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**SUPERCritical WATER OXIDATION
OF
COLORED SMOKE, DYE, AND
PYROTECHNIC COMPOSITIONS**

Final Report: Pilot Plant Conceptual Design

by

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Abstract

The existing demilitarization stockpile contains large quantities of colored smoke, spotting dye, and pyrotechnic munitions. For many years, these munitions have been stored in magazines at locations within the continental United States awaiting completion of the life-cycle. The open air burning of these munitions has been shown to produce toxic gases that are detrimental to human health and harmful to the environment. Prior efforts to incinerate these compositions have also produced toxic emissions and have been unsuccessful.

Supercritical water oxidation (SCWO) is a rapidly developing hazardous waste treatment method that can be an alternative to incineration for many types of wastes. The primary advantage SCWO affords for the treatment of this selected set of obsolete munitions is that toxic gas and particulate emissions will not occur as part of the effluent stream. Sandia is currently designing a SCWO reactor for the U. S. Army Armament Research, Development & Engineering Center (ARDEC) to destroy colored smoke, spotting dye, and pyrotechnic munitions. This report summarizes the design status of the ARDEC reactor. Process and equipment operation parameters, process flow equations or mass balances, and utility requirements for six wastes of interest are developed in this report. Two conceptual designs are also developed with all process and instrumentation detailed.

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Introduction

Supercritical water oxidation (SCWO), a method for destroying aqueous organic waste, is a relatively new technology discovered about fifteen years ago at the Massachusetts Institute of Technology.¹ It is not commercialized presently, but shows promise for detoxifying wastes in an efficient, cost-competitive, and environmentally safe manner.² SCWO occurs at moderate temperatures and pressures where the ability of water to dissolve organic compounds is greatly enhanced. The dissolved waste rapidly reacts with an oxidizer to produce innocuous combustion products.

The basic methodology of SCWO is fairly simple to describe: 1) aqueous hazardous waste is mixed with water, pressurized, and heated above its liquid/vapor critical point, 2) an oxidizing agent (oxygen, air, or hydrogen peroxide) is injected into the fluid, 3) the mixture is allowed to react for a short duration, and 4) the reaction products are cooled and separated. These products include water, inorganic salts, carbon dioxide, molecular nitrogen, and other gases depending on the composition of the waste. Typical reaction conditions are at temperatures of 550 -550 °C and pressures of approximately 250 bar.

The project addressed in this report concerns the use of SCWO as a method to destroy a selected set of U.S. Army and U.S. Navy munitions deemed to be obsolete. These materials include dyes, pyrotechnics, smokes, and other complicated chemical and energetic formulations. For many years, these dyes and other complex organic-based hazardous materials, have been stored at various locations within the continental United States awaiting completion of the munitions life-cycle. Technology development and process implementation for the demilitarization of these materials is being conducted for the U.S. Army Armament Research, Development, and Engineering Center (ARDEC).

The open air burning of these munitions produces toxic gases that are detrimental to human health and harmful to the environment. Test studies using incineration have indicated that it is incapable of treating a majority of the colored smoke/dye and pyrotechnic munitions in the demilitarization inventory in an environmentally safe manner. It appears that toxic emissions containing particulate matter are produced which serve to "lock-up" incinerators by severely plugging pollution abatement equipment.

ARDEC has established a program with Sandia to assess the feasibility of SCWO as a treatment technology for colored smokes, dyes, and pyrotechnics. If feasibility is indicated, Sandia is to design and build a 1000 gallon/day SCWO production prototype. After initial testing and evaluation, the reactor will be taken to the McAlester Army Ammunition Plant (MCAAP) in Oklahoma to begin processing military waste.

ARDEC's program at Sandia for developing a prototype reactor is divided into three Phases. Phase I has the goal of assessing the feasibility of destroying the military waste. Phase II and Phase III have the goals of designing and building the prototype reactor. For Phases II and III, a contractor is currently being identified to build the unit according to Sandia technical specifications. Based on these goals, this report: 1) develops designs in sufficient detail to provide a framework for communication between the contractor, Sandia National Labs, and ARDEC, 2) estimates the operational and capital costs for a production prototype, 3) identifies technical and cost uncertainties and how to reduce these in Phase II, and 4) provides ARDEC the necessary detail to determine whether the project can be completed within budget and schedule. The pilot plant conceptual design represented in this report, and the summary on experimental results conclude the initial Phase 1 feasibility study.

Sandia has completed a feasibility study that has examined the processing of four dyes and one pyrotechnic smoke composition using a 20 gallon/day bench scale reactor. These tests have shown that reaction with hydrogen peroxide for ten seconds at 550 °C and 270 bar will destroy greater than 99% of the organic constituents. In addition to demonstrating the success of this treatment method from a destruction efficiency perspective, this feasibility study served to identify the important issues that need to be addressed regarding process reliability. Specifically, reactor plugging by oxidation products and effects of feed materials on corrosion are two consequences of treating these military wastes that have been identified as needing further attention. These results are presented in detail in another report.

This report summarizes the design status of the ARDEC reactor. The process flow is first described, including conceptual designs and process flow sheets for six wastes of interest. These process flow sheets and schematics are the framework for the development of

detailed schematics - the beginnings of process and instrumentation diagrams (P&IDs). From these P&IDs, power requirements, a detailed capital cost assessment, and process control schemes are developed. A heat transfer and fluid mechanic (thermal-hydraulic) assessment is done for one of the conceptual designs.

The only experimental results included in this report are from salt deposition studies which were important in the formulation of the system design concepts presented here. Much of this work was conducted under the auspices of another research project. A final summary of these results is currently being developed and will be published in a separate report.

Process Flow Description

This section presents two conceptual designs of a SCWO pilot plant which differ in the salt separation subsystem. Two designs were developed; one will be chosen in Phase II prior to beginning detailed design and construction.

These designs were developed to process the six wastes of interest:

- 1) Orange dye:

- 2) Red dye:

- 3) Green Dye (Type I):

- 4) Green Dye (Type II):

5) Blue Dye (Type I):

6) Blue Dye (Type II):

7) Pyrotechnic Composition:

8) CS agent:

The Type 1 and Type 2 compositions for the green and blue dyes are listed because the alphasurine (blue) component of these dye formulations may exist as either the calcium or as the sodium salt. The available documentation suggests that either cation may have been used in production of the munitions. Even if the samples sent to Sandia show only either sodium or calcium is present, some subset

of the material may have the other metal, and as a consequence, the treatment process must be prepared to handle a combination of the two.

Description of Concepts

Two reactor concepts are presented in this report. Their differences lie in how the formation and removal of inorganic salts is handled. These conceptual designs form the basis for the process flow sheets and the P&IDs

In Concept A (see Figure 1), waste from the feed tank is intensified by the feed pump to 4000 psi and mixed with an oxidant at 20°C at the entrance of a tubular reactor. The solution is heated resistively to 420°C within the salt separation subsystem, which is demarcated from the rest of the reactor by a hot isolation (AIROP) valve. After leaving the salt separation subsystem, the solution is further heated to 550°C until the waste is destroyed. The products are cooled in the heat exchanger (HX), separated in the liquid/gas separator, and injected into the effluent collection tank and stack. Finally, the liquid is recirculated to the feed tank.

Most of the feed materials will produce inorganic acids as a product of the oxidation process. These acids can significantly enhance reactor corrosion. Consequently, these design schemes provide for the addition of NaOH (caustic soda) to the feed such that the final pH will be nearly neutral. Initial and final pH, modified by caustic soda, is a design parameter that will be studied for its effect on reactor corrosion in Phase II prior to final design completion.

In Concept A, a means is provided to clear plugs should they develop. As discussed in detail in the next section, sodium sulfate, Na_2SO_4 , and possibly other salts, are produced during the destruction of these wastes. Na_2SO_4 adheres to the reactor wall and rapidly causes plugs rendering the equipment inoperable. Any successful SCWO design must incorporate a method for removing these salts either chemically or mechanically.

In Concept A, as flow is restricted during salt formation, a pressure drop occurs across the reactor. Small scale tests have shown that the plug and the associated pressure gradient appear in the reactor sections where the feed temperature is raised from 380 °C to 420°C.

When this pressure differential reaches a predetermined amount, for example 300 psi, the waste is diverted to an identical parallel line (not shown). The plugged section is isolated and the temperature reduced to 200-350°C, allowing the salt to redissolve into the water.

Concept B (see Figure 2) is similar to Concept A, but differs in the salt separation system by avoiding the need to cycle sections of the reactor from salt collecting to rinsing temperatures. In this method, a thermocline is used to separate the salt from the solution. A thermocline is a temperature gradient that induces a density gradient from the top to the bottom of the vessel. For Na_2SO_4 , the primary salt formed in processing the military dyes, the solubility decreases to essentially zero just above the critical temperature (374°C)³ such that this salt will concentrate in solution in cooler regions. Gases exit at the top and salt collecting in the bottom of the vessel is removed by injecting water at approximately 300°C to form a brine stream. This vessel design has been patented by MODAR.⁴

Oxidizer Selection

The oxidizers that have been used in a number of laboratories as the technology has been developed include hydrogen peroxide, air, and oxygen. A cost assessment that includes power consumption, raw material, and capital equipment costs, associated with the oxidant and feed subsystems, was performed to understand the financial trade-offs involved in oxidant choice. The results are summarized in Table 1.

Parameters for the oxidant tradeoff study were as follows: A stoichiometric concentration of oxidant (no excess oxidant) and orange dye were used in the study. Operation was for a 20-hr day for 300 days and did not include any release of energy by the oxidizing process (heating value of the waste). Ancillary equipment, flow meters, tanks, etc., other than the high pressure liquid pumps, was not included. The cost of piping, vessels, heat exchangers, transformers, liquid/gas separators, and other subsystems, other than the costs associated with the oxidant and feed subsystems, was not included in the oxidant trade-off study.

The analysis shows that there is a large difference in total cost for hydrogen peroxide relative to air or oxygen. Air is slightly more expensive to use than oxygen because of energy costs associated with

compressing and heating large amounts of nitrogen which performs no useful function in the oxidation process. These costs offset the expense associated with purchasing oxygen from a supplier.

However, there are other operational issues that suggest air is likely to be the best choice despite the small additional cost. We do not recommend using oxygen if air is an adequate oxidizer because extreme care must be exercised in designing and operating systems with high pressure oxygen to prevent oxygen-related explosions. Experience at Sandia and elsewhere has shown that even with careful design and operation, accidents are possible, especially in the presence of hydrocarbons or other oxidizable organic material.

Tests at Sandia have shown that pure high pressure⁶ oxygen when reacted with methane and methanol at concentrations in excess of 5 wt% in supercritical water can initiate flames having adiabatic temperatures that would destroy current reactor designs since these flame temperatures would exceed material limitations. Oxygen, composing only 21% of air, is effectively much less reactive when dilute and, as a result, very high temperature excursions (flames) may be suppressed. Operating with air may allow organic concentrations in excess of 5 wt%. The process flow calculations presented in the next section were done for 5 wt% feed concentration. Recognizing this caveat, however, the affect of air on allowable concentration must be evaluated prior to final design detail.

It is our opinion that the difference in cost is not sufficient to warrant oxygen being chosen over air as the oxidizer. However, to date, air has not been used to destroy any of the military waste samples. The effect of air on destruction efficiencies and performance must be evaluated prior to commitment to this oxidizer, however, there is evidence in the literature suggesting that air is an adequate oxidizer.^{1,4} An oxygen system can be a backup choice that has been used to destroy organic waste by Sandia and other researchers.^{1,5}

Process Flow Sheets

Process flow sheets detail the flow rates of reactants and products. Included for review in Appendix A are the calculations for the pyrotechnic smoke, CS agent, and dyes, with and without neutralization of acid by NaOH. An example calculation sheet for the orange dye with acid neutralization is reproduced as Table 2A.

Both reactant and product composition are offered in the box, followed by calculations recording the total throughput of water, dye, and air, per day. The boxed results on the right side of the diagrams detail the compressor requirements for 20% and 100% excess oxygen. The effect of excess oxidant on performance is an engineering parameter that must be studied in Phase II prior to final design detail. The caustic soda requirement to neutralize acid formation is in addition to the oxidant and feed ratios. Addition of NaOH results in the trade-off of increased salt formation which is not desirable. The concentration of acid that will significantly decrease the lifetime of the reactor is an engineering parameter that must be studied in Phase II prior to final design detail. Finally, the effluent flow rates and composition are recorded at the bottom of these process flow calculation sheets.

The results of the analyses for all the dyes, CS, and pyrotechnic composition, are given in Table 2B. As shown, CS has the highest air requirement whereas the largest producer of salt is the orange dye. These chemical composition calculations complete the process flow schematics and allow further refinement of the various subsystems to proceed.

Performance Requirements

Calculations in this report are based on performance requirements derived from the program management plan for the ARDEC project and the destruction efficiencies and experience with the military wastes.

Primary Requirements

Daily throughput	1000 gallons/hour
Waste loading	5 wt% minimum
Man rated reactor	All components
Skid mounted	For transportation to other sites
Control	Automatic
Safety	Automatic shutdown
Location	MCAAP
Discharge requirements	TBD per State of Oklahoma
Waste	Capable of handling the military waste listed in this report
Process	SCWO

Secondary Requirements

Flow rate	50 gallon/hr minimum
Plant utilization	83%
Minimum acceptable destruction efficiency (TOC)	99%
System pressure	4000 psi
System (fluid) temperature	550°C
Residence time	Minimum 15 seconds at 550°C
Heated components	Inconel 625
Excess oxygen capacity	100%

The assembled unit will be tested on the contractor premises, disassembled and reassembled at MCAAP for operation. Since the military wastes are located throughout the continental United States and are hazardous to transport, the reactor will be moved to other waste sites after destroying the inventory at MCAAP. The unit will be mounted on several skids for transportation. This is not expected to be a difficult requirement as long as an overall modular nature of design and construction is pursued.

As discussed in the section on design definition and capital equipment costs, sufficient work has not been done to determine a minimum residence time that will efficiently destroy the wastes of interest. Tests in Sandia's SCWO reactor have shown that 10 seconds with hydrogen peroxide is sufficient to destroy greater than 99% of the organic constituents based on total organic carbon (TOC) content at 550°C. 100% excess oxidant was used during the tests conducted at 4000 psi. The test results are currently being compiled in a final report. In the conceptual designs, the liquid effluent is recirculated - not discharged to the environment. Hence, it is permissible to destroy 99% of the waste during the first pass. The secondary requirements are derived from these considerations and may change before final design.

Determination of a minimum flow rate is based on ARDEC's requirement to destroy approximately 400 lbs of waste per day. Once the plant is at system temperature and destroying waste, it is desirable to leave it on line until maintenance of a central component is necessary. It will take several hours to warm the reactor up and to shut down the unit. Experience has also shown that most problems with Sandia's reactor occur during startup and shutdown. Additionally, it is good practice to minimize thermal cycling of mechanical components as thermal cycling tends to decrease the lifetime of mechanical systems. Based on these considerations, with a plant utilization of 83%, the 400 lbs of waste can be destroyed in 20 hours at a concentration of 5 wt%.

Salt Deposition Studies

Before refining the various subsystems of the conceptual designs, it is appropriate to discuss the salt deposition studies that have been conducted in Sandia's SCWO flow reactor. Bench tests on dyes in this

tubular reactor have indicated the formation of salts, between 300°C and 400°C consistent with the chemical composition analysis. That is, calcium and sodium sulfate (CaSO_4 and Na_2SO_4) are not present in the feed but are formed as a result of the complete oxidation of the dyes. Most tests have been conducted with 0.5 wt% dye and the reactor has plugged in under 2 hours.

The test results shown in Figure 3 are typical. For this test, control was maintained until about 70 minutes when pressure transducers 1 and 2 begin to rise. Pressure transducer 1 is located at the inlet to the reactor, pressure transducer 2 is located approximately 90 cm into the reactor, and the third transducer is located at the letdown regulator. As a plug builds in the first 90 cm, a pressure differential develops between the inlet (PT1) and positions downstream (PT2 and PT3). At 80 minutes, a sharp spike is observed as PT2 jumps to a value near that of PT1. Apparently, this plug broke away and reattached farther down the tube resulting in a pressure differential between the point 90 cm into the reactor at PT2 and the outlet. As the test continued, PT1 and PT2 began to diverge indicating additional material was being deposited in the first 90 cm. The differential between PT2 and PT3 did not increase suggesting no new material was clogging the flow in this region.

During one run, the test was stopped and, after cooling, the tubing was disassembled to confirm blockage by salt; the blockage was examined by several analytical methods to confirm that it was Na_2SO_4 .

A series of tests was conducted for ARPA to better characterize the salt deposition process in conjunction with studies to evaluate SCWO for the demilitarization of chemical warfare agents. In these tests, Na_2SO_4 at 0.5 wt% loading was heated to approximately 400°C to quantify the deposition rate of Na_2SO_4 over a range of pressures and flow rates and to determine if variations in these parameters affects deposition rate. ARPA has a contract with General Atomics to explore the feasibility of using SCWO to dispose of chemical warfare agents and is expecting to have similar problems with its feedstock. Although 0.5 wt% Na_2SO_4 is only about 20% of the anticipated salt loading generated by the ARDEC waste, these results provide the information needed to evaluate the gross aspects of salt plugging in the reactor being designed in this project.

Test Description

The test conditions are summarized in Table 3. Tests 1 through 3 varied flow rate over the range available. At the high flow rates (1.5 g/s), the equipment is heat transfer limited and could not raise the fluid temperature in excess of 400°C. For tests 4 and 5 the pressure was raised to 5150 psi. In the final two tests, the pressure was lowered back to 3700 psi and the flow rate was fixed at 0.6 g/s, although there are differences between tests 1, 6, and 7 as described below.

Other than tests 2 and 7, the following procedure was adhered to:

- 1) Distilled water was used to establish a temperature profile along the reactor at the test pressure while the reactor was being heated.
- 2) After steady state was reached, the water was discontinued and distilled water with 0.5 wt% Na_2SO_4 was substituted at the same flow rate as the pure water. Control of thermal profiles was generally within 15°C.
- 3) Samples of the liquid effluent were collected during the experiment every 5 to 10 minutes.
- 4) When a pressure differential of approximately 1000 psi developed, the test was terminated by turning the heaters off, depressurizing, and stopping the flow of the Na_2SO_4 solution.
- 5) After the reactor had cooled, the plug was dissolved by flowing distilled water at 2000 psi and collecting the effluent to provide a global salt balance. Evaluation of the effluent by specific ion electrode and spectrophotometric techniques yields a deposition rate for sodium sulfate under the above conditions. Preliminary evaluation of the results from effluent analysis indicate that 95% of the salt is deposited in the reactor.

