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ABSTRACT

Batch and continuous flow reactor tests at Pacific Northwest Laboratory (PNL) have shown that organics similar to those present in the single-shell and double-shell underground storage tanks at Hanford can be decomposed in the liquid phase at relatively mild temperatures of 150°C to 350°C in an aqueous process known as hydrothermal processing (HTP). The organics will react with the abundant oxidants such as nitrite already present in the Hanford tank waste to form hydrogen, carbon dioxide, methane, and ammonia. No air or oxygen needs to be added to the system. Ferrocyanides and free cyanide will hydrolyze at similar temperatures to produce formate and ammonia and may also react with nitrates or other oxides. During testing, the organic carbon was transformed first to oxalate at ~310°C and completely oxidized to carbonate at ~350°C accompanied by hydroxide consumption. Solids were formed at higher temperatures, causing a small-diameter outlet tube to plug. The propensity for plugging was reduced by diluting the feed with concentrated hydroxide.

INTRODUCTION

Low temperature hydrothermal processing (HTP) is a thermal-chemical autogenous processing method adapted to address the destruction of organic and ferrocyanide contaminants in Hanford tank waste. Nearly 30% of the 177 underground radioactive waste storage tanks containing these materials on the Hanford Site have been identified as safety issues due to the potential for uncontrolled reactions between reductants (organics and ferrocyanides) and oxidants (e.g. nitrite) and the generation of flammable gases from the degradation of organics. HTP can be used to accelerate the naturally occurring reactions in tank waste in a controlled manner whereby safety hazards can be eliminated and downstream feed specification process requirements can be met. With HTP, organics react with oxidants such as nitrate and nitrite already present in the waste. Ferrocyanides and free cyanide will hydrolyze at similar temperatures and may also react with nitrates or other oxidants present in the waste. No air or oxygen needs to be added to the system. The continuous processing equipment consists of a plug-flow, tubular reactor system designed to accommodate the

temperature, pressure, gas generation, and heat release associated with decomposition of the reactive species.

This paper discusses laboratory-scale experiments conducted in the batch and continuous modes with organic tank waste simulants at various temperatures and conditions, and presents a preliminary heat and material balance for a 20-gpm HTP system. The simulants were representative of the double-shell slurry waste stored in Tank 241-SY-101. The experimental approach, results, and process evaluation are given here.

EXPERIMENTAL APPROACH

Hydrothermal processing tests were performed as batch reactions and in a continuous flow reactor. Batch reactions using simulated wastes containing a single organic component were conducted in 100-mL Teflon-lined Parr reaction bombs, obtained from Parr Instrument Company, Moline, Illinois. These vessels were heated in a convection oven to maximum temperatures of 200°C and 243°C and were held at temperature for 1 hour. The Teflon liner prevented higher reaction temperatures from being used. Inorganic components of the waste simulant used in batch reactions are given in Table I. Organic components were HEDTA, EDTA, sodium citrate, NTA, paraffin oil (stand-in for NPH), sodium glycolate, and glycine. Because hydroxide ions may be consumed in the process, companion batch reactions were performed in which the hydroxide content was doubled and tripled relative to the reference composition.

Additional testing with EDTA was conducted with a 1-L continuous flow reactor. The continuous flow reactor system included a 1-L 304L stainless steel tubular reactor made of 1 in. ID, 2 in. OD tubing, a feeding system, a product recovery system, and a data acquisition and control system. Only the supernatant liquid phase of simulated waste, collected by centrifugation at room temperature, was used in these tests. The waste contained approximately 1.5 g/L organic carbon, as EDTA. The supernatant liquid was chosen to minimize the potential for reactor plugging that might be caused by solids precipitation in the small-bore reactor outlet. Solubilities of many ionic compounds are known to decrease rapidly with increased temperature near or above the critical temperature of water(1). Reaction temperatures ranged from 250°C to 350°C, with waste simulant residence times in the hottest zone of the reactor of approximately 5 minutes.

Preliminary corrosion tests were performed with 304L and Inconel U-bend coupons to evaluate stress corrosion cracking at reaction conditions. Stress corrosion cracking was not observed with either material when exposed to the feed material at 350°C for several hours.

