor, Cooldown and Separation, and Pressure Regulation. Each subsystem can be modified easily without affecting the operation of another subsystem. Note that the feed and oxidizer may be preheated separately or together depending on the configuration of the valves supplying the preheat system.

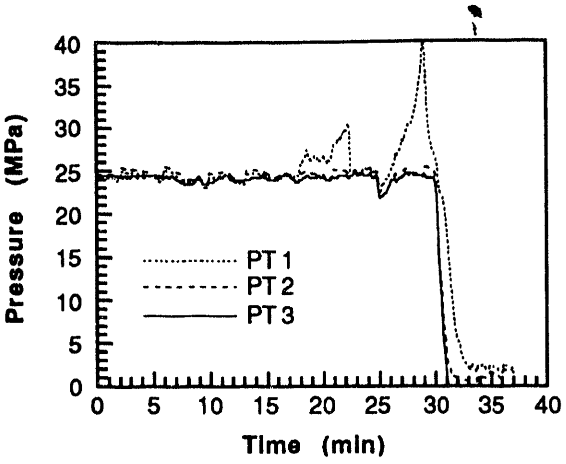

Figure 2. System pressure. PT 1 is at the inlet to the reactor before any heaters. PT 2 is located 140 cm into the reactor in the initial heat-up section. PT 3 is located at the end of the system just before the pressure letdown regulator.

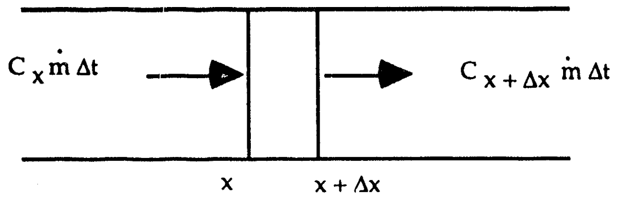

Figure 3. Mass balance on a volume element in the reactor.

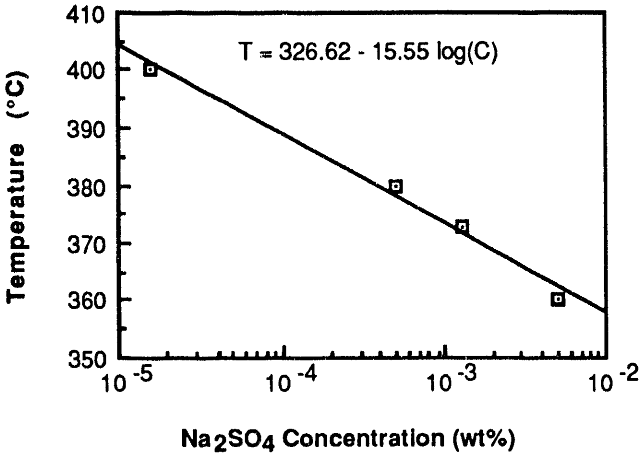

Figure 4. Temperature-composition Na_2SO_4-H_2O phase diagram at 250 bar. This phase diagram is an "effective" solubility curve.

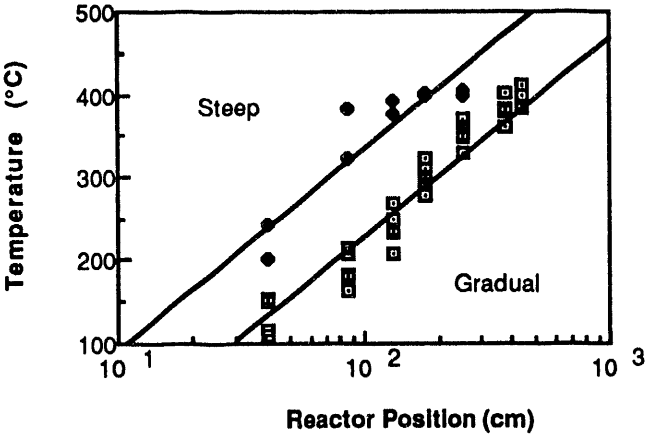

Figure 5. Gradual and steep temperature profiles. Experimentally measured fluid temperature as a function of reactor position.

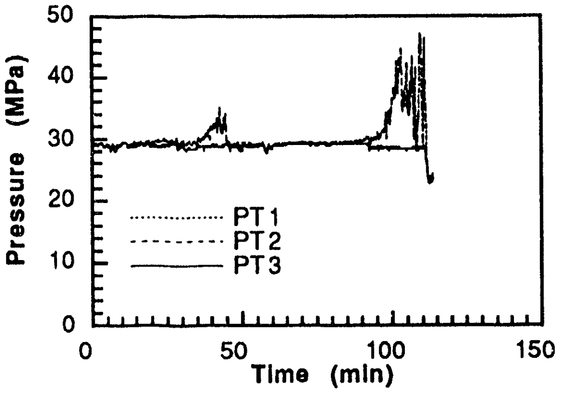

Figure 6. System pressure. PT 1 is at the inlet to the reactor before any heaters. PT 2 is located 140 cm into the reactor in the initial heat-up section. PT 3 is located at the end of the system just before the pressure letdown.

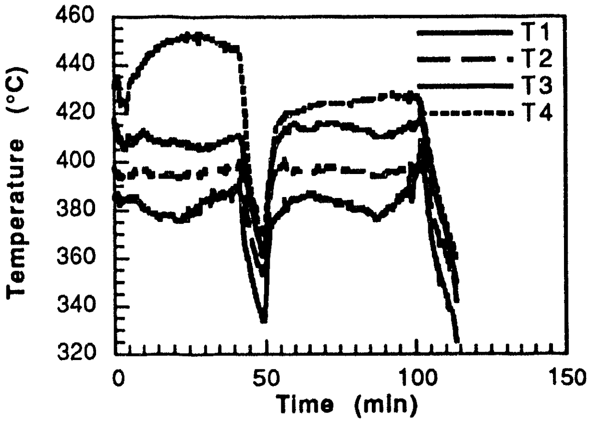

Figure 7. Plot of the four thermocouples covering the last 350 cm of the reactor. Positions of thermocouples: T1 = 370 cm, T2 = 440 cm, T3 = 570 cm, T4 = 710 cm.

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