Several operating method variations were explored over these seven tests. As plugging began to develop during tests 2 and 7, the feed heaters were turned off and pure water was reintroduced in place of the Na_2SO_4 to attempt to dissolve the salt plug as the temperature fell. For tests 1 and 4, a different axial temperature profile was impressed on the reactor.

Results and Discussion

The measured temperature profiles for all tests are shown in Figure 4. For tests 1 and 4, and tests 2, 3, 5, 6, and 7, respectively, the profiles are approximately the same.

Plugging occurred from 18 to 48 minutes as summarized in Table 4.

All raw pressure data is shown in Figures 5 through 11. The character of the data is similar to that presented earlier for the organic dye.

Before discussing tests 2 and 7, specifically, some qualitative observations are possible. Plugging occurs significantly sooner for test 1, which had a steeper temperature profile, but identical input flow rate, when compared to tests 6 and 7. Possibly, the salt deposition takes place over a greater area for the latter two tests. Plugging occurs sooner for test 2 than test 6, where the only difference between the tests is the input flow rate. In this comparison, the flow rate of salt into the reactor is twice as great for test 2 than it is for test 6. Actual deposition rates cannot be determined until the effluent analyses are complete, however, the reduced time to plugging is probably related to the increased flow rate, and therefore, increased rate at which salt is introduced to the reactor. Note, that despite the increased flow rate for test 3 relative to test 2, the time to plugging increases and does not support this hypothesis.

As plugging occurred during test 2 (the first peak in Figure 6), the Na_2SO_4 and heat were turned off and an attempt was made to clear the plug by flowing pure water through the reactor. The spikes that occur between 30 and 40 minutes are due to the operator turning the feed water on and off (attempting to prevent bursting a rupture disk) and not to a plug clearing a little and then building up again. Eventually the plug clears at about 45 minutes and the Na_2SO_4 is reestablished.

A second attempt at actively clearing the plug was made in test 7 (see Figure 11). This time the plug was cleared more systematically and there was less concern about rupturing a relief line. All furnaces were turned off when the pressure on the upstream side of the plug had reached 5000 psi (about 42 minutes) and flow of Na_2SO_4 was switched to pure water. The temperature profile in the reactor over

the last 10 feet is shown in Figure 12 as a function of time. The four curves in Figure 12 represent the time histories of the last four thermocouples in the reactor. Their initial conditions can be read as the last four solid triangles in Figure 2. When the heat was turned off at 42 minutes, the temperatures dropped rapidly and fell below 380°C at 48 minutes. The pressure differential immediately dropped indicating that plug had cleared. The the furnaces were subsequently turned back on. At 52 minutes the Na₂SO₄ flow was reestablished. At about 95 minutes, plugging again began to affect upstream pressure. This time Na₂SO₄ was diverted to pure water and the furnaces were left on. As the pressure continued to grow, shutdown was initiated. Apparently, the plug will not clear without reducing temperature.

Test 7 is consistent with work by Armellini and Tester³ on the temperature-composition phase behavior of Na₂SO₄ in water at supercritical conditions. A figure is reproduced from their paper as Figure 13. Plotted in the figure is the solubility of Na₂SO₄ in a single phase liquid region demarcated by the solid line. At 380°C, 0.55 wt% of salt can coexist in a single phase; any excess will precipitate out as a solid.

Scale-up Estimates

The results reported above are useful for scaling-up from the bench scale to a pilot scale size with 2.5 wt% salt loading. The reactor designs presented in this report are for 5 wt% organic loading. After oxidation, approximately half of this waste is converted into salt. Hence, this scale-up argument is directly applicable to Concept A.

As a hypothesis, we propose that the plugging is directly related to the cross-sectional area of the tube, to the kinematic and thermal development of the flow, and to the concentration of salt.

To estimate the plugging time for a scaled-up reactor, thermal and kinematic similitude are first enforced. For thermal similitude, the mixture must be heated from ambient to 400°C between 3 feet and 20 feet as in the above tests. For kinematic similitude, the velocities of the fluid particles in the scaled up version, V_s , must equal the velocities in the above tests, V_t :

$$V_s = V_t \quad (1)$$

The scaled or pilot plant flow rate, $\dot{m}_s$, is on the order of 50 times the test flow rates, $\dot{m}_t$:

$$\dot{m}_s = 50 \dot{m}_t \quad (2)$$

Now,

$$\dot{m}_s = \rho_s A_s V_s = 50 \rho_t A_t V_t \quad (3)$$

Since kinematic and thermal similarity are being enforced:

$$A_s = 50 A_t \quad (4)$$

The inner diameter of the bench test reactor is 0.188 inch. Hence, to maintain kinematic and thermal similitude, the pilot version should have an inside diameter of 1.343 inch.

Plugging occurred between 23 and 48 min during the tests at 4000 psi with salt loading of 0.5 wt%. If the time to plugging is directly related to concentration, at 2.5 wt% salt loading, the bench scale size will plug in

$$23 \text{ to } 48 \text{ minutes} \times (0.5 \text{ wt\%/} 2.5 \text{ wt\%})$$

$$= 4.6 \text{ to } 9.6 \text{ minutes}$$

We hypothesize that the time to plugging in the tests, 20 minutes, would be reduced due to the increase in salt loading from 0.5 wt% to 2.5 wt%. If our hypotheses are correct, even though the tubing of the pilot version has an area of 50 times the bench scale, it too will quickly plug because the salt deposition rate in the pilot version is 50 times that in the bench scale reactor.

The data presented in Figure 3 was generated using hydrogen peroxide as the oxidant. If air is the oxidant, additional experimentation to confirm these scaling arguments should be done. It is also unknown if the deposition rate would remain the same for a

tube having a diameter of 1.343 inch; possibly the salt plug that would form could not be supported by the larger area. It should be noted that an attractive feature of this technology, in addition to the destruction of organic component, is the potential removal of the salt from the effluent stream.

A final parameter to check to insure kinematic similarity is whether the flow regimes are similar for the pilot scale. This is violated, somewhat, because the Reynolds number for the scaled version is several times the Reynolds number for the bench model. This means that the flow in the scaled-up version will transition more quickly to turbulent flow. However, at 380°C where the salt is precipitating out at 1.2 g/s flow rate in the test, the Reynolds number is approximately 5000 and is presumed turbulent.

Although Na_2SO_4 is the most prevalent salt produced from the ARDEC feed streams, other salts not studied to date, but are listed on the process flow sheets, include CaSO_4 , KCl , NaCl , and MgO .

We do not have solubility data for CaSO_4 and MgO at supercritical conditions and therefore cannot speculate if its behavior will be like Na_2SO_4 . These salts are not soluble in pure water and are not likely to be soluble at supercritical conditions either. However, NaCl may behave differently. Figure 14 is reproduced from the work of Armellini and Tester, and shows the temperature-composition diagram for NaCl and water. The supercritical mixture will transition through a vapor-liquid region, and finally into a vapor-solid region where we anticipate it will plug the reactor at about 460°C. We believe that KCl will behave similarly.

To summarize this section, a major technical problem to overcome to be able to use SCWO to destroy military wastes is the formation of salts and their subsequent deposits following oxidation of the organic itself. The next section develops the conceptual designs for both the tubular reactor and vessel-type reactor in sufficient detail to estimate capital cost.

Design Definition and Capital Equipment Costs

Both concepts, shown in Figures 15 and 16, were developed in sufficient detail to estimate operational and capital equipment cost. Again, these concepts differ only in the reactor/salt separation

subsystem. A tubular reactor is proposed as Concept A and a vessel-type reactor is proposed as Concept B. Each concept consists of a mix & feed subsystem, an air compressor subsystem, a reactor/salt separation subsystem, a salt or brine letdown subsystem, a high-pressure (H.P.) water subsystem, and a liquid/gas/solid separation & letdown subsystem.

Start-up and Operation

To begin operation, air is intensified in the pressure tank by the compressor and metered into the reactor and separator to the desired system pressure. Likewise, cascading pressures are established in the salt letdown system for salt letdown vessel 1 and 2 by regulating air into these vessels. Salt letdown pressures are initially set by the regulators.

After system pressure is established, air flow rate is set by flow control valve, FCV1, and system pressure is maintained by the combination of the pressure transducer, PT, and the flow control valve, FCV, attached to the gas effluent line of the separator.

Distilled water is then pumped by a diaphragm-type pump, HPLP, into the reactor at the desired flow rate. This will cause the control system to make adjustments in the letdown valve system. Feedback between FM1 and the compressor flow control valve, FCV1, adjusts FCV1 to increase flow as desired by operator or computer.

For the tubular design, the temperature profile in the reactor is then established by radiatively or resistively heating the inconel tubing while flowing distilled water and air. For the vessel design (Concept B), either the tubing must similarly be heated and/or the reactor vessel must be heated.

After the desired temperature profile is established with pure water and air, diluted waste with NaOH and air is directed to the first section of the reactor (section 1) and heated to 420°C. In sections 2 and 3, the feed and air are then heated to 550°C for a minimum residence time of 15 seconds.

At the present time, insufficient work has been done to determine a minimum residence time that will efficiently destroy the wastes of interest. There are several issues involved. First, the wastewater

discharge option and acceptable destruction efficiencies compatible with the options, whether to McAlester's pink water treatment plant, the sewage treatment plant, or the ground, have not been determined. Second, tests have not been performed with air to determine destruction efficiencies as a function of residence time. Third, the treated waste water is recirculated. Tests in the MER with the ARDEC wastes have shown that 10 seconds with hydrogen peroxide is sufficient to destroy greater than 99% of the organic constituents. Any residual organic remains in the circulating water.

Salt removal is achieved in Concept A by cycling a section of the reactor from a salt deposition mode to a rinsing mode. As salt accumulates in section 1, a differential pressure is detected by the pressure transducers (PTs). When a sufficiently large pressure difference is detected, for example 300 psi, AV1 is shut and AV3 is opened to divert the reacting flow to section 2. Simultaneously, AV2 is opened, injecting pure water into the reactor. This water is allowed to pass through the 550°C section, section 3, for a certain period of time, for example 1 minute, to remove any residual organic present in section 1. The heaters in section 1 between 200 and 425°C are then turned off. AV4 is shut and AV5 is opened diverting the water to the salt letdown system. Section 1 is available for continued operation after the plug clears. As discussed in the previous section, this sequence of operations may have to occur approximately every 5 to 10 minutes with 5 wt% organic waste.'

For Concept B, distilled water and air are brought to temperature and then waste is injected by gradually increasing waste concentration. Due to the heat of combustion of the waste, external electrical power is gradually throttled back to maintain temperature control. A clean fuel like isopropyl alcohol may be used as an intermediary between complex waste and pure water to establish operating conditions. This may require a separate pumping system not included in the cost estimate.

In Concept B, salt is removed by injecting water into the vessel. A thermocline from top to bottom of about 300°C separates the salt from the reacting solution⁴ as discussed previously.

Liquid, gas, and any residual solids that migrate entirely through the reactor section are separated by gravity in the final subsystem; the solution is brought to ambient temperature by chilled water in the heat exchanger, HX, before the gravity separator. The primary

effluents from the system are brine and gas, but provision is made to analyze the circulating liquid. Additional effluents may occur from the water purifier but are not quantified at this time. For example, since 95% of the sodium sulfate formed as a product is expected to end up in the brine stream, 5% may be left in the circulating stream. It is not obvious that this residual sodium sulfate should be allowed back into the reactor and a provision for a "purifier" is made in the P&IDs. Similarly, due to corrosion, nickel and chromium may arrive in the effluent in ppm quantities and we may not want to circulate these back into the reactor. This must be studied further in Phase II.

Cost Estimate

A materials list with associated cost by subsystem is included for each concept in Appendix B. In Table 5, the cost by subsystem is summarized. The cost was calculated by requesting quotations from vendors based on preliminary design and specification, and then increased by 20%.

Regardless of design configuration, tubular or vessel, the overall cost of the reactor/salt separation and letdown subsystem is estimated to be the same. Approximately 60% of the cost is due to the reactor, whether tubular or vessel. Approximately 45% of the cost of the liquid/gas/solid separation and letdown system is primarily due to the analyzers. Provision in capital cost is made for both an on-line gas chromatograph and an on-line total organic carbon analyzer. At this time, it is not certain that a gas chromatograph is needed at all; perhaps specific analyzers to monitor regulated effluents such as CO will suffice.

Included as miscellaneous equipment is a house air system (to drive valves), the control system, and a chiller to recirculate the coolant. Not included is the cost of a water purifier in the circulation line should it be required.

Control

After start-up, control is entirely automatic. Air is metered into the reactor through FCV1 and mixed with waste in the vessel in Concept B; in Concept A air is mixed with waste at a pipe tee before the reactor subsystem. The feed flow rate is determined by the speed of

the HPLP motor, which is adjusted electrically; the feed flow rate is monitored by FM2. All flow control valves are adjusted electrically by stepping-type motors, or pneumatically, and interfaced to the appropriate flow meter. Compensation for variations in flow rate occur automatically.

All waste is destroyed with an excess oxygen flow rate that needs to be determined experimentally on the bench scale. Initially, pure water is flowing into the reactor with air during start-up. The pure water flow rate is systematically throttled while beginning the introduction of the feed into the reactor. At first, only 0.5 wt% waste is fed into the reactor with a large excess oxygen concentration. The liquid effluent is tested for destruction efficiency. Oxidant concentration is adjusted and the liquid effluent is periodically analyzed for destruction efficiency. Even if destruction efficiencies fall, to say, 90% this is not critical at this point because the liquid effluent is all recirculated.

Trace unreacted organic remains in the water and is recirculated to the feed inlet - not discharged to the drain. This is one of the primary advantages of this technology over competitive methods. Based on periodic analysis of the liquid effluent an acceptable excess oxygen flow rate is established; it is then doubled and the feed concentration is increased to 1 wt%. Due to the heat of combustion, external electrical power to the reactor subsystem is reduced by local temperature controllers. This progressive ratcheting continues until the desired feed concentration is reached.

Pressure transducers (PTs) are located upstream and downstream of the reactor subsystem, and at 20, 200, and 420°C joints in the reactor for Concept A. They are located on the air, waste, and effluent lines in Concept B. All pressure transducers, thermocouples, flow rates, destruction efficiencies, gaseous effluent composition, and liquid levels are monitored by automatic computer data acquisition and control. Remote control is exercised by electric, pneumatic, or electropneumatic means, as appropriate.

Both brine and liquid effluent levels are controlled by differential pressure transducers, DPTs, interfaced to flow control valves, FCVs. Local control is initiated by progressively opening an orifice if the level increases, and progressively decreasing the diameter of this orifice if the level falls. Tanks are monitored by liquid level

indicators, LLIs, that actuate an alarm on the control console if they near filling.

Tanks are sized to permit destruction of the organic in a day without circulation of the liquid effluent or disposal of the brine stream. However, with the 500-gallon mixing tank, two batches of waste must be mixed per day to meet the 1000 gal/day flow rate.

During normal operation, all solenoid valves are actuated at the control console; all air-operated valve/solenoid valve combinations have a logic structure so they are normally closed except for the emergency depressurization valves connected to the emergency vent vessel, which have a normally open logic structure. In an accident scenario, power is interrupted to the control consoles, initiating the following automatic and simultaneous actions: 1) the power is shut to the furnaces, 2) the high pressure pumps are turned off, 3) water, waste, and air flow rates are interrupted, and 4) the depressurization lines are opened. Loss of electrical power or house air also depressurizes the system due to this logic structure. The system is mechanically-safed from overpressurization by the relief devices, RDs.

Abnormal conditions that would initiated the emergency shutdown are: 1) loss of electrical power, 2) loss of pneumatic power, 3) overpressurization and, 4) increase in temperature beyond material specification.

For Concept A, switching between sections 1 and 2 is automatic. The process control system that integrates this would be based on a 50-Mhz 486-PC with analog-to-digital interfaces. Several process control programs are available, such as Genesis (a trademark of Iconics) or PCDM (a trademark of Honeywell), that simplify the development of a supervisory control program and process display. Amenable to total system control, these programs also gather and retain process information for historical and process improvement purposes.

Reaction flow rates, reaction pressure, and reaction temperature are the three process control variables. Reaction flow rates (air and diluted waste flow rates) are maintained by the compressor and the HPLP. Adjustment is determined by total organic carbon (TOC) analysis. System pressure is maintained at the separator by the free surface in the separator. A servo-controlled flow control valve and

pressure transducer maintain target pressure. A letdown valve controls liquid level in the separator metering effluent into the effluent tank. Reaction temperature is controlled locally by temperature controllers interfaced to thermocouples placed either in the reacting medium or on the vessel as appropriate.

Heat Transfer Assessment

As discussed previously, Na_2SO_4 is deposited in the reactor in the heat-up region below 425°C and can be dissolved by pure water at 380°C or below. By dividing the tubular reactor into three heated sections, the sections can be isolated. The second section can then be flushed periodically with pure water to remove salt build-up. In addition, this division allows the reactor to be more compact than if the reactor were a single section.

In order to calculate the energy required per section, the heat flux per section, and the length of each section, the tubular reactor is first divided as shown in Figure 17; the fluid, predominantly air and water, is heated from 20°C to 200°C in section 1, 200°C to 425°C in section 2, and 425°C to 550°C in section 3. Section 3 also contains an insulated section to provide additional residence time at an elevated temperature.

Neglecting the heat of combustion and the properties of the organic, the energy Q that must be transferred to the fluid to raise the temperature in each section from the inlet temperature T_i to the outlet temperature T_o is

$$Q = \dot{m}_t (h_o - h_i) \quad (5)$$

where $\dot{m}_t$ is the total mass flow rate, h_o is the total enthalpy at the outlet of the section, and h_i is the total enthalpy at the inlet of each section.

The thermodynamic and transport properties of water and air are obtained from an in-house computer program derived from the NBS/NRC steam tables. A basic model of transport is employed by weighting thermodynamic, and later transport properties, of the predominantly air and water mixture, by mass flow rate. Neglecting

the properties of the organic constituent, the weighted enthalpy h_t is thus

$$h_t = \frac{\dot{m}_w}{\dot{m}_t} h_w + \frac{\dot{m}_a}{\dot{m}_t} h_a \quad (6)$$

where $\dot{m}_w$, and $\dot{m}_a$, are the mass flow rate of water and air, respectively.