Pre- and post-test chemical analyses were performed selectively on the simulated wastes to evaluate the nature and extent of organic destruction. Ammonia

concentrations were evaluated using an ammonia-specific electrode, which was standardized in basic ammonium chloride solutions. Analyses included total organic carbon (TOC); anion concentrations, using ion chromatography (IC); and elemental, using inductively coupled argon plasma spectroscopy (ICP). Selective samples were examined using x-ray diffraction (XRD) to identify crystalline solids and using differential scanning calorimetry (DSC) before and after HTP treatment to evaluate the reduction in reaction potential. Tests were performed to assess the rates and stoichiometry of gas generation for heat-treated and untreated simulated wastes.

Hydroxide ion concentrations in batch reactions were determined by titration. Barium chloride was added to a sample aliquot to precipitate barium carbonate. The sample was filtered, and the filtrate titrated to pH 7. Potassium oxalate was then added to complex aluminum hydroxide, thus freeing 3 moles of hydroxide ions per aluminum atom present. This solution was titrated to pH 7. Hydroxide ion concentrations were calculated from the total amount of standard acid used.

EXPERIMENTAL RESULTS

The experiments conducted using HTP on simulated Tank 101-SY waste provided information on changes in organic, hydroxide, nitrate, and nitrite ion concentrations, at various temperatures; overall reaction stoichiometry; and solids formation.

Changes in Carbon, Hydroxide, Nitrate, and Nitrite Ion Concentrations in the Continuous Flow Reactor

Total organic carbon concentrations remained largely unchanged in continuous flow experiments up to approximately 300°C, but fell rapidly with increased temperature from 300°C to 350°C, using waste residence times of approximately 5 minutes. Changes in TOC content as a function of reactor temperature are given in Figure 1. In these experiments, EDTA was the sole organic constituent. Organic carbon that was not converted to carbonate was essentially all present as oxalate. Oxalate concentrations as a function of temperature are also included in Figure 1, determined using IC. At temperatures up to approximately 280°C, oxalate formation was minimal. At temperatures equal to or greater than 310°C, however, TOC and oxalate concentrations were essentially identical. At 350°C, TOC values were reduced by approximately a factor of 30 relative to the initial value, indicating large-scale conversion to carbonate.

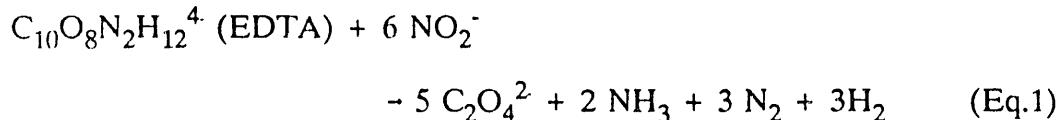
As was observed during the 1-L batch reactions, a decrease in the hydroxide concentration was apparent. The lowering of the hydroxide content was most evident following heat treatment above 300°C. The base content was lowered by more than 1 mole/kg waste at 350°C in the continuous flow experiments, which is approximately identical to 1 mole base reduction per mole organic carbon converted to carbonate. As was found in batch reactions, consumption of hydroxide ions appeared to be associated

with the complete conversion of organic carbon to carbonate ions, but not to oxalate or other partial degradation products.

Nitrite concentrations were lowered in the flow reactor as the temperature was increased, while nitrate ion concentrations, within experimental error, were not affected. Although experimental scatter was appreciable, approximately one-half mole of nitrite was consumed for every mole of organic carbon that was converted to carbonate. The lack of a decrease in nitrate ion concentrations with increased temperature would imply that the nitrate ion remained unreactive under present experimental conditions, similar to the results of batch reactions performed at lower temperatures.

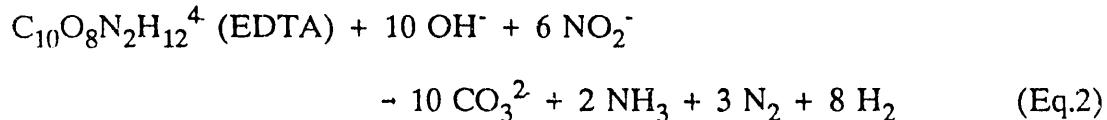
Overall Reaction Stoichiometry

Based on the results of batch and continuous flow tests, a simplified stoichiometry of degradation reactions can be given. The overall reaction anticipated for the conversion of EDTA to oxalate (as opposed to complete destruction to carbonate) is



Equation (1) assumes that nitrite was the primary oxidant, and that nitrate ions were inactive. The extent of reduction of nitrite ions was qualitatively consistent with both batch and continuous flow test results (approximately one-half mole nitrite ion consumption per mole organic carbon). Note that no base is consumed in this reaction. All of the reaction products given in Equation (1) have been identified in both batch and continuous flow tests. The stoichiometry for formation of ammonia reflects conversion only of organic nitrogen. Clearly, from batch test results, a smaller quantity of ammonia also derives from inorganic nitrogen. Nitrous oxide appeared to react further to yield nitrogen.