From the process flow calculations, the mass flow rates of the air to destroy the CS agent is 36.25 scfm; CS is the agent requiring the greatest amount of air. Using equations (5) and (6), and setting $\dot{m}_w = 1000$ gal/day and $\dot{m}_a = 36.25$ scfm, yields

$$\begin{aligned} Q_1 &= 44.03 \text{ kW} \\ Q_2 &= 100.95 \text{ kW} \\ Q_3 &= 35.27 \text{ kW} . \end{aligned}$$

The total power required to raise the mixture from ambient temperature to 550°C, $Q_1 + Q_2 + Q_3 = Q_t$, is then 180.25 kW. As shown in Appendix C, the heat loss from radiation and convection (including the additional length in the third section) is less than the heating value of the waste at 5 wt% if the tubing is wrapped; with high temperature insulation. 180.25 kW plus about 5% more for losses (see Appendix C) is a maximum energy demand on startup - it is reduced significantly due to self-heating of the air/water mixture by oxidation of the waste. This maximum energy demand is also valid for the vessel configuration.

The length of each section is found by breaking the section into smaller zones and integrating in finite difference fashion over all zones. For the i^{th} zone,

$$Q_i = \dot{m}_t (h_o - h_i)_i \quad (7)$$

where,

$$Q_i = q'' A_w = h_l \Delta T A_w \quad (8)$$

where q'' and A_w are the impressed heat flux and wetted area of zone i , respectively; h_i is the local heat transfer coefficient and ΔT is the temperature difference between the wall and fluid at the outlet of zone i .

The local heat transfer coefficient, h_i , is related to the Nusselt, Nu , by the equation

$$h_i = Nu k_t / D \quad (9)$$

where D is the tube diameter; k_t is the weighted thermal conductivity. h_i is also related to the Reynolds number through the equation⁷

$$Nu = 0.023 Re_t^{0.8} Pr_t^{0.33} \quad (10)$$

where Re_t and Pr_t are the weighted Reynolds number and Prandtl number, respectively. Re_t and Pr_t are weighted by the transport properties of viscosity and thermal conductivity, similar to what was done with the enthalpy in equation (6).

Equations (7) through (10) are solved simultaneously per zone by guessing the heat flux and integrating forward for a section. Wall temperature is calculated at each zone by equation (8) and if not exceeded by certain criteria, the heat flux is increased and the entire section integrated through, again. The product is the length of each section:

$$\begin{aligned} L_1 &= 1.750 \text{ m} \\ L_2 &= 6.024 \text{ m} \\ L_3 &= 8.368 \text{ m.} \end{aligned}$$

To calculate the additional length required for 15 seconds of residence time, the weighted mass flow rate, $\dot{m}_t$, is divided by the cross-sectional area A and the weighted density, ρ_t , to give the velocity at the end of section 3:

$$V = \frac{\dot{m}_t}{A \rho_t} \quad (11)$$

Multiplying the velocity by 15 seconds gives $L_r = 12.69$ m. These results are summarized in Table 6. Reynolds Number, heat flux, density, and other important variables as a function of distance along the pipe are all recorded in Appendix C for review. The wall thickness is also determined as 0.315 inch in Appendix C.

A potential configuration is shown in Figure 18 for the final section. The entire 21 meters of length ($L_3 + L_r$) has been configured inside an insulated shell having dimensions of 0.7 meters in diameter and about 3 meters long.

Summary

In addition to deciding on reactor configuration (pressure vessel or tubular) and beginning detailed layout design, the following tasks will be done in Phase II over the next year and one-half:

- 1) The pyrotechnic will be destroyed on Sandia's existing bench scale reactor using hydrogen peroxide as the oxidant. The flow reactor will be reconfigured for air and the pyrotechnic rerun. At this time the reactor is not designed to precisely control air flow rate and it must be modified. It is, however, designed to precisely control hydrogen peroxide flow rate; a modification to the safe operating procedure is necessary to do this test. Mass balance or closure has not been emphasized on the dyes. It will be attempted on the pyrotechnic. This will begin to confirm the chemical composition calculations in this report and experimentally characterize any operational problems with the destruction of the pyrotechnic with air. The pyrotechnic has all the major groups of salts and acids that have been identified by the chemical composition sheets other than HCl.

- 2) Although we understand the salt deposition problem better now than we did in June '92, we have not done enough testing to fully characterize it. We propose in the short term to experimentally analyze this problem for NaCl, KCl, and sodium phosphate. Phosphorous compounds have not been explicitly studied in this

report but are expected to be a class of compounds that the Army may wish to destroy in the future.

3) Corrosion studies will be conducted with the pyrotechnic with first hydrogen peroxide as the oxidant, and then air, to begin to characterize the corrosion process. It is expected that the first few tests will indicate the direction that this program should take. In addition, recent and ongoing work done by General Atomics in this area will be reviewed. Probably, as with the salt studies, erosion and corrosion tests will be done with specific chemicals, KCl, NaCl, HCl, and H₂SO₄, with different pH, and modified by acid neutralization. Screening studies on this task have already begun.

4) Flames can be initiated in supercritical water depending on the organic concentration. Sandia will conduct tests on a highly flammable fuel at high temperature with air and pure oxygen. This will be done to set an upper limit on allowable concentration of organic.

5) Tests with air will be done with each waste to experimentally characterize the waste, as was done by calculation in this report.

6) Several salt separation schemes will be attempted. Specifically, a shunt or switching scheme will be attempted for effectiveness (Concept A), and a transpiration-cooled tube proposed by Aérojet may be evaluated.

A transpiration-cooled tube may prevent the adherence of the salt against the wall of a tubular vessel, but it is in its earliest stages of development. Conceptually, the waste and water flow in an inner tube that is porous. Oxidant and water are preheated and introduced into an outer shell flowing through the porous inner wall. The inward fluid motion establishes a boundary layer on the inside of the porous wall preventing the reacting medium from interacting with the wall. Ideally, the reacting medium is restricted to an inner core eliminating corrosion and salt-deposition problems.

7) Only 0.5 wt% waste has been destroyed at this time. No control difficulties were observed from the energy liberated by this process, although the energy released at this concentration would not be expected to raise the fluid temperature much more than 25 °C. However, at 10 times this concentration, the energy released is significant. How this energy is managed and what the optimum

control scheme is for management, needs to be explored in Phase II. This is not viewed as a major impediment to development but cannot be neglected.

All tasks for Phase I have been completed. Progress reports on destruction efficiencies for all dyes have been delivered and a final laboratory report, including initial destruction efficiencies of the pyrotechnic, is planned for release in August, 1993. An RFQ has been issued by Sandia for contract bids to begin Phase II. Selection of a final contractor will occur in August 1993.

Detailed design, construction, and resolution of issues raised in this report and the lab feasibility study begin nearly simultaneously and/or overlap. Although the military wastes have been successfully destroyed with hydrogen peroxide on a bench scale and an attempt has been made to characterize the feed stocks in this report, salt-deposition, deviation from hydrogen peroxide as the oxidant, and the corrosion issues raised in this report indicate it is important to more fully characterize the wastes and their effect on reactor corrosion and system performance to reduce risk. The estimates in this report indicate that the funds allotted for capital equipment in the original program statement are adequate. It is not possible to evaluate whether funds allotted for detailed design and construction are adequate before bids are received.

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CONCEPT A

Drawn By Larry Hoffa

Figure 1. Process Flow Design (Concept A).

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Figure 2. Process Flow Design (Concept B).

Table 1. Summary of Oxidizer Trade-off Study.

Hydrogen Peroxide

Power Consumption	\$122/day
Raw Material (Cost of H ₂ O ₂)	\$1000/day
Capital Equipment Cost (Includes leased H ₂ O ₂ Storage Tank)	\$20,000+(\$200/month)
Total	\$359,000/Year

Air

Power Consumption	\$143/day
Raw Material	\$0/day
Capital Equipment Cost	\$48,000
Total	\$90,000/Year

Oxygen

Power Consumption	\$127/day
Raw Material (Cost of O ₂)	\$24/day
Capital Equipment Cost (Includes leased O ₂ Storage Tank)	\$27,100+(\$375/month)
Total	\$76,900/Year

Table 2A. Chemical Composition Analysis.

Orange Dye

100% Acid Orange 10

MW(Molecular Weight) = 452.37

Chemical Composition Calculation for Orange Dye

This calculation estimates the amount of oxygen required to decompose the organic components of orange dye and the products generated from the oxidation. The calculation is based on 1000 gal/day of chemical waste stream at 5% concentration and 20 hours per day of operation.

Name	wt %	composition							MW
Acid Orange 10	100	16	10	2	2	7	2	0	452.3749
Air	100	0	0	138	0	37	0	0	2524.9024
NaOH	100	0	2	0	2	2	0	0	79.99434
CO2	100	16	0	0	0	32	0	0	704.1592
N2	100	0	0	140	0	0	0	0	1960.938
H2O	100	0	12	0	0	6	0	0	108.09204
Na2SO4	100	0	0	0	4	8	2	0	284.0824

Oxygen Requirement

Weight ratio: MW (air)/MW(dye) = 5.5814379

Density of waste stream (assume water) = 1 kg/lit

Waste stream per day " 1000 g/d x 3.79 l/g = 3785.4 l/d x 1 kg/l = 3785.4 kg/d

5% of dye = 3785.4 kg/d x 0.05 = 189.27 kg/d

Air required per day = 189.27 x MW(air)/MW(dye) = 1056.4 kg/d

The system is operated at 20 hr/day: " 1056.3987 + (20 x 60) min/d = 0.88033 kg/min

at 60 °F and 14.7 psia, density (air) = 0.0763 lb/ft³ x 0.45 kg/lb = 0.03461 kg/ft³

Air required in SCFM = 0.8803323 kg/min + 0.03 kg/ft³ = 25.436 SCFM

100% allowance for oxygen, " 25.436014 SCFM x 2 = **50.87 SCFM**

20% allowance for oxygen, " 25.436014 SCFM x 1.2 = **30.52 SCFM**

NaOH Requirement

Weight ratio: MW (NaOH)/MW(dye) = 0.176832

NaOH per day = Dye/day x MW (NaOH/dye) = 189.27 kg/d x weight ratio = 33.469 kg/d

Products

Name	MW ratio	dye/day	Product/day (kg/d)
CO2	1.56	x 189	= 294.61452 kg/d
N2	4.33	x 189	= 820.4406 kg/d
H2O	0.24	x 189	= 45.224835 kg/d
Na2SO4	0.63	x 189	= 118.85778 kg/d

Table 2B. Summary - Chemical Composition Analysis.

Chemical Name	Formula	Air Req'd (SCFM)	NaOH Req'd (kg/d)	Salt Produced * (kg/d)
Orange Dye	$C_{16}H_{10}N_2Na_2O_7S_2$	25.44	33.47	118.86 (Na_2SO_4)
Red Dye	$C_{18}H_{13}N_3O_8S_2Na_2$ (80%) $C_{16}H_9N_4Na_3O_9S_2$ (20%)	24.25	26.61	104.56 (Na_2SO_4)
Green Dye (I)	$C_{16}H_9N_4Na_3O_9S_2$ (80%) $C_{27}H_{31}N_2NaO_6S_2$ (20%)	23.902	19.35	99.47 (Na_2SO_4)
Green Dye (II)	$C_{16}H_9N_4Na_3O_9S_2$ (80%) $Ca(C_{27}H_{31}N_2O_7S_2)_2$ (20%)	22.63	18.12	96.39 (Na_2SO_4 & $CaSO_4$)
Blue Dye (I)	$C_{27}H_{31}N_2NaO_6S_2$ (30%) $NaC_{37}H_{36}N_3O_6S_2$ (20%) $C_{12}H_{22}O_{11}$ (50%)	30.48	18.46	43.70 (Na_2SO_4)
Blue Dye (II)	$Ca(C_{27}H_{31}N_2O_7S_2)_2$ (30%) $NaC_{37}H_{36}N_3O_6S_2$ (20%) $C_{12}H_{22}O_{11}$ (50%)	28.56	16.61	39.07 (Na_2SO_4 & $CaSO_4$)
CS	$C_{10}H_5ClN_2$	36.25	40.14	58.64 ($NaCl$)
Pyrotechnic	$KClO_3$ (31.5%) $C_{12}H_{22}O_{11}$ (18%) $MgCO_3$ (3.5%) $C_{24}H_{12}O$ (4.7%) $C_{17}H_{10}O$ (9.4%) $C_{28}H_{21}O_2N_2$ (32.9%)	24.602	0**	36.27 (KCl)

* Results from the process calculation with added NaOH.

** Calculations using NaOH were not done since no significant quantities of acid are directly formed by oxidation of pyrotechnic.

Figure 3. Pressure trace for organic feed (typical).

Table 3. Test conditions for Na₂SO₄ experiment

<u>Test No.</u>	<u>Pressure (psi)</u>	<u>Temperature (C)</u>	<u>Flowrate (gm/s)</u>
1	3700	400	0.6
2	3700	400	1.2
3	3700	400	1.5
4	5150	400	0.6
5	5150	400	1.2
6	3700	400	0.6
7	3700	400	0.6

Table 4. Time that Na₂SO₄ is discontinued.

<u>Test No.</u>	<u>Time (minutes)</u>
1	28
2	23
3	37
4	26
5	18
6	48
7	41

Figure 4. Temperature profile for all tests.

Figure 5. Test #1 (0.5 wt% Na_2SO_4 , $\dot{m} = 0.6 \text{ gm/s}$)

Figure 6. Test #2 (0.5 wt% Na_2SO_4 , $\dot{m} = 1.2 \text{ gm/s}$)

Figure 7. Test #3 (0.5 wt% Na_2SO_4 , $\dot{m} = 1.5 \text{ gm/s}$)

Figure 8. Test #4 (0.5 wt% Na_2SO_4 , $\dot{m} = 0.6 \text{ gm/s}$)

Figure 9. Test #5 (0.5 wt% Na_2SO_4 , $\dot{m} = 1.2 \text{ gm/s}$)

Figure 10. Test #6 (0.5 wt% Na_2SO_4 , $\dot{m} = 0.6 \text{ gm/s}$)

Figure 11. Test #7 (0.5 wt% Na_2SO_4 , $\dot{m} = 0.6 \text{ gm/s}$)

Figure 12. Temperature profile as a function of time over the last 10 feet of the reactor.

Figure 13. Temperature-composition $\text{Na}_2\text{SO}_4\text{-H}_2\text{O}$ phase diagram at 250 bar (reproduced from Armellini and Tester).

Figure 14. Temperature-composition $\text{NaCl-H}_2\text{O}$ phase diagram at 250 bar (reproduced from Armellini and Tester).

Figure 15. P&ID for Concept A.

ARDEC
P & ID
CONCEPT B (U)

Figure 16. P&ID for Concept B.

Table 5. Capital Equipment Estimate by Subsystem.

Mix and Feed	\$92,500
H. P. Air Compressor	\$104,500
H. P. Water	\$23,100
Reactor/Salt Separation/Salt Letdown	\$308,000
Liquid/Gas/Solid/Separation and Letdown	\$231,400
Miscellaneous Equipment	\$30,000
Total	\$789,500

See detailed estimate in Appendix B.

Figure 17. Tubular reactor divided into three sections.

Table 6. Summary- Heat Transfer Assessment.

<u>Section</u>	<u>Q (kW)</u>	<u>L(m)</u>
1	44.03	1.75
2	100.95	6.024
3	35.27	8.368*

*Does not include the residual section of 12.69 m.

Figure 18. Typical configuration.

Appendix A. Process Flow Sheets

This appendix contains two sets of process flow calculations for the following wastes, with and without added NaOH as the neutralizer.

1) Orange dye:

2) Red dye:

3) Green Dye (Type I):

4) Green Dye (Type II):

5) Blue Dye (Type I):

6) Blue Dye (Type II):

7) Pyrotechnic Composition:

KClO_3 (31.5%)

$\text{C}_{12}\text{H}_{22}\text{O}_{11}$ (18%)

MgCO_3 (3.5%)

$\text{C}_{24}\text{H}_{12}\text{O}$ (4.7%)

$\text{C}_{17}\text{H}_{10}\text{O}$ (9.4%)

$\text{C}_{28}\text{H}_{21}\text{O}_2\text{N}_2$ (32.9%)

8) CS agent:

$\text{C}_{10}\text{H}_5\text{ClN}_2$ (100%)

Orange Dye

100% Acid Orange 10

$\text{C}_{16}\text{H}_{10}\text{N}_2\text{Na}_2\text{O}_7\text{S}_2$ MW(Molecular Weight) = 452.37

Chemical Composition Calculation for Orange Dye

This calculation estimates the amount of oxygen required to decompose the organic components of orange dye and the products generated from the oxidation. The calculation is based on 1000 gal/day of chemical waste stream at 5% concentration and 20 hours per day of operation.

Name	wt %	composition							MW
Acid Orange 10	100	C	H	N	Na	O	S	Ca	
Air	100	0	0	138	0	37	0	0	2524.9024
CO2	100	16	0	0	0	32	0	0	704.1592
N2	100	0	0	140	0	0	0	0	1960.938
H2O	100	0	8	0	0	4	0	0	72.06136
H2SO4	100	0	2	0	0	4	1	0	98.07754
Na2SO4	100	0	0	0	2	4	1	0	142.0412

Oxygen Requirement

Weight ratio:	MW (air)/MW(dye)	=	5.5814379						
Density of waste stream (assume water)		=	1	kg/lit					
Waste stream per day	» 1000 g/d	x	3.79 l/g	=	3785.4 l/d	x	1 kg/l	=	3785.4 kg/d
	5% of dye	=	3785.4 kg/d	x	0.05	=		=	189.27 kg/d
	Air required per day	=	189.27	x	MW(air)/MW(dye)	=		=	1056.4 kg/d
The system is operated at 20 hr/day:	» 1056.3987	+	(20 x 60) min/d	=		=		=	0.88033 kg/min
at 60 °F and 14.7 psia, density (air)	=	0.0763 lb/ft3	x	0.45 kg/lb	=		=	=	0.03461 kg/ft3
	Air required in SCFM	=	0.8803323 kg/min	+	0.03 kg/ft3	=		=	25.436 SCFM
100% allowance for oxygen,	» 25.436014 SCFM	x	2	=		=		=	50.87 SCFM
20% allowance for oxygen,	» 25.436014 SCFM	x	1.2	=		=		=	30.52 SCFM

Products

Name	MW ratio		dye/day		Product/day (kg/d)
CO2	1.56	x	189	=	294.61452 kg/d
N2	4.33	x	189	=	820.4406 kg/d
H2O	0.16	x	189	=	30.14989 kg/d
H2SO4	0.22	x	189	=	41.03485 kg/d
Na2SO4	0.31	x	189	=	59.428889 kg/d

Red Dye

80% Amido Naphthol Red G

$C_{18}H_{13}N_3O_8S_2Na_2$ MW(Molecular Weight) = 509.43

20% Tartrazine

$C_{16}H_9N_4Na_3O_9S_2$ MW(Molecular Weight) = 534.37

Chemical Composition Calculation for Red Dye

This calculation estimates the amount of oxygen required to decompose the organic components of red dye and the products generated from the oxidation. The calculation is based on 1000 gal/day of chemical waste stream at 5% concentration and 20 hours per day of operation.

Name	wt %	Composition							MW
		C	H	N	Na	O	S	Ca	
Amido Naphthol	80	18	13	3	2	8	2	0	509.43
Tartrazine	20	16	9	4	3	9	2	0	534.37
Air (80%)	80	0	0	154	0	41.5	0	0	2821
Air (20%)	20	0	0	130	0	35	0	0	2380.9
CO2(80%)	80	18	0	0	0	36	0	0	792.18
CO2(20%)	20	16	0	0	0	32	0	0	704.16
N2 (80%)	80	0	0	157	0	0	0	0	2199.1
N2 (20%)	20	0	0	134	0	0	0	0	1876.9
H2O (80%)	80	0	11	0	0	5.5	0	0	99.084
H2O (20%)	20	0	8	0	0	4	0	0	72.061
H2SO4(80%)	80	0	2	0	0	4	1	0	98.078
H2SO4(20%)	20	0	1	0	0	2	0.5	0	49.039
Na2SO4(80%)	80	0	0	0	2	4	1	0	142.04
Na2SO4(20%)	20	0	0	0	3	6	1.5	0	213.06

Oxygen Requirement

$$\begin{aligned}
 \text{Weight ratio: } & \text{MW(air)/MW(dye)@80\%} = 2821 + 509 = 5.5376 \\
 & \text{MW(air)/MW(dye)@20\%} = 2381 + 534 = 4.4554 \\
 & \text{" MW(air)/MW(dye) (net)} = 5.3212
 \end{aligned}$$

$$\text{Density of waste stream (assume water)} = 1 \text{ kg/lit}$$

$$\text{Waste stream per day} = 1000 \text{ g/d} \times 3.785 \text{ l/g} = 3785.4 \text{ l/d} \times 1 \text{ kg/l} = 3785.4 \text{ kg/d}$$

$$5\% \text{ of dye} = 3785.4 \text{ kg/d} \times 0.05 = 189.27 \text{ kg/d}$$

$$\text{Air required per day} = 189.27 \times \text{MW(air)/MW(dye)} = 1007.1 \text{ kg/d}$$

$$\text{The system is operated 20 hr/day:} = 1007.1 + (20 \times 60) \text{ min/d} = 0.8393 \text{ kg/min}$$

$$\text{at 60 °F and 14.7 psia, density (air)} = 0.0763 \text{ lb/ft}^3 \times 0.454 \text{ kg/lb} = 0.0346 \text{ kg/ft}^3$$

$$\text{" Air required in SCFM} = 0.8393 \text{ kg/min} + 0.035 \text{ kg/ft}^3 = 24.25 \text{ SCFM}$$

$$100\% \text{ allowance for oxygen,} = 24.25 \text{ SCFM} \times 2 = 48.50 \text{ SCFM}$$

$$20\% \text{ allowance for oxygen,} = 24.25 \text{ SCFM} \times 1.2 = 29.10 \text{ SCFM}$$

Products

Name	MW ratio		net	dye/day		Product/day (kg/d)
	80%	20%				
CO2	1.555	1.318	1.508	x	189	= 285.34 kg/d
N2	4.317	3.512	4.156	x	189	= 786.58 kg/d
H2O	0.195	0.135	0.183	x	189	= 34.56 kg/d
H2SO4	0.193	0.092	0.172	x	189	= 32.63 kg/d
Na2SO4	0.279	0.399	0.303	x	189	= 57.31 kg/d

Green Dye (I)

80% Tartrazine

$\text{C}_{16}\text{H}_9\text{N}_4\text{Na}_3\text{O}_9\text{S}_2$ MW(Molecular Weight) = 534.37

20% Alphazurine 2G

$\text{C}_{27}\text{H}_{31}\text{N}_2\text{NaO}_6\text{S}_2$ MW(Molecular Weight) = 566.68

Chemical Composition Calculation for Green Dye - Type I

This calculation estimates the amount of oxygen required to decompose the organic components of green dye (type I) and the products generated from the oxidation. The calculation is based on 1000 gal/day of chemical waste stream at 5% concentration and 20 hours per day of operation.

Name	wt %	Composition							MW
		C	H	N	Na	O	S	Ca	
Tartrazine	80	16	9	4	3	9	2	0	534.37
Alphazurine	20	27	31	2	1	6	2	0	566.68
Air (80%)	80	0	0	130	0	35	0	0	2380.9
Air (20%)	20	0	0	260	0	70	0	0	4761.7
CO2(80%)	80	16	0	0	0	32	0	0	704.16
CO2(20%)	20	27	0	0	0	54	0	0	1188.3
N2 (80%)	80	0	0	134	0	0	0	0	1876.9
N2 (20%)	20	0	0	262	0	0	0	0	3669.8
H2O (80%)	80	0	8	0	0	4	0	0	72.061
H2O (20%)	20	0	28	0	0	14	0	0	252.21
H2SO4 (80%)	80	0	1	0	0	2	0.5	0	49.039
H2SO4 (20%)	20	0	3	0	0	6	1.5	0	147.12
Na2SO4(80%)	80	0	0	0	3	6	1.5	0	213.06
Na2SO4(20%)	20	0	0	0	1	2	0.5	0	71.021

Oxygen Requirement

Weight ratio:	MW(air)/MW(dye)@80%	=	2381	+	534	=	4.4554
	MW(air)/MW(dye)@20%	=	4762	+	567	=	8.4029
	" MW(air)/MW(dye) (net)					=	5.2449

Density of waste stream (assume water) = 1 kg/lit

$$\text{Waste stream per day} \quad \gg \quad 1000 \text{ g/d} \quad \times \quad 3.785 \text{ l/g} \quad = \quad 3785.4 \text{ l/d} \quad \times \quad 1 \text{ kg/l} \quad = \quad 3785.4 \text{ kg/d}$$
$$5\% \text{ of dye} = 3785.4 \text{ kg/d} \times 0.05 = 189.27 \text{ kg/d}$$
$$\text{Air required per day} = 189.27 \times \text{MW}(\text{air})/\text{MW}(\text{dye}) = 992.71 \text{ kg/d}$$

The system is operated 20 hr/day: " 992.71 + (20 x 60) min/d = 0.8273 kg/min

$$\text{at } 60^\circ\text{F and } 14.7 \text{ psia, density (air) } = 0.0763 \text{ lb/ft}^3 \times 0.454 \text{ kg/lb} = 0.0346 \text{ kg/ft}^3$$

» Air required in SCFM = $0.8273 \text{ kg/min} + 0.035 \text{ kg/lit} = 23.902 \text{ SCFM}$

100% allowance for oxygen,	"	23.902 SCFM	x	2	=	47.80 SCFM
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20% allowance for oxygen,	"	23.902 SCFM	x	1.2	=	28.68 SCFM
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Products

Name	MW ratio		net		dye/day		Product/day (kg/d)
	80%	20%					
CO2	1.318	2.097	1.474	x	189	=	278.90 kg/d
N2	3.512	6.476	4.105	x	189	=	776.97 kg/d
H2O	0.135	0.445	0.197	x	189	=	37.27 kg/d
H2SO4	0.092	0.26	0.125	x	189	=	23.72 kg/d
Na2SO4	0.399	0.125	0.344	x	189	=	65.12 kg/d

Green Dye (II)

80% Tartrazine

20% Alphazurine 2G

Chemical Composition Calculation for Green Dye - Type II

This calculation estimates the amount of oxygen required to decompose the organic components of green dye (type II) and the products generated from the oxidation. The calculation is based on 1000 gal/day of chemical waste stream at 5% concentration and 20 hours per day of operation.

Name	wt %	Composition							MW
		C	H	N	Na	O	S	Ca	
Tartrazine	80	16	9	4	3	9	2	0	534.37
Alphazurine	20	54	82	4	0	24	4	1	1339.6
Air (80%)	80	0	0	130	0	35	0	0	2380.9
Air (20%)	20	0	0	512	0	138	0	0	9379.3
CO2(80%)	80	16	0	0	0	32	0	0	704.16
CO2(20%)	20	54	0	0	0	108	0	0	2376.5
N2 (80%)	80	0	0	134	0	0	0	0	1876.9
N2 (20%)	20	0	0	516	0	0	0	0	7227.5
H2O (80%)	80	0	8	0	0	4	0	0	72.061
H2O (20%)	20	0	76	0	0	38	0	0	684.58
H2SO4(80%)	80	0	1	0	0	2	0.5	0	49.039
H2SO4(20%)	20	0	6	0	0	12	3	0	294.23
Na2SO4(80%)	80	0	0	0	3	6	1.5	0	213.06
CaSO4	20	0	0	0	0	4	1	1	136.14

Oxygen Requirement

Weight ratio: $MW(\text{air})/MW(\text{dye})@80\% = 2381 + 534 = 4.4554$
 $MW(\text{air})/MW(\text{dye})@20\% = 9379 + 1340 = 7.0016$
 " $MW(\text{air})/MW(\text{dye}) (\text{net}) = 4.9647$

Density of waste stream (assume water) = 1 kg/lit

Waste stream per day " 1000 g/d x 3.785 l/g = 3785.4 l/d x 1 kg/l = 3785.4 kg/d

5% of dye = 3785.4 kg/d x 0.05 = 189.27 kg/d

Air required per day = 189.27 x $MW(\text{air})/MW(\text{dye}) = 939.66 \text{ kg/d}$

The system is operated 20 hr/day: " 939.66 + (20 x 60) min/d = 0.7831 kg/min

at 60 °F and 14.7 psia, density (air) = 0.0763 lb/ft³ x 0.454 kg/lb = 0.0346 kg/ft³

" Air required in SCFM = 0.7831 kg/min + 0.035 kg/ft³ = 22.625 SCFM

100% allowance for oxygen, " 22.625 SCFM x 2 = **45.25 SCFM**

20% allowance for oxygen, " 22.625 SCFM x 1.2 = **27.15 SCFM**

Products

Name	MW ratio		net		dye/day		Product/day (kg/d)
	80%	20%					
CO2	1.318	1.774	1.409	x	189	=	266.68 kg/d
N2	3.512	5.395	3.889	x	189	=	736.06 kg/d
H2O	0.135	0.511	0.21	x	189	=	39.76 kg/d
H2SO4	0.092	0.22	0.117	x	189	=	22.21 kg/d
Na2SO4	0.399	-	0.319	x	189	=	60.37 kg/d
CaSO4	-	0.102	0.02	x	189	=	3.85 kg/d

Blue Dye (I)

30% Alphazurine B

20% Acid Fast Violet

50% Sugar

Chemical Composition Calculation for Blue Dye - Type I

This calculation estimates the amount of oxygen required to decompose the organic components of blue dye (type I) and the products generated from the oxidation. The calculation is based on 1000 gal/day of chemical waste stream at 5% concentration and 20 hours per day of operation.

Name	wt %	Composition							MW
		C	H	N	Na	O	S	Ca	
Alphazurine B	30	27	31	2	1	6	2	0	566.68
Acid Fast Violet	20	37	36	3	1	6	2	0	705.83
Sugar	50	12	22	0	0	11	0	0	342.3
Air (30%)	30	0	0	260	0	70	0	0	4761.7
Air (20%)	20	0	0	344	0	92.5	0	0	6298.2
Air (50%)	50	0	0	89	0	24	0	0	1630.6
CO2(30%)	30	27	0	0	0	54	0	0	1188.3
CO2(20%)	20	37	0	0	0	74	0	0	1628.4
CO2(50%)	50	12	0	0	0	24	0	0	528.12
N2 (30%)	30	0	0	262	0	0	0	0	3669.8
N2 (20%)	20	0	0	347	0	0	0	0	4860.3
N2 (50%)	50	0	0	89	0	0	0	0	1246.6
H2O (30%)	30	0	28	0	0	14	0	0	252.21
H2O (20%)	20	0	33	0	0	16.5	0	0	297.25
H2O (50%)	50	0	22	0	0	11	0	0	198.17
H2SO4(30%)	30	0	3	0	0	6	1.5	0	147.12
H2SO4(20%)	20	0	3	0	0	6	1.5	0	147.12
Na2SO4(30%)	30	0	0	0	1	2	0.5	0	71.021
Na2SO4(20%)	20	0	0	0	1	2	0.5	0	71.021

Oxygen Requirement

Weight ratio:	MW(air)/MW(dye)@30%	=	4762	+	567	=	8.4029
	MW(air)/MW(dye)@20%	=	6298	+	706	=	8.9231
	MW(air)/MW(dye)@50%	=	1631	+	342	=	4.7636
	" MW(air)/MW(dye) (net)					=	6.6873

Density of waste stream (assume water) = 1 kg/lit

$$\text{Waste stream per day} \quad " \quad 1000 \quad \text{g/d} \quad \times \quad 3.785 \quad \text{l/g} \quad = \quad 3785.4 \quad \text{l/d} \quad \times \quad 1 \quad \text{kg/l} \quad = \quad 3785.4 \quad \text{kg/d}$$
$$5\% \text{ of dye} = 3785.4 \text{ kg/d} \times 0.05 = 189.27 \text{ kg/d}$$
$$\text{Air required per day} = 189.27 \times \frac{\text{MW}(\text{air})}{\text{MW}(\text{dye})} = 1265.7 \text{ kg/d}$$

The system is operated 20 hr/day: " 1265.7 + (20 x 60) min/d = 1.0547 kg/min

$$\text{at } 60^\circ\text{F and } 14.7 \text{ psia, density (air) } = 0.0763 \text{ lb/ft}^3 \times 0.454 \text{ kg/lb} = 0.0346 \text{ kg/ft}^3$$

» Air required in SCFM = 1.0547 kg/min + 0.035 kg/ft³ = 30.476 SCFM

100% allowance for oxygen,	"	30.476 SCFM	x	2	=	60.95 SCFM
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20% allowance for oxygen,	"	30.476 SCFM	x	1.2	"	36.57 SCFM
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Products

Name	MW ratio					dye/day		Product/day (kg/d)
	30%	20%	50%	net				
CO2	2.097	2.307	1.543	1.862	x	189	=	352.40 kg/d
N2	6.476	6.886	3.642	5.141	x	189	=	973.01 kg/d
H2O	0.445	0.421	0.579	0.507	x	189	=	96.00 kg/d
H2SO4	0.26	0.208	0	0.12	x	189	=	22.63 kg/d
Na2SO4	0.125	0.101	0	0.058	x	189	=	10.93 kg/d

Blue Dye (II)

30% Alphazurine 2G

20% Acid Fast Violet

50% Sugar

Chemical Composition Calculation for Blue Dye - Type II

This calculation estimates the amount of oxygen required to decompose the organic components of blue dye (type II) and the products generated from the oxidation. The calculation is based on 1000 gal/day of chemical waste stream at 5% concentration and 20 hours per day of operation.

Name	wt %	Composition							MW
		C	H	N	Na	O	S	Ca	
Alphazurine B	30	54	82	4	0	24	4	1	1339.6
Acid Fast Violet	20	37	36	3	1	6	2	0	705.83
Sugar	50	12	22	0	0	11	0	0	342.3
Air (30%)	30	0	0	512	0	138	0	0	9379.3
Air (20%)	20	0	0	344	0	92.5	0	0	6298.2
Air (50%)	50	0	0	89	0	24	0	0	1630.6
CO2(30%)	30	54	0	0	0	108	0	0	2376.5
CO2(20%)	20	37	0	0	0	74	0	0	1628.4
CO2(50%)	50	12	0	0	0	24	0	0	528.12
N2 (30%)	30	0	0	516	0	0	0	0	7227.5
N2 (20%)	20	0	0	347	0	0	0	0	4860.3
N2 (50%)	50	0	0	89	0	0	0	0	1246.6
H2O (30%)	30	0	76	0	0	38	0	0	684.58
H2O (20%)	20	0	33	0	0	16.5	0	0	297.25
H2O (50%)	50	0	22	0	0	11	0	0	198.17
H2SO4(30%)	30	0	6	0	0	12	3	0	294.23
H2SO4(20%)	20	0	3	0	0	6	1.5	0	147.12
CaSO4(30%)	30	0	0	0	0	4	1	1	136.14
NaSO4(20%)	20	0	0	0	1	2	0.5	0	71.021

Oxygen Requirement

Weight ratio: MW(air)/MW(dye)@30% = 9379 + 1340 = 7.0016
 MW(air)/MW(dye)@20% = 6298 + 706 = 8.9231
 MW(air)/MW(dye)@50% = 1631 + 342 = 4.7636 MW(air)/MW(dye) (net) = 6.2669

Density of waste stream (assume water) = 1 kg/lit

Waste stream per day " 1000 g/d x 3.785 l/g = 3785.4 l/d x 1 kg/l = 3785.4 kg/d

5% of dye = 3785.4 kg/d x 0.05 = 189.27 kg/d

Air required per day = 189.27 x MW(air)/MW(dye) = 1186.1 kg/d

The system is operated 20 hr/day: " 1186.1 + (20 x 60) min/d = 0.9884 kg/min

at 60 °F and 14.7 psia, density (air) = 0.0763 lb/ft3 x 0.454 kg/lb = 0.0346 kg/ft3

" Air required in SCFM = 0.9884 kg/min + 0.035 kg/ft3 = 28.56 SCFM

100% allowance for oxygen, " 28.56 SCFM x 2 = **57.12 SCFM**

20% allowance for oxygen, " 28.56 SCFM x 1.2 = **34.27 SCFM**

Products

Name	MW ratio				dye/day	Product/day (kg/d)
	30%	20%	50%	net		
CO2	1.774	2.307	1.543	1.765	x 189	= 334.07 kg/d
N2	5.395	6.886	3.642	4.817	x 189	= 911.65 kg/d
H2O	0.511	0.421	0.579	0.527	x 189	= 99.75 kg/d
H2SO4	0.22	0.208	0	0.108	x 189	= 20.36 kg/d
CaSO4	0.102	0	0	0.03	x 189	= 5.77 kg/d
Na2SO4	0	0.101	0	0.02	x 189	= 3.81 kg/d

Pyrotechnic Composition

31.5% Potassium Chlorate

KClO_3 MW(Molecular Weight) = 122.55

18% Lactose

$\text{C}_{12}\text{H}_{22}\text{O}_{11}$ MW(Molecular Weight) = 342.30

3.5% Magnesium Carbonate

MgCO_3 MW(Molecular Weight) = 84.32

4.7% $\text{C}_{24}\text{H}_{12}\text{O}$ MW(Molecular Weight) = 316.36

9.4% Benzanthrone

$\text{C}_{17}\text{H}_{10}\text{O}$ MW(Molecular Weight) = 230.27

32.9% $\text{C}_{28}\text{H}_{21}\text{O}_2\text{N}_2$ MW(Molecular Weight) = 417.49

Note: Calculations using NaOH were not done since no significant quantities of acid are directly formed by oxidation of pyrotechnic.