If the final product is carbonate rather than oxalate, the anticipated overall reaction is



In this case, 10 moles of hydroxide are consumed per mole of EDTA present initially. The results of batch reactions as well as continuous flow reactions are qualitatively in agreement with the above equations. In continuous flow reactions, a conversion of 1 mole organic carbon/kg sample to carbonate was accompanied by a 1 mole/kg sample reduction in the hydroxide ion concentration.

Consumption of base following Equation (2) could certainly lead to extensive precipitation of aluminum-containing salts. Unless additional base is added to the waste mixture, the phase gibbsite $[Al(OH)_3]$ may form in the place of sodium aluminate (2, 3). The solubility of gibbsite decreases rapidly with reductions in the hydroxide ion content at approximately pH 14.

Solids Formation in the Continuous Flow Reactor

Lowered solubilities of waste simulant components, particularly for temperatures greater than 300°C, tended to cause the continuous flow reactor to plug. Plugging tendencies were accentuated by the small size of the reactor outlet tubing. Using the supernatant phase of the waste simulant composition given in Table I, the reactor became plugged at approximately 310°C. X-ray diffraction analysis of solids collected from within the reactor showed them to be composed of sodium nitrate (35 wt%), sodium nitrite (30 wt%), sodium oxalate (20 wt%), and sodium carbonate monohydrate (10 wt%), plus perhaps a few trace phases. Sodium oxalate and sodium carbonate are degradation products of EDTA. Salts containing aluminum were not detected; however, aluminum may have been present as an amorphous solid and not particularly visible in the XRD spectrum. Ion chromatography analyses revealed that aluminum was present in the solids, in concentrations similar to its concentration in the waste feed.

The supernatant phase of the waste simulant was then diluted by 20 vol% with 10 molar sodium hydroxide in an attempt to prevent precipitation of amorphous aluminum hydroxide at reactor temperatures. The temperature range without plugging by solids was extended to 350°C by this action. The addition of base should have prevented aluminum hydroxide formation, whose solubility is known to fall rapidly with decreased base content near a hydroxide concentration of 1 molar (2). Of course, it is clear that solids in addition to aluminum-containing precipitates were also formed, largely unrelated to base content. It is believed that a combination of dilution with concentrated base and the use of a reactor outlet of larger bore would be sufficient to circumvent reactor plugging throughout the temperature range used here.

PROCESS EVALUATION

The data from the laboratory-scale testing was compiled into a preliminary heat and material balance. In addition to actual process data, the hypothesized chemical reactions have been used to provide the most conservative balance.

Assumptions

A number of assumptions were made to allow the mass and energy balances to be estimated without having comprehensive data on the proposed process or waste stream. The process operating conditions obtained from laboratory data are based on undiluted waste. Hence, it is assumed that these conditions will also apply to the diluted waste.

The key assumptions made when performing the energy and material balances for the HTP are summarized below.

- Feed Stream: SY1-SIM-92A diluted with 3 volumes of water per volume of stimulant.
- Feed Processing Rate: 20 gpm.
- Feed Stream Temperature and Pressure: 25°C (77°F) at 30 psi (assumed the waste will be pumped from a feed tank to the HTP pump inlet).
- Reactor Temperature and Pressure: 350°C (660°F) at 3000 psi (based on favorable results obtained from lab tests at this temperature and pressure).
- High Pressure Pump Efficiency: 70% (preliminary estimate).
- Reactor Outlet Stream: cooled to 100°C (210°F) before pressure letdown (relatively high outlet temperature will help keep constituents in solution).
- Vent Gas: saturated with water vapor at 100°C (210°F).
- Very limited thermodynamic data on brines (concentrated salt solution) at elevated temperatures and pressures exist; therefore, thermodynamic data for water were used.
- Tank waste and dilution solution were assumed to be ideal (i.e., constant volume in an ideal solution).
- All the carbon in the waste feed stream is present as EDTA.
- All of the EDTA reacts with nitrite and hydroxide ions to form carbonate ion, H₂N₂, and NH₃ with a heat of reaction of 2.37×10^6 J/g-mole. The assumption of complete reaction will result in conservative estimates of off-gas volumes for later design of any off-gas treatment system. However, it may result in overestimating the chemical energy produced in the reactor. Hence, until better chemistry data are available from ongoing experiments, it will be assumed that the net production of energy from the chemical reactions is zero. This will result in over estimation of the trim heater energy requirements.