Chemical Composition Calculation for Pyrotechnic

This calculation estimates the amount of oxygen required to decompose the organic components of pyrotechnic and the products generated from its oxidation. The calculation is based on 1000 gal/day of chemical waste stream at 5% concentration and 20 hours per day of operation.

Name	wt %	Composition									MW
		C	H	N	Na	O	S	K	Mg	Cl	
KClO ₃	31.5	0	0	0	0	3	0	1	0	1	122.55
Lactose	18	12	22	0	0	11	0	0	0	0	342.3
MgCO ₃	3.5	1	0	0	0	3	0	0	1	0	84.321
C ₂₄ H ₁₂ O	4.7	24	12	0	0	1	0	0	0	0	316.36
Benzanthrone	9.4	17	10	0	0	1	0	0	0	0	230.27
C ₂₈ H ₂₁ O ₂ N ₂	32.9	28	21	2	0	2	0	0	0	0	417.49
Air (18%)	18	0	0	89	0	24	0	0	0	0	1630.6
Air (4.7%)	4.7	0	0	197	0	53	0	0	0	0	3607.3
Air (9.4%)	9.4	0	0	141	0	38	0	0	0	0	2582.9
Air (32.9%)	32.9	0	0	240	0	64.5	0	0	0	0	4393.6
KCl(31.5%)	31.5	0	0	0	0	0	0	1	0	1	74.555
O ₂ (31.5%)	31.5	0	0	0	0	3	0	0	0	0	47.998
MgO(3.5%)	3.5	0	0	0	0	1	0	0	1	0	40.311
CO ₂ (18%)	18	12	0	0	0	24	0	0	0	0	528.12
CO ₂ (3.5%)	3.5	1	0	0	0	2	0	0	0	0	44.01
CO ₂ (4.7%)	4.7	24	0	0	0	48	0	0	0	0	1056.2
CO ₂ (9.4%)	9.4	17	0	0	0	34	0	0	0	0	748.17
CO ₂ (32.9%)	32.9	28	0	0	0	56	0	0	0	0	1232.3
N ₂ (18%)	18	0	0	89	0	0	0	0	0	0	1246.6
N ₂ (4.7%)	4.7	0	0	197	0	0	0	0	0	0	2759.3
N ₂ (9.4%)	9.4	0	0	141	0	0	0	0	0	0	1974.9
N ₂ (32.9%)	32.9	0	0	242	0	0	0	0	0	0	3389.6
H ₂ O (18%)	18	0	22	0	0	11	0	0	0	0	198.17
H ₂ O (4.7%)	4.7	0	12	0	0	6	0	0	0	0	108.09
H ₂ O (9.4%)	9.4	0	10	0	0	5	0	0	0	0	90.077
H ₂ O (32.9%)	32.9	0	21	0	0	10.5	0	0	0	0	189.16

Oxygen Requirement

Weight ratio: MW(air)/MW(dye)@18% = 1631 + 342 = 4.764
 MW(air)/MW(dye)@4.7% = 3607 + 316 = 11.4
 MW(air)/MW(dye)@9.4% = 2583 + 230 = 11.22
 MW(air)/MW(dye)@32.9% = 4394 + 417 = 10.52

» MW(air)/MW(dye) (net) = 5.91

Density of waste stream (assume water) = 1 kg/lit

Waste stream per day » 1000 g/d x 3.785 l/g = 3785 l/d x 1 kg/l = 3785.4 kg/d

5% of dye = 3785 kg/d x 0.05 = 189.27 kg/d

Air required per day = 189.3 x MW(air)/MW(dye) = 1118.6 kg/d

Oxygen is produced from KClO₃ disassociation, the air requirement can be reduced.

MW(O₂)/MW(dye)@31.5% = 48 + 123 = 0.392

O₂ / day = 189.3 * 0.315 * 0.39 = 23.35 kg/d

equivalent air/day (23.15% O₂) = 23.35 + 0.23 = 100.87 kg/d

The net air required per day = 1119 - 101 = 1017.7 kg/d

The system is operated 20 hr/day: » 1018 + (20 x 60) min/d = 0.8481 kg/min

at 60 °F and 14.7 psia, density (air) = 0.076 lb/ft³ x 0.4536 kg/lb = 0.0345 kg/ft³

» Air required in SCFM = 0.848 kg/min + 0.0345 kg/ft³ = 24.602 SCFM

100% excess oxygen, » 24.6 SCFM x 2 = **49.20 SCFM**

20% excess oxygen, » 24.6 SCFM x 1.2 = **29.52 SCFM**

Products

Name	MW_ratio					net	<u>dye/day</u>			<u>Product/day (kg/d)</u>
	18.0%	3.5%	4.7%	9.4%	32.9%					
CO2	1.543	0.522	3.339	3.249	2.952	1.73	x	189.3	=	327.32 kg/d
* N2	3.642	0	8.722	8.577	8.119	4.54	x	189.3	=	859.82 kg/d
H2O	0.579	0	0.342	0.391	0.453	0.31	x	189.3	=	57.94 kg/d
- KCl(31.5%)	-	-	-	-	-	0.19	x	189.3	=	36.27 kg/d
O2(31.5%)	-	-	-	-	-	0.12	x	189.3	=	23.35 kg/d
MgO(3.5%)	-	-	-	-	-	0.02	x	189.3	=	3.17 kg/d

CS

100% CS

C₁₀H₅ClN₂ MW(Molecular Weight) = 188.62

C₁₀H₅ClN₂ + 11 O₂ + 41 N₂ --> 10 CO₂ + 2 H₂O + 42 N₂ + HCl

Chemical Composition Calculation for CS

This calculation estimates the amount of oxygen required to decompose the organic components of CS and the products generated from the oxidation. The calculation is based on 1000 gal/day of chemical waste stream at 5% concentration and 20 hours per day of operation.

Name	wt %	composition							MW
		C	H	N	Na	O	Cl	Ca	
CS	100	10	5	2	0	0	1	0	188.61775
Air	100	0	0	82	0	22	0	0	1500.5362
CO2	100	10	0	0	0	20	0	0	440.0995
N2	100	0	0	84	0	0	0	0	1176.5628
H2O	100	0	4	0	0	2	0	0	36.03068
HCl	100	0	1	0	0	0	1	0	36.46097

Oxygen Requirement

$$\text{Weight ratio: } \text{MW (air)/MW(cs)} = 7.9554347$$

$$\text{Density of waste stream (assume water)} = 1 \text{ kg/lit}$$

$$\text{Waste stream per day} = 1000 \text{ g/d} \times 3.79 \text{ l/g} = 3785.4 \text{ l/d} \times 1 \text{ kg/l} = 3785.4 \text{ kg/d}$$

$$5\% \text{ of cs} = 3785.4 \text{ kg/d} \times 0.05 = 189.27 \text{ kg/d}$$

$$\text{Air required per day} = 189.27 \times \text{MW(air)/MW(cs)} = 1505.73 \text{ kg/d}$$

$$\text{The system is operated at 20 hr/day: } = 1505.7251 \div (20 \times 60) \text{ min/d} = 1.25477 \text{ kg/min}$$

$$\text{at 60 °F and 14.7 psia, density (air)} = 0.0763 \text{ lb/ft}^3 \times 0.45 \text{ kg/lb} = 0.03461 \text{ kg/ft}^3$$

$$\text{Air required in SCFM} = 1.2547709 \text{ kg/min} \div 0.03 \text{ kg/ft}^3 = 36.2549 \text{ SCFM}$$

$$100\% \text{ allowance for oxygen, } = 36.254913 \text{ SCFM} \times 2 = \boxed{72.51 \text{ SCFM}}$$

$$20\% \text{ allowance for oxygen, } = 36.254913 \text{ SCFM} \times 1.2 = \boxed{43.51 \text{ SCFM}}$$

Products

Name	MW ratio		cs/day		Product/day (kg/d)
CO2	2.33	x	189	=	441.62139 kg/d
N2	6.24	x	189	=	1180.6314 kg/d
H2O	0.19	x	189	=	36.155276 kg/d
HCl	0.19	x	189	=	36.587054 kg/d

Orange Dye

100% Acid Orange 10

MW(Molecular Weight) = 452.37

Chemical Composition Calculation for Orange Dye

This calculation estimates the amount of oxygen required to decompose the organic components of orange dye and the products generated from the oxidation. The calculation is based on 1000 gal/day of chemical waste stream at 5% concentration and 20 hours per day of operation.

Name	wt %	composition							MW
		C	H	N	Na	O	S	Ca	
Acid Orange 10	100	16	10	2	2	7	2	0	452.3749
Air	100	0	0	138	0	37	0	0	2524.9024
NaOH	100	0	2	0	2	2	0	0	79.99434
CO2	100	16	0	0	0	32	0	0	704.1592
N2	100	0	0	140	0	0	0	0	1960.938
H2O	100	0	12	0	0	6	0	0	108.09204
Na2SO4	100	0	0	0	4	8	2	0	284.0824

Oxygen Requirement

Weight ratio: $\text{MW (air)}/\text{MW(dye)} = 5.5814379$

Density of waste stream (assume water) = 1 kg/lit

Waste stream per day » 1000 g/d x 3.79 l/g = 3785.4 l/d x 1 kg/l = 3785.4 kg/d

5% of dye = 3785.4 kg/d x 0.05 = 189.27 kg/d

Air required per day = 189.27 x MW(air)/MW(dye) = 1056.4 kg/d

The system is operated at 20 hr/day: » 1056.3987 + (20 x 60) min/d = 0.88033 kg/min

at 60 °F and 14.7 psia, density (air) = 0.0763 lb/ft³ x 0.45 kg/lb = 0.03461 kg/ft³

Air required in SCFM = 0.8803323 kg/min + 0.03 kg/ft³ = 25.436 SCFM

100% allowance for oxygen, » 25.436014 SCFM x 2 = **50.87 SCFM**

20% allowance for oxygen, » 25.436014 SCFM x 1.2 = **30.52 SCFM**

NaOH Requirement

Weight ratio: $\text{MW (NaOH)}/\text{MW(dye)} = 0.176832$

NaOH per day = Dye/day x MW (NaOH/dye) = 189.27 kg/d x weight ratio = 33.469 kg/d

Products

Name	MW ratio		dye/day		Product/day (kg/d)
CO2	1.56	x	189	=	294.61452 kg/d
N2	4.33	x	189	=	820.4406 kg/d
H2O	0.24	x	189	=	45.224835 kg/d
Na2SO4	0.63	x	189	=	118.85778 kg/d

Red Dye

80% Amido Naphthol Red G

20% Tartrazine

Chemical Composition Calculation for Red Dye

This calculation estimates the amount of oxygen required to decompose the organic components of red dye and the products generated from the oxidation. The calculation is based on 1000 gal/day of chemical waste stream at 5% concentration and 20 hours per day of operation.

Name	wt %	Composition							MW
		C	H	N	Na	O	S	Ca	
Amido Naphthol	80	18	13	3	2	8	2	0	509.43
Tartrazine	20	16	9	4	3	9	2	0	534.37
Air (80%)	80	0	0	154	0	41.5	0	0	2821
Air (20%)	20	0	0	130	0	35	0	0	2380.9
NaOH (80%)	80	0	2	0	2	2	0	0	79.994
NaOH (20%)	20	0	1	0	1	1	0	0	39.997
CO2(80%)	80	18	0	0	0	36	0	0	792.18
CO2(20%)	20	16	0	0	0	32	0	0	704.16
N2 (80%)	80	0	0	157	0	0	0	0	2199.1
N2 (20%)	20	0	0	134	0	0	0	0	1876.9
H2O (80%)	80	0	15	0	0	7.5	0	0	135.12
H2O (20%)	20	0	10	0	0	5	0	0	90.077
Na2SO4(80%)	80	0	0	0	4	8	2	0	284.08
Na2SO4(20%)	20	0	0	0	4	8	2	0	284.08

Oxygen Requirement

Weight ratio: $MW(\text{air})/MW(\text{dye})@80\% = 2821 + 509 = 5.5376$
 $MW(\text{air})/MW(\text{dye})@20\% = 2381 + 534 = 4.4554$
" $MW(\text{air})/MW(\text{dye}) \text{ (net)} = 5.3212$

Density of waste stream (assume water) = 1 kg/lit

Waste stream per day " 1000 g/d x 3.785 l/g = 3785.4 l/d x 1 kg/l = 3785.4 kg/d

5% of dye = 3785.4 kg/d x 0.05 = 189.27 kg/d

Air required per day = 189.27 x $MW(\text{air})/MW(\text{dye}) = 1007.1 \text{ kg/d}$

The system is operated 20 hr/day: " 1007.1 + (20 x 60) min/d = 0.8393 kg/min

at 60 °F and 14.7 psia, density (air) = 0.0763 lb/ft³ x 0.454 kg/lb = 0.0346 kg/ft³

" Air required in SCFM = 0.8393 kg/min + 0.035 kg/ft³ = 24.25 SCFM

100% allowance for oxygen, " 24.25 SCFM x 2 = **48.50 SCFM**

20% allowance for oxygen, " 24.25 SCFM x 1.2 = **29.10 SCFM**

NaOH Requirement

Weight ratio: $MW(\text{NaOH})/MW(\text{dye})@80\% = 79.99 + 509 = 0.157$
 $MW(\text{NaOH})/MW(\text{dye})@20\% = 40 + 534 = 0.0748$
" $MW(\text{NaOH})/MW(\text{dye}) \text{ (net)} = 0.1406$

NaOH per day = Dye/day x MW (NaOH/dye) = 189.27 kg/d x weight ratio = 26.61 kg/d

Products

Name	MW ratio		net		dye/day		Product/day (kg/d)
	80%	20%					
CO2	1.555	1.318	1.508	x	189	=	285.34 kg/d
N2	4.317	3.512	4.156	x	189	=	786.58 kg/d
H2O	0.265	0.169	0.246	x	189	=	46.54 kg/d
Na2SO4	0.558	0.532	0.552	x	189	=	104.56 kg/d

Green Dye (I)

80% Tartrazine

$\text{C}_{16}\text{H}_9\text{N}_4\text{Na}_3\text{O}_9\text{S}_2$ MW(Molecular Weight) = 534.37

20% Alphazurine 2G

$\text{C}_{27}\text{H}_{31}\text{N}_2\text{NaO}_6\text{S}_2$ MW(Molecular Weight) = 566.68

Chemical Composition Calculation for Green Dye - Type I

This calculation estimates the amount of oxygen required to decompose the organic components of green dye (type I) and the products generated from the oxidation. The calculation is based on 1000 gal/day of chemical waste stream at 5% concentration and 20 hours per day of operation.

Name	wt %	Composition							MW
		C	H	N	Na	O	S	Ca	
Tartrazine	80	16	9	4	3	9	2	0	534.37
Alphazurine	20	27	31	2	1	6	2	0	566.68
Air (80%)	80	0	0	130	0	35	0	0	2380.9
Air (20%)	20	0	0	260	0	70	0	0	4761.7
NaOH (80%)	80	0	1	0	1	1	0	0	39.997
NaOH (20%)	20	0	3	0	3	3	0	0	119.99
CO2(80%)	80	16	0	0	0	32	0	0	704.16
CO2(20%)	20	27	0	0	0	54	0	0	1188.3
N2 (80%)	80	0	0	134	0	0	0	0	1876.9
N2 (20%)	20	0	0	262	0	0	0	0	3669.8
H2O (80%)	80	0	10	0	0	5	0	0	90.077
H2O (20%)	20	0	34	0	0	17	0	0	306.26
Na2SO4(80%)	80	0	0	0	4	8	2	0	284.08
Na2SO4(20%)	20	0	0	0	4	8	2	0	284.08

Oxygen Requirement

Weight ratio: $MW(\text{air})/MW(\text{dye})@80\% = 2381 + 534 = 4.4554$
 $MW(\text{air})/MW(\text{dye})@20\% = 4762 + 567 = 8.4029$
" $MW(\text{air})/MW(\text{dye}) \text{ (net)} = 5.2449$

Density of waste stream (assume water) = 1 kg/lit

Waste stream per day " 1000 g/d x 3.785 l/g = 3785.4 l/d x 1 kg/l = 3785.4 kg/d

5% of dye = 3785.4 kg/d x 0.05 = 189.27 kg/d

Air required per day = 189.27 x $MW(\text{air})/MW(\text{dye}) = 992.71 \text{ kg/d}$

The system is operated 20 hr/day: " 992.71 + (20 x 60) min/d = 0.8273 kg/min

at 60 °F and 14.7 psia, density (air) = 0.0763 lb/ft³ x 0.454 kg/lb = 0.0346 kg/ft³

" Air required in SCFM = 0.8273 kg/min + 0.035 kg/ft³ = 23.902 SCFM

100% allowance for oxygen, " 23.902 SCFM x 2 = **47.80 SCFM**

20% allowance for oxygen, " 23.902 SCFM x 1.2 = **28.68 SCFM**

NaOH Requirement

Weight ratio: $MW(\text{NaOH})/MW(\text{dye})@80\% = 40 + 534 = 0.0748$
 $MW(\text{NaOH})/MW(\text{dye})@20\% = 120 + 567 = 0.2117$
" $MW(\text{NaOH})/MW(\text{dye}) \text{ (net)} = 0.1022$

NaOH per day = Dye/day x MW (NaOH/dye) = 189.27 kg/d x weight ratio = 19.349 kg/d

Products

Name	MW ratio		net		dye/day		Product/day (kg/d)
	80%	20%					
CO2	1.318	2.097	1.474	x	189	=	278.90 kg/d
N2	3.512	6.476	4.105	x	189	=	776.97 kg/d
H2O	0.169	0.54	0.243	x	189	=	45.98 kg/d
Na2SO4	0.532	0.501	0.526	x	189	=	99.47 kg/d

Green Dye (II)

80% Tartrazine

20% Alphazurine 2G

Chemical Composition Calculation for Green Dye - Type II

This calculation estimates the amount of oxygen required to decompose the organic components of green dye (type II) and the products generate from the oxidation. The calculation is based on 1000 gal/day of chemical waste stream at 5% concentration and 20 hours per day of operation.

Name	wt %	Composition							MW
		C	H	N	Na	O	S	Ca	
Tartrazine	80	16	9	4	3	9	2	0	534.37
Alphazurine	20	54	82	4	0	24	4	1	1339.6
Air (80%)	80	0	0	130	0	35	0	0	2380.9
Air (20%)	20	0	0	512	0	138	0	0	9379.3
NaOH(80%)	80	0	1	0	1	1	0	0	39.997
NaOH(20%)	20	0	6	0	6	6	0	0	239.98
CO2(80%)	80	16	0	0	0	32	0	0	704.16
CO2(20%)	20	54	0	0	0	108	0	0	2376.5
N2 (80%)	80	0	0	134	0	0	0	0	1876.9
N2 (20%)	20	0	0	516	0	0	0	0	7227.5
H2O (80%)	80	0	10	0	0	5	0	0	90.077
H2O (20%)	20	0	88	0	0	44	0	0	792.67
Na2SO4(80%)	80	0	0	0	4	8	2	0	284.08
Na2SO4(20%)	20	0	0	0	6	12	3	0	426.12
CaSO4	20	0	0	0	0	4	1	1	136.14

Oxygen Requirement

Weight ratio: $MW(\text{air})/MW(\text{dye})@80\% = 2381 + 534 = 4.4554$
 $MW(\text{air})/MW(\text{dye})@20\% = 9379 + 1340 = 7.0016$
" $MW(\text{air})/MW(\text{dye}) \text{ (net)} = 4.9647$

Density of waste stream (assume water) = 1 kg/lit

Waste stream per day " 1000 g/d x 3.785 l/g = 3785.4 l/d x 1 kg/l = 3785.4 kg/d
5% of dye = 3785.4 kg/d x 0.05 = 189.27 kg/d
Air required per day = 189.27 x $MW(\text{air})/MW(\text{dye}) = 939.66 \text{ kg/d}$
The system is operated 20 hr/day: " 939.66 + (20 x 60) min/d = 0.7831 kg/min
at 60 °F and 14.7 psia, density (air) = 0.0763 lb/ft3 x 0.454 kg/lb = 0.0346 kg/ft3
" Air required in SCFM = 0.7831 kg/min + 0.035 kg/ft3 = 22.625 SCFM
100% allowance for oxygen, " 22.625 SCFM x 2 = **45.25 SCFM**
20% allowance for oxygen, " 22.625 SCFM x 1.2 = **27.15 SCFM**

NaOH Requirement

Weight ratio: $MW(\text{NaOH})/MW(\text{dye})@80\% = 40 + 534 = 0.0748$
 $MW(\text{NaOH})/MW(\text{dye})@20\% = 240 + 1340 = 0.1791$
" $MW(\text{NaOH})/MW(\text{dye}) \text{ (net)} = 0.0957$

NaOH per day = Dye/day x MW (NaOH/dye) = 189.27 kg/d x weight ratio = 18.115 kg/d

Products

Name	MW ratio		net		dye/day		Product/day (kg/d)
	80%	20%					
CO2	1.318	1.774	1.409	x	189	=	266.68 kg/d
N2	3.512	5.395	3.889	x	189	=	736.06 kg/d
H2O	0.169	0.592	0.253	x	189	=	47.92 kg/d
Na2SO4	0.532	0.318	0.489	x	189	=	92.54 kg/d
CaSO4		0.102	0.02	x	189	=	3.85 kg/d

Blue Dye (I)

30% Alphazurine B

$\text{C}_{27}\text{H}_{31}\text{N}_2\text{NaO}_6\text{S}_2$ MW(Molecular Weight) = 566.68

20% Acid Fast Violet

$\text{NaC}_{37}\text{H}_{36}\text{N}_3\text{O}_6\text{S}_2$ MW(Molecular Weight) = 705.83

50% Sugar

$\text{C}_{12}\text{H}_{22}\text{O}_{11}$ MW(Molecular Weight) = 342.30

Chemical Composition Calculation for Blue Dye - Type I

This calculation estimates the amount of oxygen required to decompose the organic components of blue dye (type I) and the products generated from the oxidation. The calculation is based on 1000 gal/day of chemical waste stream at 5% concentration and 20 hours per day of operation.

Name	wt %	Composition							MW
		C	H	N	Na	O	S	Ca	
Alphazurine B	30	27	31	2	1	6	2	0	566.68
Acid Fast Violet	20	37	36	3	1	6	2	0	705.83
Sugar	50	12	22	0	0	11	0	0	342.3
Air (30%)	30	0	0	260	0	70	0	0	4761.7
Air (20%)	20	0	0	344	0	92.5	0	0	6298.2
Air (50%)	50	0	0	89	0	24	0	0	1630.6
NaOH (30%)	30	0	3	0	3	3	0	0	119.99
NaOH (20%)	20	0	3	0	3	3	0	0	119.99
CO2(30%)	30	27	0	0	0	54	0	0	1188.3
CO2(20%)	20	37	0	0	0	74	0	0	1628.4
CO2(50%)	50	12	0	0	0	24	0	0	528.12
N2 (30%)	30	0	0	262	0	0	0	0	3669.8
N2 (20%)	20	0	0	347	0	0	0	0	4860.3
N2 (50%)	50	0	0	89	0	0	0	0	1246.6
H2O (30%)	30	0	34	0	0	17	0	0	306.26
H2O (20%)	20	0	39	0	0	19.5	0	0	351.3
H2O (50%)	50	0	22	0	0	11	0	0	198.17
Na2SO4(30%)	30	0	0	0	4	8	2	0	284.08
Na2SO4(20%)	20	0	0	0	4	8	2	0	284.08

Oxygen Requirement

Weight ratio:	MW(air)/MW(dye)@30%	=	4762	+	567	=	8.4029
	MW(air)/MW(dye)@20%	=	6298	+	706	=	8.9231
	MW(air)/MW(dye)@50%	=	1631	+	342	=	4.7636
	” MW(air)/MW(dye) (net)					=	6.6873

Density of waste stream (assume water) = 1 kg/lit

$$\text{Waste stream per day} \quad " \quad 1000 \quad \text{g/d} \quad \times \quad 3.785 \quad \text{l/g} \quad = \quad 3785.4 \quad \text{l/d} \quad \times \quad 1 \quad \text{kg/l} \quad = \quad 3785.4 \quad \text{kg/d}$$

$$5\% \text{ of dye} = 3785,4 \text{ kg/d} \times 0.05 = 189.27 \text{ kg/d}$$

$$\text{Air required per day} = 189.27 \times \text{MW}(\text{air})/\text{MW}(\text{dye}) = 1265.7 \text{ kg/d}$$

The system is operated 20 hr/day: " 1265.7 + (20 x 60) min/d = 1.0547 kg/min

$$\text{at } 60^\circ\text{F and } 14.7 \text{ psia, density (air) } = 0.0763 \text{ lb/ft}^3 \times 0.454 \text{ kg/lb} = 0.0346 \text{ kg/ft}^3$$

$$\text{Air required in SCFM} = 1.0547 \text{ kg/min} + 0.035 \text{ kg/ft}^3 = 30.476 \text{ SCFM}$$

100% allowance for oxygen,	»	30.476 SCFM	x	2	=	60.95 SCFM
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20%	allowance for oxygen,	"	30.476 SCFM	x	1.2	=	36.57 SCFM
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NaOH Requirement

Weight ratio:	MW(NaOH)/MW(dye)@30% =	120	+	567	=	0.2117
	MW(NaOH)/MW(dye)@20% =	120	+	706	=	0.17
	” MW(NaOH)/MW(dye) (net)				=	0.0975

$$\text{NaOH per day} = \text{Dye/day} \times \text{MW (NaOH/dye)} = 189.27 \text{ kg/d} \times \text{weight ratio} = 18.458 \text{ kg/d}$$

Products

Name	MW ratio					dye/day		Product/day (kg/d)
	30%	20%	50%	net				
CO2	2.097	2.307	1.543	1.862	x	189	=	352.40 kg/d
N2	6.476	6.886	3.642	5.141	x	189	=	973.01 kg/d
H2O	0.54	0.498	0.579	0.551	x	189	=	104.31 kg/d
Na2SO4	0.501	0.402	0	0.231	x	189	=	43.70 kg/d

Blue Dye (II)

30% Alphazurine 2G

20% Acid Fast Violet

50% Sugar

Chemical Composition Calculation for Blue Dye - Type II

This calculation estimates the amount of oxygen required to decompose the organic components of blue dye (type II) and the products generated from the oxidation. The calculation is based on 1000 gal/day of chemical waste stream at 5% concentration and 20 hours per day of operation.

Name	wt %	Composition							MW
		C	H	N	Na	O	S	Ca	
Alphazurine B	30	54	82	4	0	24	4	1	1339.6
Acid Fast Violet	20	37	36	3	1	6	2	0	705.83
Sugar	50	12	22	0	0	11	0	0	342.3
Air (30%)	30	0	0	512	0	138	0	0	9379.3
Air (20%)	20	0	0	344	0	92.5	0	0	6298.2
Air (50%)	50	0	0	89	0	24	0	0	1630.6
NaOH (30%)	30	0	6	0	6	6	0	0	239.98
NaOH (20%)	20	0	3	0	3	3	0	0	119.99
CO2(30%)	30	54	0	0	0	108	0	0	2376.5
CO2(20%)	20	37	0	0	0	74	0	0	1628.4
CO2(50%)	50	12	0	0	0	24	0	0	528.12
N2 (30%)	30	0	0	516	0	0	0	0	7227.5
N2 (20%)	20	0	0	347	0	0	0	0	4860.3
N2 (50%)	50	0	0	89	0	0	0	0	1246.6
H2O (30%)	30	0	88	0	0	44	0	0	792.67
H2O (20%)	20	0	39	0	0	19.5	0	0	351.3
H2O (50%)	50	0	22	0	0	11	0	0	198.17
Na2SO4(30%)	30	0	0	0	6	12	3	0	426.12
Na2SO4(20%)	20	0	0	0	4	8	2	0	284.08
CaSO4	30	0	0	0	0	4	1	1	136.14

Oxygen Requirement

Weight ratio: $MW(\text{air})/MW(\text{dye})@30\% = 9379 + 1340 = 7.0016$
 $MW(\text{air})/MW(\text{dye})@20\% = 6298 + 706 = 8.9231$
 $MW(\text{air})/MW(\text{dye})@50\% = 1631 + 342 = 4.7636$ " $MW(\text{air})/MW(\text{dye}) (\text{net}) = 6.2669$

Density of waste stream (assume water) = 1 kg/lit

Waste stream per day " 1000 g/d x 3.785 l/g = 3785.4 l/d x 1 kg/l = 3785.4 kg/d

5% of dye = 3785.4 kg/d x 0.05 = 189.27 kg/d

Air required per day = 189.27 x $MW(\text{air})/MW(\text{dye}) = 1186.1 \text{ kg/d}$

The system is operated 20 hr/day. " 1186.1 + (20 x 60) min/d = 0.9884 kg/min

at 60 °F and 14.7 psia, density (air) = 0.0763 lb/ft³ x 0.454 kg/lb = 0.0346 kg/ft³

" Air required in SCFM = 0.9884 kg/min + 0.035 kg/ft³ = 28.56 SCFM

100% allowance for oxygen, " 28.56 SCFM x 2 = **57.12 SCFM**

20% allowance for oxygen, " 28.56 SCFM x 1.2 = **34.27 SCFM**

NaOH Requirement

Weight ratio: $MW(\text{NaOH})/MW(\text{dye})@30\% = 240 + 1340 = 0.1791$
 $MW(\text{NaOH})/MW(\text{dye})@20\% = 120 + 706 = 0.17$
" $MW(\text{NaOH})/MW(\text{dye}) (\text{net}) = 0.0877$

NaOH per day = Dye/day x $MW(\text{NaOH}/\text{dye}) = 189.27 \text{ kg/d} \times \text{weight ratio} = 16.607 \text{ kg/d}$

Products

Name	MW ratio				dye/day		Product/day (kg/d)
	30%	20%	50%	net			
CO2	1.774	2.307	1.543	1.765	x	189	= 334.07 kg/d
N2	5.395	6.886	3.642	4.817	x	189	= 911.65 kg/d
H2O	0.592	0.498	0.579	0.567	x	189	= 107.23 kg/d
Na2SO4	0.318	0.402	0	0.176	x	189	= 33.30 kg/d
CaSO4	0.102	0	0	0.03	x	189	= 5.77 kg/d

C S

100% C S

C₁₀H₅ClN₂ MW(Molecular Weight) = 188.62

Chemical Composition Calculation for CS

This calculation estimates the amount of oxygen required to decompose the organic components of CS and the products generated from the oxidation. The calculation is based on 1000 gal/day of chemical waste stream at 5% concentration and 20 hours per day of operation.

Name	wt %	composition								MW
CS	100	10	5	2	0	0	1	0	0	188.61775
Air	100	0	0	82	0	22	0	0	0	1500.5362
NaOH	100	0	1	0	1	1	0	0	0	39.99717
CO2	100	10	0	0	0	20	0	0	0	440.0995
N2	100	0	0	84	0	0	0	0	0	1176.5628
H2O	100	0	6	0	0	3	0	0	0	54.04602
NaCl	100	0	0	0	1	0	1	0	0	58.4428

Oxygen Requirement

$$\text{Weight ratio:} \quad \text{MW (air)/MW(cs)} = 7.9554347$$

$$\text{Density of waste stream (assume water)} = 1 \text{ kg/lit}$$

$$\text{Waste stream per day} = 1000 \text{ g/d} \times 3.79 \text{ l/g} = 3785.4 \text{ l/d} \times 1 \text{ kg/l} = 3785.4 \text{ kg/d}$$

$$5\% \text{ of cs} = 3785.4 \text{ kg/d} \times 0.05 = 189.27 \text{ kg/d}$$

$$\text{Air required per day} = 189.27 \times \text{MW(air)/MW(cs)} = 1505.73 \text{ kg/d}$$

$$\text{The system is operated at 20 hr/day:} = 1505.7251 \div (20 \times 60) \text{ min/d} = 1.25477 \text{ kg/min}$$

$$\text{at 60 °F and 14.7 psia, density (air)} = 0.0763 \text{ lb/ft}^3 \times 0.45 \text{ kg/lb} = 0.03461 \text{ kg/ft}^3$$

$$\text{Air required in SCFM} = 1.2547709 \text{ kg/min} \div 0.03 \text{ kg/ft}^3 = 36.2549 \text{ SCFM}$$

$$100\% \text{ allowance for oxygen,} = 36.254913 \text{ SCFM} \times 2 = \boxed{72.51 \text{ SCFM}}$$

$$20\% \text{ allowance for oxygen,} = 36.254913 \text{ SCFM} \times 1.2 = \boxed{43.51 \text{ SCFM}}$$

NaOH Requirement

$$\text{Weight ratio:} \quad \text{MW (NaOH)/MW(cs)} = 0.2120541$$

$$\text{NaOH per day} = \text{cs/day} \times \text{MW (NaOH/cs)} = 189.27 \text{ kg/d} \times \text{weight ratio} = 40.1355 \text{ kg/d}$$

Products

Name	MW ratio		cs/day		Product/day (kg/d)
CO2	2.33	x	189	=	441.62139 kg/d
N2	6.24	x	189	=	1180.6314 kg/d
H2O	0.29	x	189	=	54.232914 kg/d
NaCl	0.31	x	189	=	58.644898 kg/d

Appendix B. Cost Estimate Breakdown

The cost of all components is recorded for the tubular configuration. For the vessel configuration, the cost of the reactor/salt separation/letdown subsystem, is approximately the same within the uncertainty of the estimates. As discussed in the body of the report, the actual quotations have been multiplied by 1.2 to account for an expected increase due to time and detail.