Heat and Material Balances

The heat and material balances are based upon the equipment configuration shown in Figure 2, Preliminary Process Flow Diagram. Pre-diluted 101-SY tank waste enters the system at 25°C (77°F) and low pressure (<50 psig). The feed is then

pressurized to 3000 psi in a high pressure pump. It has been assumed that the temperature of the feed will not increase as a result of passing through the pump. The pressurized feed is heated to approximately 300°C (570°F) in a heat exchanger that recovers heat from the processed feed. The temperature of the feed is then boosted to the desired reaction temperature by passing the feed through the trim heater heat exchanger. The organic constituents are converted to carbonates or oxalates in a tubular packed bed reactor. Approximately 80% of the heat in the processed feed stream is recovered in the preheat exchanger. The temperature of the processed feed is kept above 100°C (210°F) to keep salts in solution. The cooled processed feed is then passed through a pressure letdown valve into a separator where the gas and liquid phases are separated. A summary of stream compositions, pressures, and temperatures is shown in Table I. The component flows are based on conversion to carbonates as shown in Equation (2).

Energy Evaluation

A 50-hp pump is required to deliver 20 gpm at 3000 psi; the total energy required to heat the feed is 8.1×10^6 Btu/hr assuming approximately 10% heat losses in the system, 80% recovery in the preheat exchanger, and no heat of reaction.

The net energy release from conversion to oxalate (Equation 1) is 3.8×10^5 Btu/hr and for conversion to carbonate reaction is 4.9×10^5 Btu/hr. The energy release from (Equation 2) is not expected to overheat the system since it represents only 33% of the trim heater capacity and 66% of the system heat losses.

SUMMARY

Low temperature hydrothermal processing of simulated Hanford double-shell slurry wastes was found to be a potentially effective means to lower the energy content of organic waste components, as well as a method to substantially lower the capacity of these simulants to produce further flammable gases under typical tank waste storage conditions. Nitrite ions served as the primary oxidant in the temperature range of 200°C to 350°C, under both batch and continuous flow conditions, whereas nitrate ions appeared to be inactive. For the EDTA, organic carbon was converted to oxalate and then to carbonate, depending on reaction temperatures and times. Based on limited testing, nitrite/nitrate ions apparently were sufficiently active to inhibit the stress corrosion cracking of stainless steel in the caustic, chloride-containing simulants at elevated temperatures. Plugging of the continuous flow reactor was encountered at temperatures greater than 300°C, due to diminished solubilities of inorganic solids and a small-diameter reactor outlet. Dilution with concentrated base lessened reactor plugging.