MIX & FEED SUBSYSTEM				
DESCRIPTION	QTY	COST EA.	NOTES	LINE TOTAL
PUMP - NAOH	1	2400	PERISTALTIC WITH DIGITAL BATCH CTL	2400
PUMP - MIX	1	2000	PERISTALTIC VARIABLE WITH CONTROL	2000
PUMP - FEED	1	1800	CENTRIFUGAL SEALESS MAG.DRIVE	1800
PUMP - WATER	1	1800	CENTRIFUGAL SEALESS MAG.DRIVE	1800
PUMP - H.P. LIQUID HPLP	1	22,500	HP DIAPHRAGM METERING PUMP, 50GAL/HR	22,500
STROKE CONTROL	1	3600	JORDAN ELECTRIC STROKE ACTUATOR	3600
PULSATION DAMPER	1	3600	INLINE DAMPER	3600
TANK - NAOH (55 GAL)	1	600	GRAD., PP, WITH FLOOR STAND	600
TANK - MIX (500 GAL)	1	2700	GRAD., H.D. P.E., CL. TOP, WITH EL. STAND	2700
TANK - FEED (1000 GAL)	1	4400	GRAD., H.D. P.E., CL. TOP, WITH EL. STAND	4400
TANK - WATER (1000 GAL)	1	1900	GRAD., H.D. P.E., FLAT BOTTOM, NO STAND	1900
WASTE FEED	1	6,000	SCREW	6,000
MIXER - MIX TANK	1	1700	1/3 HP GEAR DRIVE FIXED MOUNT	1700
MIXER - FEED TANK	1	2300	3/4 HP GEAR DRIVE FIXED MOUNT	2300
AIR OP VALVE AV	2	700	H.P. TAPER SEAL, NC PISTON ACT. & SV	1400
AIR OP VALVE AV	3	600	1/2" NPT SS BALL, NC ACT. & SV	1800
AIR OP VALVE AV	5	500	1/4" NPT SS BALL, NC ACT. & SV	2500
HAND VALVE HV	7	200	1/2" NPT SS BALL HAND	1400
VALVE - PROPORTION PV	2	1700	CONTROL VALVE WITH AIR POSITIONER	3400
CHECK VALVE CV	3	200	H.P. BALL CHECK	600
RUPTURE DISC RD	1	300	STRAIGHT SAFETY HEAD BODY	300
FLOW METER FM	1	1400	TURBINE	1400
LIQUID LEVEL INDICATOR LLI	2	600	MIX & FEED	1200
LIQUID LEVEL INDICATOR LLI	1	400	WATER	400
LIQUID LEVEL INDICATOR LLI	1	400	DRUM	400
PRESSURE TRANSDUCER PT	1	1200	O-7500 PSI	1200
OPT. MIX INDICATOR	1	12,000		12,000
PH MONITOR PH	1	600		600
TUBING		5,000		5,000
MISC FITTINGS		1600		1600
SUBSYSTEM TOTAL				92,500

AIR COMPRESSOR SUBSYSTEM					
DESCRIPTION		QTY	COST EA.	NOTES	LINE TOTAL
COMPRESSOR - AIR		1	79,000	H.P. RECIP. PISTON, 5000PSI, 78 SCFM	79,000
PRESSURE TANK - AIR		1	14,500	RACK, 8 ASME, 454 SCF EACH @ 5KSI	14,500
AIR OP VALVE	AV	3	700	H.P. TAPER SEAL, NC PISTON ACT. & SV	2100
VALVE - FLOW CONTROL	FCV	1	1900	CONTROL VALVE WITH AIR POSITIONER	1900
CHECK VALVE	CV	1	200	H.P. AIR, SOFT SEAT	200
RUPTURE DISC	RD	1	300	STRAIGHT SAFETY HEAD BODY	300
FLOW METER	FM	1	1500	TURBINE	1500
PRESSURE TRANSDUCER	PT	2	1200	O-7500 PSI	2400
TUBING			2000		2000
MISC. FITTINGS			600		600
				SUBSYSTEM TOTAL	104,500
H.P. WATER SUBSYSTEM					
PUMP - H.P. LIQUID	HPLP	1	12,000	HP DIAPHRAGM METERING PUMP, 25GAL/HR	12,000
STROKE CONTROL		1	3600	JORDAN ELECTRIC STROKE ACTUATOR	3600
AIR OP VALVE	AV	3	700	H.P. TAPER SEAL, NC PISTON ACT. & SV	2100
AIR OP VALVE	AV	1	600	1/2" NPT SS BALL, NC ACT. & SV	600
HAND VALVE	HV	1	200	1/2" NPT SS EALL HAND	200
CHECK VALVE	CV	1	200	H.P. BALL CHECK	200
RUPTURE DISC	RD	1	300	STRAIGHT SAFETY HEAD BODY	300
PRESSURE TRANSDUCER	PT	1	1200	O-7500 PSI	1200
FLOW METER	FM	1	1400	TURBINE	1400
TUBING			1000		1000
MISC. FITTINGS			500		500
				SUBSYSTEM TOTAL	23,100

REACTOR / SALT SEPARATION / LETDOWN SUBSYSTEM				
DESCRIPTION	QTY	COST EA.	NOTES	LINE TOTAL
TUBULAR - REACTOR WITH		180,000	INCONEL 625, 1.343 ID, 2.089 OD	180,000
(2) TUBULAR SALT SEPARATOR			3 SECTIONS, WITH 2 PARALLEL SALT	
WITH TRANSFORMER &			SECTIONS, ALL RESISTIVELY HEATED	
HEATER CONTROLS				
VESSEL - SALT LETDOWN	2	9,500	BOLTED CLOSURE VESSEL	19,000
TANK - BRINE (1000 GAL)	1	6,000	CONICAL BOTTOM	6,000
PUMP - BRINE	1	1400	PERISTALTIC FIXED OUTPUT	1400
AIR OP VALVE AV NO	2	700	H.P. TAPER SEAL, NO PISTON ACT. & SV	1400
AIR OP VALVE AV	2	700	H.P. TAPER SEAL, NC PISTON ACT. & SV	1400
AIR OP VALVE AV	4	10,000	H.P., HIGH TEMP., NC PISTON ACT. & SV	40,000
AIR OP VALVE AV	2	600	1/2" NPT SS BALL, NC ACT. & SV	1200
AIR OP VALVE AV	1	500	1/4" NPT SS BALL, NC ACT. & SV	500
VALVE - FLOW CONTROL FCV	2	3200	CONTROL VALVE WITH AIR POSITIONER	6400
VALVE - FLOW CONTROL FCV	1	10,000	H.P., H.T. LET DOWN VALVE WITH AIR ACT	10,000
PRESSURE REGULATOR	2	1200	WITH AIR ACTUATOR POSITIONER	2400
BACKPRESSURE REGULATOR	2	1800	WITH AIR ACTUATOR POSITIONER	3600
RUPTURE DISC RD	2	300	STRAIGHT SAFETY HEAD BODY	600
FILTER	1	300		300
FLOW METER FM	1	1800	TURBINE	1800
LIQUID LEVEL INDICATOR LLI	1	600	BRINE TANK	600
PRESSURE TRANSDUCER PT	6	1600	O-7500 PSI @ HIGH TEMP.	9600
DIFFERENTIAL PRESSURE DPT	2	2200		4400
THERMOCOUPLE TC	11	400	H.P.	4400
TUBING		10,000		10,000
MISC. FITTINGS		3000		3000
			SUBSYSTEM TOTAL	308,000

LIQUID / GAS / SOLID SEPARATION SUBSYSTEM					
DESCRIPTION		QTY	COST EA.	NOTES	LINE TOTAL
HEAT EXCHANGER	HX	1	20,400	316 SHELL INCONEL 625 TUBE	20,400
COOLING RECIRCULATION		1	18,000		18,000
VESSEL - LIQUID/GAS/SOLIDS 1		1	18,000	316 BOLTED CLOSURE	18,000
VESSEL - LIQUID/GAS/SOLIDS 2		1	12,000	316 BOLTED CLOSURE	12,000
VESSEL - EMERGENCY VENT		1	14,200	500 GAL SS LOW PRESSURE	14,200
TANK - EFFLUENT(1000 GAL)		1	4400	GRAD., H.D. P.E., WITH EL. STAND	4400
PUMP - RECIRCULATION		1	1800	CENTRIFUGAL SEALESS MAG.DRIVE	1800
AIR OP VALVE	AV NO	2	700	H.P. TAPER SEAL, NO PISTON ACT. & SV	1400
AIR OP VALVE	AV	6	700	H.P. TAPER SEAL, NC PISTON ACT. & SV	4200
AIR OP VALVE	AV	2	600	1/2" NPT SS BALL, NC ACT. & SV	1200
AIR OP VALVE	AV	5	500	1/4" NPT SS BALL, NC ACT. & SV	2500
HAND VALVE	HV	1	200	1/2" NPT SS BALL HAND	200
VALVE - FLOW CONTROL	LDV	1	2100	L.P. LIQUID, LET DOWN VALVE, AIR ACT	2100
VALVE - FLOW CONTROL	LDV	1	5000	H.P. LIQUID, LET DOWN VALVE, AIR ACT	5000
VALVE - FLOW CONTROL	FCV	1	5000	H.P. GAS, LET DOWN VALVE WITH AIR ACT	5000
CHECK VALVE	CV	1	200	H.P. BALL CHECK	200
BACKPRESSURE REGULATOR		1	1800	WITH AIR ACTUATOR POSITIONER	1800
RUPTURE DISC	RD	1	300	STRAIGHT SAFETY HEAD BODY	300
FILTER		3	300		900
LIQUID ANALYZER TOC		1	48,000		48,000
GAS ANALYZER GC		1	60,000		60,000
PRESSURE TRANSDUCER	PT	1	1200	O-7500 PSI	1200
DIFFERENTIAL PRESSURE	DPT	1	2200		2200
LIQUID LEVEL INDICATOR	LLI	2	600	EFFLUENT	1200
THERMOCOUPLE	TC	1	400	H.P.	400
TUBING			3600		3600
MISC. FITTINGS			1200		1200
SUBSYSTEM TOTAL					231,400

Appendix C. Heat Transfer Calculations

This appendix contains the thermodynamic and heat transfer calculations for the supercritical oxidation prototype reactor (tubular configuration). The reactor thickness is first calculated. The total energy required to raise the fluid mixture from 20 °C to 550 °C is determined. Then, the heat flux at the ends of each section is calculated; the maximum heat flux for each section is also determined. Finally, the length of the reactor is determined by dividing the total energy required for each section by the product of heat flux and internal circumference; in addition, the length required for a 15 second residence time is included.

Results are presented for fluid and wall temperature, heat flux, and other heat transfer variables, along the reactor. Total heat lost from the reactor is also estimate at the end of this section.

Design Criteria

For calculation purposes, the tubular reactor is divided into three sections: a 20 °C to 200 °C section, a 200 °C to 425 °C section, and a 425 °C to 550 °C section. Section 3 also contains an insulated section for a residence time of 15 seconds. The configuration of the tubular reactor is shown below.

All calculations are for a water flow rate of 1000 gal/day with a 5 wt % chemical waste concentration. The material of the tubular reactor is Inconel 625 and the maximum allowable working pressure and temperature are 5000 psi and 625 °C, respectively.

I. Reactor Thickness

The inner diameter of the tubular reactor (concept A) is 1.343 in. Using a maximum allowable working pressure of 5000 psi at 625 °C wall temperature, and Inconel 625, the maximum allowable stress is 21 ksi (Ref, ASME Section VIII, Div I, ANSI Table UNF 23.3, P 368).

The minimum required thickness of the tube is calculated as follows,

$$t = \frac{PR_i}{SE - 0.6P} \quad (\text{Ref, ASME, ANSI UG-27, P.24})$$

where P = maximum allowable working pressure, ksi
 R_i = internal radius, in, = $1.342/2 = 0.672$ in
 S = maximum allowable stress, ksi
 E = joint efficiency

$$t = \frac{(5 \text{ ksi}) (0.672 \text{ in})}{(21 \text{ ksi}) (0.65) - 0.6(5 \text{ ksi})}$$

$$t = 0.315 \text{ in}$$

The outer diameter of the tube is then:

$$D_o = 1.343 + 2(0.315) = 1.973 \text{ in}$$

II. Total Energy Required

The energy required for each section is calculated as follows:

$$Q = \dot{m} (H_o - H_i)$$

where Q = Heat required, kW
 $\dot{m}$ = Mass flow rate, kg/s
 H_o = Enthalpy at outlet, kJ/kg
 H_i = Enthalpy at inlet, kJ/kg

Since the process fluid is a mixture of water and air, weighted thermodynamic and transport properties are calculated based on mass flow ratios.

Weighted heat transfer properties:

$$X_n = \frac{\dot{m}_{air}}{\dot{m}_{total}} X_{na} + \frac{\dot{m}_{water}}{\dot{m}_{total}} X_{nw}$$

where $\dot{m}_w$ = mass flow rate of water
 $\dot{m}_a$ = mass flow rate of air
 $\dot{m}_w$ = total mass flow rate

The X_n is a fluid mechanic property,

H enthalpy
h heat transfer coefficient
k thermal conductivity
 μ viscosity of the fluid
 ρ density of the fluid
 c_p specific heat

From process flow calculations, the mass flow rates of water and air for the CS agent (which has the highest oxidant requirement among the wastes to be treated) are 1000 gal/day and 36.25 scfm respectively, or

$$\dot{m}_w = 0.0526 \text{ kg/s}$$

$$\dot{m}_a = 0.0209 \text{ kg/s}$$

$$\dot{m}_t = \dot{m}_w + \dot{m}_a = 0.0526 \text{ Kg/s} + 0.0209 \text{ kg/s} = 0.0735 \text{ kg/s}$$

Let,

$$\phi_w = \frac{\dot{m}_w}{\dot{m}_t}$$

$$\phi_a = \frac{\dot{m}_a}{\dot{m}_t}$$

$$\phi_w = (0.0526) \div (0.0735) = 0.716$$

$$\phi_a = (0.0209) \div (0.0735) = 0.284$$

The thermodynamic and transport properties of water in this calculation are obtained from an in-house computer program:

T = 20°C (293°K)	$H_w = 110.184 \text{ kJ/kg}$
T = 200°C (473°K)	$H_w = 864.362 \text{ kJ/kg}$
T = 425°C (698°K)	$H_w = 2682.317 \text{ kJ/kg}$
T = 550°C (823°K)	$H_w = 3296.496 \text{ kJ/kg}$

For air, the enthalpy in kJ/kg is (Ref: Thermodynamic Properties in SI, W. C. Reynolds, P.9),

P(MPa)	Temp (K)					
	300	400	500	700	800	900
20	425.39	554.95	657.23	878.29	990.07	1103.34
30	417.41	541.77	657.3	882.29	995.34	1109.58

By linear interpolation,

P(MPa)	Temperature (K)			
	300	473	700	823
20	425.39	629.61	878.29	1016.12
30	417.41	626.11	882.29	1021.62

At $P = 28.37$ MPa (280 atm), the enthalpy of air is:

$T = 300^\circ\text{K}$ ($\sim 293^\circ\text{K}$)	$H_a = 418.71$ kJ/kg
$T = 473^\circ\text{K}$	$H_a = 626.68$ kJ/kg
$T = 700^\circ\text{K}$ ($\sim 698^\circ\text{K}$)	$H_a = 881.64$ kJ/kg
$T = 823^\circ\text{K}$	$H_a = 1020.72$ kJ/kg

The enthalpy of the process fluid is then:

$$H_t = \phi_w H_w + \phi_a H_a$$

$$\begin{aligned} H_{20} &= (0.716) H_{20w} + (0.284) H_{20a} \\ &= (0.716)(110.184 \text{ kJ/kg}) + (0.284)(418.71 \text{ kJ/kg}) \\ &= 197.81 \text{ kJ/kg} \end{aligned}$$

$$\begin{aligned} H_{200} &= (0.716)(864.362 \text{ kJ/kg}) + (0.284)(626.68 \text{ kJ/kg}) \\ &= 796.86 \text{ kJ/kg} \end{aligned}$$

$$\begin{aligned} H_{425} &= (0.716)(2682.317 \text{ kJ/kg}) + (0.284)(881.64 \text{ kJ/kg}) \\ &= 2170.29 \text{ kJ/kg} \end{aligned}$$

$$\begin{aligned} H_{550} &= (0.716)(3296.496 \text{ kJ/kg}) + (0.284)(1020.72 \text{ kJ/kg}) \\ &= 2650.18 \text{ kJ/kg} \end{aligned}$$

The heat required in kW for each section is finally:

$$Q_1 = \dot{m}_t (H_{200} - H_{20})$$

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$$Q_1 = (0.0735 \text{ kg/s}) (796.86 - 197.81) \text{ kJ/kg}$$

$$Q_1 = 44.03 \text{ kW}$$

$$Q_2 = (0.0735 \text{ kg/s}) (2170.29 - 796.86) \text{ kJ/kg}$$

$$Q_2 = 100.95 \text{ kW}$$

$$Q_3 = (0.0735 \text{ kg/s}) (2650.18 - 2170.29) \text{ kJ/kg}$$

$$Q_3 = 35.27 \text{ kW}$$

$$Q_T = Q_1 + Q_2 + Q_3$$

$$= 44.03 + 100.95 + 35.27$$

$$Q_T = 180.25 \text{ kW}$$

II. Heat Flux

To determine heat flux for each section:

$$q'' = h \Delta T$$

where q'' = heat flux, kW/m²
 h = heat transfer coefficient, kW/m² °C
 ΔT = temperature between the wall and fluid

Note: the heat flux is limited by the maximum wall temperature of the tube.

$$h = \frac{Nu \cdot k}{D}$$

where Nu = Nusselt number, f(Re, Pr)
 k = thermal conductivity, kW/m °C
 D = pipe diameter, meter

$$Nu = 0.023 Re^{0.8} Pr^{0.33} \text{ (Ref : Engineering Thermodynamics by W. C. Reynolds)}$$

where Re = Reynolds number
 Pr = Prandtl number

The Reynolds and Prandtl number are given by:

$$Re = \frac{VD\rho}{\mu}$$

where V = velocity, m/s

ρ = density of the fluid, kg/m³
 μ = viscosity of the fluid, kg/m-s

Since $\dot{m} = \rho A V$, where A is the cross-sectional area of the pipe

$$\rho = \frac{\dot{m}}{A V}$$

$$\begin{aligned}
 Re &= \frac{V D \dot{m}}{A V \mu} \\
 &= \frac{4 D \dot{m}}{\pi D^2 \mu} \\
 &= \frac{4 \dot{m}}{\pi D \mu}
 \end{aligned}$$

$$D = 1.343 \text{ in} \times 0.0254 \text{ m/in} = 0.0341 \text{ m}$$

For water at 280 atm:

Temperature (°C)	Viscosity 10 ⁷ (kg/m-s)	Specific Heat (kJ/kg)	Thermal conductivity (W/m-°C)
20	9926.4	4.104	0.611
200	1408.0	4.357	0.686 ;
425	304.3	9.276	0.118
550	330.8	3.426	0.105

For air, the viscosity in 10⁷ kg/m-s is (Ref: Handbook of Physical Properties of Liquids and Gases P.627):

P(Bar)	Temp (K)						
	290	300	450	500	700	800	850
250	256.0	256.0	286.3	300.5	358	386	399.3
300	277.0	275.5	295.6	308.4	362	389.9	402.9
280	268.6	267.7	291.88	305.24	360.4	388.3	401.5

By linear interpolation,

At 280 bar (~280 atm),

$$\begin{aligned}
 T = 20^\circ\text{C} (293^\circ\text{K}) \quad \mu &= 0.268 \times 10^{-4} \text{ kg/m-s} \\
 T = 200^\circ\text{C} (473^\circ\text{K}) \quad \mu &= 0.298 \times 10^{-4} \text{ kg/m-s}
 \end{aligned}$$

$$\begin{aligned} T = 425^{\circ}\text{C} (698^{\circ}\text{K}) \quad \mu &= 0.360 \times 10^{-4} \text{ kg/m-s} \\ T = 550^{\circ}\text{C} (823^{\circ}\text{K}) \quad \mu &= 0.394 \times 10^{-4} \text{ kg/m-s} \end{aligned}$$