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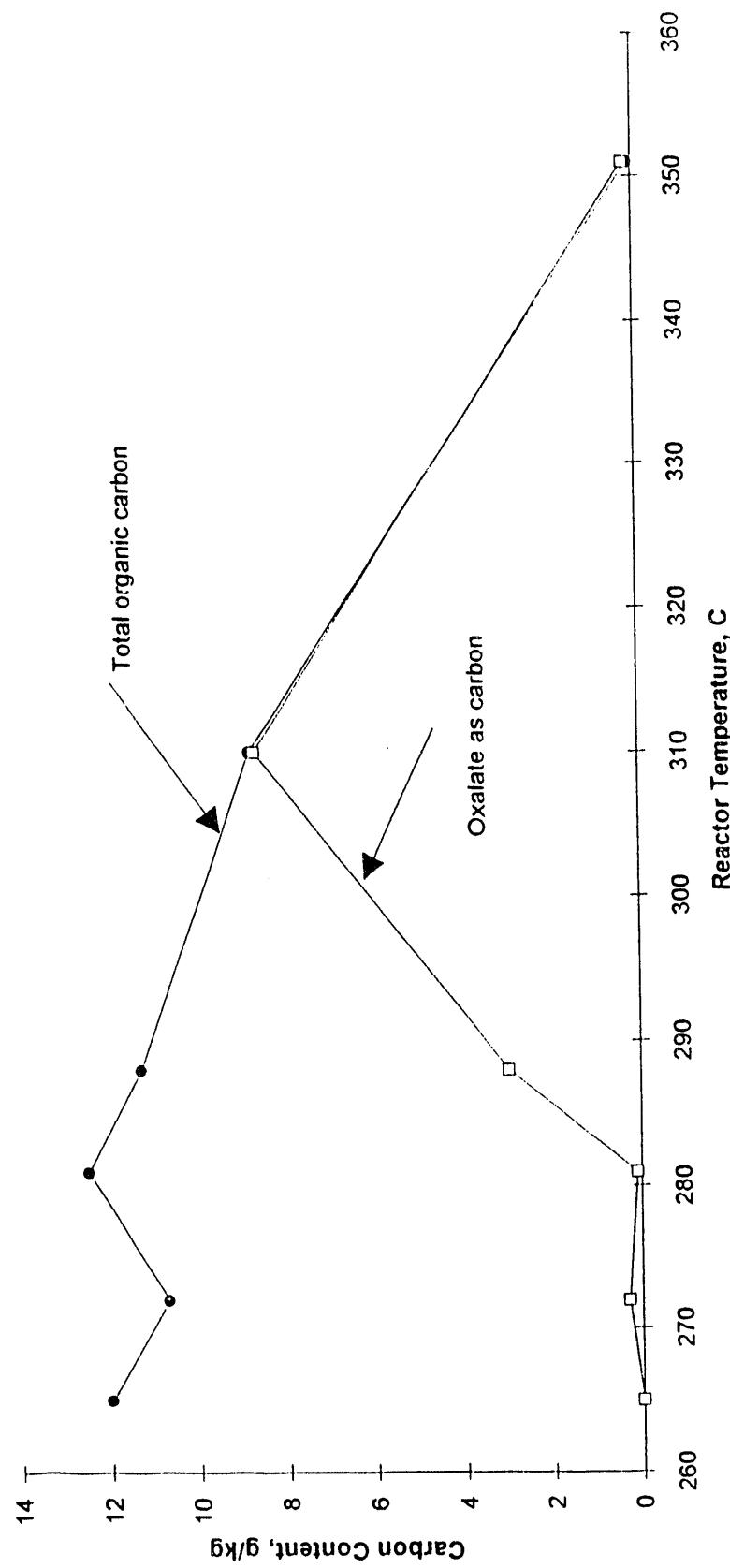
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Table 1. Summary of Stream Compositions

Parameter	Waste	Feed			Gas Outlet	Liquid Outlet
		P1	P5	P8		
Temperature, C		25	350	100	100	
Pressure, psig		30	3000	0	0	
Flowrate, ft ³ /hr		160	160	2817	159	
Component		Composition, wt %				
TOC	1.52	0.51	0	-	-	0
Na	19.6	6.59	6.69	-	-	6.69
Al	3.6	1.21	1.229	-	-	1.229
Cl	1.5	0.50	0.512	-	-	0.512
PO4	1.1	0.37	0.376	-	-	0.376
NO2	10.8	3.63	2.496	-	-	2.496
NO3	9.5	3.19	3.243	-	-	3.243
CO3	1.5	0.50	3.11	-	-	3.11
Fl	0.12	0.04	0.041	-	-	0.041
OH	3.1	1.04	0.323	-	-	0.323
SO4	0.19	0.06	0.065	-	-	0.065
Cr	0.35	0.12	0.119	-	-	0.119
Cu	0.35	0.12	0.119	-	-	0.119
Fe	0.026	0.009	0.009	-	-	0.009
Ni	0.0078	0.003	0.003	-	-	0.003
Ca	0.02	0.007	0.007	-	-	0.007
K	0.26	0.087	0.087	-	-	0.089
H2O	40.4	79.96	75.4	61.9	75.4	
Other	6.0562	2.04	0	-	-	2.067
N2	-	-	-	-	-	23.9
H2	-	-	-	-	-	4.5
NH3	-	-	-	-	-	9.7

Figure 1 Effect of Temperature on TOC and Oxalate Concentrations



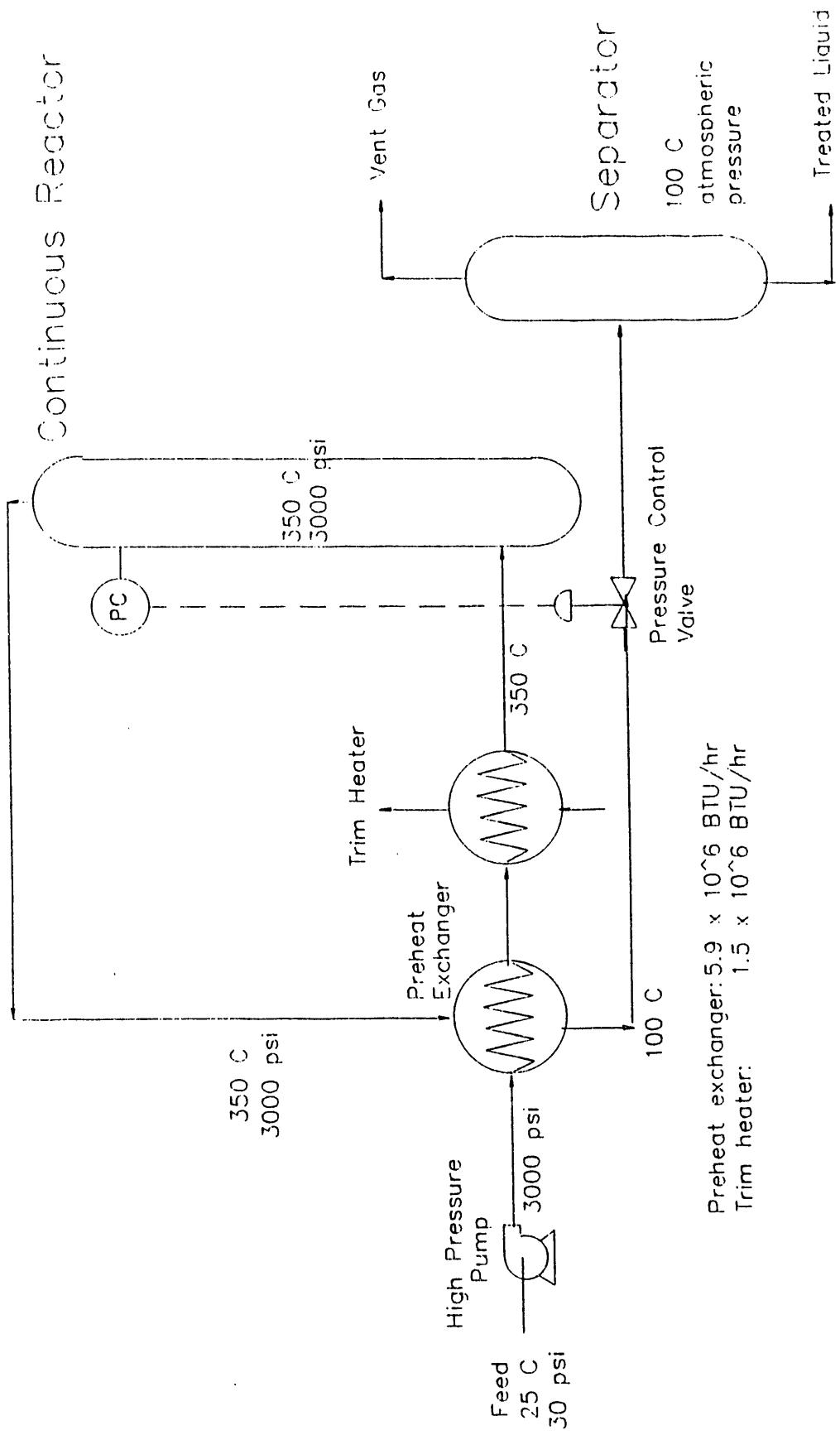


Figure 2 Preliminary Flowsheet for the Low Temperature Hydrothermal Reactor

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