The viscosity of the process fluid at a particular temperature is:

$$\mu_t = \phi_w \mu_w + \phi_a \mu_a$$

$$\begin{aligned} \mu_{20} &= (0.716) \mu_{20w} + (0.284) \mu_{20a} \\ &= (0.716) (9.9264 \times 10^{-4} \text{ kg/m-s}) + (0.284) (0.268 \times 10^{-4} \text{ kg/m-s}) \\ &= 7.183 \times 10^{-4} \text{ kg/m-s} \end{aligned}$$

$$\begin{aligned} \mu_{200} &= (0.716) (1.408 \times 10^{-4} \text{ kg/m-s}) + (0.284) (0.298 \times 10^{-4} \text{ kg/m-s}) \\ &= 1.093 \times 10^{-4} \text{ kg/m-s} \end{aligned}$$

$$\begin{aligned} \mu_{425} &= (0.716) (0.3043 \times 10^{-4} \text{ kg/m-s}) + (0.284) (0.360 \times 10^{-4} \text{ kg/m-s}) \\ &= 0.320 \times 10^{-4} \text{ kg/m-s} \end{aligned}$$

$$\begin{aligned} \mu_{550} &= (0.716) (0.3308 \times 10^{-4} \text{ kg/m-s}) + (0.284) (0.394 \times 10^{-4} \text{ kg/m-s}) \\ &= 0.349 \times 10^{-4} \text{ kg/m-s} \end{aligned}$$

The Reynolds number is then calculated as:

$$\begin{aligned} \text{Re}_{20} &= \frac{4 \dot{m}_i}{\pi D \mu_{20}} \\ &= 4(0.0735 \text{ kg/s}) \div \pi (0.0340\text{m})(7.183 \times 10^{-4} \text{ kg/m-s}) \\ &= 3831 \end{aligned}$$

$$\begin{aligned} \text{Re}_{200} &= 4(0.0735 \text{ kg/s}) \div \pi (0.0340\text{m})(1.093 \times 10^{-4} \text{ kg/m-s}) \\ &= 25182 \end{aligned}$$

$$\begin{aligned} \text{Re}_{425} &= 4(0.0735 \text{ kg/s}) \div \pi (0.0340\text{m})(0.320 \times 10^{-4} \text{ kg/m-s}) \\ &= 85746 \end{aligned}$$

$$\begin{aligned} \text{Re}_{550} &= 4(0.0735 \text{ kg/s}) \div \pi (0.0340\text{m})(0.349 \times 10^{-4} \text{ kg/m-s}) \\ &= 78867 \end{aligned}$$

The Prandtl number is,

$$\text{Pr} = \frac{\mu C_p}{k}$$

where C_p = specific heat, kJ/kg °C
 k = thermal conductivity, W/m-°C

The specific heat of air in kJ/kg°C is :(Ref: Handbook of Physical Properties of Liquids and Gases P.597),

P(Bar)	Temp (K)					
	290	300	475	700	800	850
200	1.291	1.266	1.112	1.114	1.128	1.136
300	1.341	1.316	1.139	1.129	1.140	1.147
280	1.331	1.306	1.134	1.126	1.138	1.145

By linear interpolation,

At 280 bar (~280 atm),

$T = 20^\circ\text{C} (293^\circ\text{K}) \quad C_p = 1.324 \text{ kJ/kg}^\circ\text{C}$
 $T = 200^\circ\text{C} (473^\circ\text{K}) \quad C_p = 1.134 \text{ kJ/kg}^\circ\text{C}$
 $T = 425^\circ\text{C} (698^\circ\text{K}) \quad C_p = 1.126 \text{ kJ/kg}^\circ\text{C}$
 $T = 550^\circ\text{C} (823^\circ\text{K}) \quad C_p = 1.141 \text{ kJ/kg}^\circ\text{C}$

The specific heat of the fluid at a particular temperature is:

$$C_{pt} = \phi_w C_{pw} + \phi_a C_{pa}$$

$$\begin{aligned} C_{p20} &= (0.716) \mu_{20w} + (0.284) \mu_{20a} \\ &= (0.716) (4.104 \text{ kJ/kg}^\circ\text{C}) + (0.284) (1.324 \text{ kJ/kg}^\circ\text{C}) \\ &= 3.314 \text{ kJ/kg}^\circ\text{C} \end{aligned}$$

$$\begin{aligned} C_{p200} &= (0.716) (4.357 \text{ kJ/kg}^\circ\text{C}) + (0.284) (1.134 \text{ kJ/kg}^\circ\text{C}) \\ &= 3.442 \text{ kJ/kg}^\circ\text{C} \end{aligned}$$

$$\begin{aligned} C_{p425} &= (0.716) (9.276 \text{ kJ/kg}^\circ\text{C}) + (0.284) (1.126 \text{ kJ/kg}^\circ\text{C}) \\ &= 6.959 \text{ kJ/kg}^\circ\text{C} \end{aligned}$$

$$\begin{aligned} C_{p550} &= (0.716) (3.426 \text{ kJ/kg}^\circ\text{C}) + (0.284) (1.141 \text{ kJ/kg}^\circ\text{C}) \\ &= 2.776 \text{ kJ/kg}^\circ\text{C} \end{aligned}$$

The thermal conductivity of air in $10^3 \text{ W/m}^\circ\text{C}$ is (Ref: Handbook of Physical Properties of Liquids and Gases P.631):

P(Bar)	Temp (K)					
	300	450	500	700	750	800
250	42.0	46.0	48.3	57.3	59.4	61.4
300	45.5	48.0	50.1	58.4	60.4	62.4
280	44.0	47.2	49.38	57.96	60.0	62.0

By linear interpolation,

At 280 bar (~280 atm),

$$T = 20^{\circ}\text{C} (293^{\circ}\text{K}) \quad k = 0.0441 \text{ W/m}^{\circ}\text{C}$$

$$T = 200^{\circ}\text{C} (473^{\circ}\text{K}) \quad k = 0.0482 \text{ W/m}^{\circ}\text{C}$$

$$T = 425^{\circ}\text{C} (698^{\circ}\text{K}) \quad k = 0.058 \text{ W/m}^{\circ}\text{C}$$

$$T = 550^{\circ}\text{C} (823^{\circ}\text{K}) \quad k = 0.0629 \text{ W/m}^{\circ}\text{C}$$

The thermal conductivity of the fluid at a particular temperature is:

$$k_t = \phi_w k_w + \phi_a k_a$$

$$\begin{aligned} k_{20} &= (0.716) k_{20w} + (0.284) k_{20a} \\ &= (0.716) (0.611 \text{ W/m}^{\circ}\text{C}) + (0.284) (0.0441 \text{ W/m}^{\circ}\text{C}) \\ &= 0.45 \text{ W/m}^{\circ}\text{C} \end{aligned}$$

$$\begin{aligned} k_{200} &= (0.716) (0.686 \text{ W/m}^{\circ}\text{C}) + (0.284) (0.0482 \text{ W/m}^{\circ}\text{C}) \\ &= 0.628 \text{ W/m}^{\circ}\text{C} \end{aligned}$$

$$\begin{aligned} k_{425} &= (0.716) (0.118 \text{ W/m}^{\circ}\text{C}) + (0.284) (0.058 \text{ W/m}^{\circ}\text{C}) \\ &= 0.101 \text{ W/m}^{\circ}\text{C} \end{aligned}$$

$$\begin{aligned} k_{550} &= (0.716) (0.105 \text{ W/m}^{\circ}\text{C}) + (0.284) (0.0629 \text{ W/m}^{\circ}\text{C}) \\ &= 0.093 \text{ W/m}^{\circ}\text{C} \end{aligned}$$

The Prandtl number is then calculated:

$$\begin{aligned} \text{Pr}_{20} &= \frac{\mu_{20} C_{p20}}{k_{20}} \\ &= \frac{(7.183 \times 10^{-4} \text{ Kg/m-s}) (3.314 \text{ kJ/kg}^{\circ}\text{C})(1000 \text{ J/kJ})}{0.45 \text{ W/m}^{\circ}\text{C}} \\ &= 5.29 \end{aligned}$$

$$\begin{aligned} \text{Pr}_{200} &= \frac{(1.093 \times 10^{-4} \text{ Kg/m-s}) (3.442 \text{ kJ/kg}^\circ\text{C})(1000 \text{ J/kJ})}{0.628 \text{ W/m}^\circ\text{C}} \\ &= 0.60 \end{aligned}$$

$$\begin{aligned} \text{Pr}_{425} &= \frac{(0.320 \times 10^{-4} \text{ Kg/m-s}) (6.959 \text{ kJ/kg}^\circ\text{C})(1000 \text{ J/kJ})}{0.101 \text{ W/m}^\circ\text{C}} \\ &= 2.205 \end{aligned}$$

$$\begin{aligned} \text{Pr}_{550} &= \frac{(0.349 \times 10^{-4} \text{ Kg/m-s}) (2.776 \text{ kJ/kg}^\circ\text{C})(1000 \text{ J/kJ})}{0.093 \text{ W/m}^\circ\text{C}} \\ &= 1.042 \end{aligned}$$

The Nusselt number and heat transfer coefficient in $\text{W/m}^2 \text{ }^\circ\text{C}$ are,

$$\begin{aligned} \text{Nu}_{20} &= 0.023 \text{ Pr}_{20}^{1/3} \text{Re}_{20}^{0.8} \\ &= 0.023 (5.29)^{1/3} (3831)^{0.8} \\ &= 29.48 \end{aligned}$$

$$\begin{aligned} \text{Nu}_{200} &= 0.023 (0.60)^{1/3} (25182)^{0.8} \\ &= 64.37 \end{aligned}$$

$$\begin{aligned} \text{Nu}_{425} &= 0.023 (2.205)^{1/3} (85746)^{0.8} \\ &= 264.05 \end{aligned}$$

$$\begin{aligned} \text{Nu}_{550} &= 0.023 (1.042)^{1/3} (78867)^{0.8} \\ &= 192.36 \end{aligned}$$

$$\begin{aligned} h_{20} &= \text{Nu}_{20} \frac{k_{20}}{D_{20}} \\ &= 29.48 \frac{0.45}{0.0341} \\ &= 389.03 \text{ W/m}^2 \text{ }^\circ\text{C} \end{aligned}$$

$$\begin{aligned} h_{200} &= 64.37 \frac{0.628}{0.0341} \\ &= 1185.47 \text{ W/m}^2 \text{ }^\circ\text{C} \end{aligned}$$

$$\begin{aligned} h_{425} &= 264.05 \frac{0.101}{0.0341} \\ &= 782.08 \text{ W/m}^2 \text{ }^\circ\text{C} \end{aligned}$$

$$\begin{aligned}
 h_{550} &= 192.36 \frac{0.093}{0.0341} \\
 &= 524.62 \text{ W/m}^2 \text{ } ^\circ\text{C}
 \end{aligned}$$

The heat flux at the ends of each section is:

$$\begin{aligned}
 q''_{20} &= h_{20} (T_w - T_f) \\
 &= (389.03 \text{ W/m}^2 \text{ } ^\circ\text{C})(625 - 20)^\circ\text{C} \\
 &= 235.363 \text{ kW/m}^2
 \end{aligned}$$

$$\begin{aligned}
 q''_{200} &= (1185.47 \text{ W/m}^2 \text{ } ^\circ\text{C})(625 - 200)^\circ\text{C} \\
 &= 503.825 \text{ kW/m}^2
 \end{aligned}$$

$$\begin{aligned}
 q''_{425} &= (782.08 \text{ W/m}^2 \text{ } ^\circ\text{C})(625 - 425)^\circ\text{C} \\
 &= 156.416 \text{ kW/m}^2
 \end{aligned}$$

$$\begin{aligned}
 q''_{550} &= (524.62 \text{ W/m}^2 \text{ } ^\circ\text{C})(625 - 550)^\circ\text{C} \\
 &= 39.346 \text{ kW/m}^2
 \end{aligned}$$

The maximum heat flux is limited by the maximum wall temperature and is the minimum for each section:

$$q''_1 = q''_{20} = 235.363 \text{ kW/m}^2$$

$$q''_2 = q''_{425} = 156.416 \text{ kW/m}^2$$

$$q''_3 = q''_{550} = 39.346 \text{ kW/m}^2$$

IV. Reactor Length

The reactor length, based on the energy required and maximum heat flux for each section, is calculated as follows:

$$Q = A q''$$

$$A = \pi D L$$

$$L = \frac{Q}{\pi D q''}$$

$$\begin{aligned}
 L_1 &= \frac{Q_1}{\pi D q''_1} \\
 &= \frac{44.03 \text{ kW}}{\pi (0.0341 \text{ m}) (235.363 \text{ kW/m}^2)} \\
 &= 1.75 \text{ m}
 \end{aligned}$$

$$\begin{aligned}
 L_2 &= \frac{100.95 \text{ kW}}{\pi (0.0341 \text{ m}) (156.416 \text{ kW/m}^2)} \\
 &= 6.024 \text{ m}
 \end{aligned}$$

$$\begin{aligned}
 L_3 &= \frac{35.27 \text{ kW}}{\pi (0.0341 \text{ m}) (39.346 \text{ kW/m}^2)} \\
 &= 8.368 \text{ m}
 \end{aligned}$$

The length required for a 15 second residence time is determined by the average velocity at the end of section 3:

$$\begin{aligned}
 \dot{m} &= \rho A V \\
 \text{where } \rho &= \text{density of the fluid} \\
 A &= \text{cross-sectional area of the flow}
 \end{aligned}$$

At 550 °C and 280 atm, the density of the fluid is 95.16 kg/m³,

$$\begin{aligned}
 V &= \frac{\dot{m}}{\rho A} \\
 &= \frac{0.0735 \text{ kg/s}}{(95.16 \text{ kg/m}^3) (\pi (0.0341 \text{ m})^2/4)} \\
 &= 0.846 \text{ m/s}
 \end{aligned}$$

$$\begin{aligned}
 L_r &= t V \\
 &= (15 \text{ sec})(0.846 \text{ m/s}) \\
 &= 12.69 \text{ m}
 \end{aligned}$$

The total length is,

$$\begin{aligned}
 L_t &= L_1 + L_2 + L_3 + L_r \\
 &= 1.75 + 6.024 + 8.368 + 12.69 \text{ m} \\
 &= 28.83 \text{ m}
 \end{aligned}$$

V. Finite difference calculations

As explained in the main body of the report, each section is divided into zones and integrated forward to predict positional fluid temperature, wall temperature, heat flux, density, Reynolds number, and heat transfer coefficient. Table A1 records the thermal hydraulic results for review; they are also recorded graphically in Figures A1 through A6. Whereas the fluid temperature increases monotonically (with position) the wall temperature is quite variable (c.f., Figures A1 and A2). Variability in impressed heat flux (c.f., Figure A3) combined with large changes in fluid-mechanic properties over the temperature range drives this variation. These detailed calculations and the discrete calculations from the previous section agree within 10 %. The difference is due to the finite difference scheme employed.

Table A1. Thermal-hydraulic predictions.

The heat transfer properties of the process fluid are estimated by a computer program, preheat.6, with following input conditions. The physical properties of air and water : incorporated in the computing program based on the weight ratio, however, single phase liquid fluid is assumed when using the heat transfer equation.

Input Data

Diameter (cm)	3.41122	Mass Flow Rate (gm/s)	73.5
Number of Sections	3	Inlet Temperature (°C)	20
Number of Subsections/section	10	Pressure (bar)	280
Length of Section 1 (cm)	175	Maximum Wall Temperature (°C)	625
Length of Section 2 (cm)	602.4		
Length of Section 3 (cm)	836.8		

Section/ Subsection	Fluid Temp (°C)	Wall Temp (°C)	Length (cm)	Heat Flux (J/cm2/s)	Density (g/cm3)	Enthalpy (J/g)	Viscosity (g/cm/s)	Thermal Cond (W/cm/°)	Specific Heat (J/g/°)	Heat X Coef (W/cm2)	Reynolds No.	Nusselt No.
1/1	37.4456	624.2906	17.5	22.64	0.80661	192.36647	0.00718	0.0045	3.31068	0.03858	3822.72	29.2517
1/2	54.8849	535.4719	35	22.64	0.79822	249.95027	0.005	0.0047	3.31188	0.04711	5489.06	34.17613
1/3	72.3491	482.1141	52.5	22.64	0.78871	307.59329	0.00373	0.00486	3.30716	0.05525	7348.98	38.74499
1/4	89.8211	449.6503	70	22.64	0.77832	365.36274	0.00293	0.00498	3.30569	0.06292	9365.53	43.07181
1/5	107.2698	430.4572	87.5	22.64	0.76717	423.27242	0.00239	0.00506	3.31008	0.07005	11493.00	47.19192
1/6	124.6701	420.1826	105	22.64	0.75537	481.29877	0.00201	0.00511	3.31931	0.07661	13683.19	51.104
1/7	142.0034	416.1483	122.5	22.64	0.74301	539.41422	0.00173	0.00514	3.33213	0.08258	15892.22	54.80491
1/8	159.2532	416.6136	140	22.64	0.73012	597.60073	0.00152	0.00515	3.34827	0.08797	18084.17	58.30449
1/9	176.3998	420.3984	157.5	22.64	0.71672	655.85045	0.00136	0.00514	3.36842	0.09279	20232.20	61.62761
1/10	193.4177	426.6721	175	22.64	0.70281	714.16234	0.00123	0.00511	3.39388	0.09706	22318.33	64.81119
2/1	233.9576	390.8387	235.24	15.8171	0.68838	772.53904	0.00113	0.00507	3.42625	0.10082	24332.67	67.90066
2/2	273.1451	419.5789	295.48	15.8171	0.65101	914.46077	0.00095	0.00489	3.5445	0.10802	28918.68	75.33464
2/3	310.2116	450.3676	355.72	15.8171	0.60947	1057.7336	0.00083	0.00461	3.74731	0.11285	33214.33	83.50583
2/4	344.071	480.7844	415.96	15.8171	0.56224	1203.1282	0.00073	0.0042	4.10226	0.1157	37530.59	93.96726
2/5	372.898	507.8588	476.2	15.8171	0.50611	1352.7685	0.00065	0.00363	4.8184	0.1172	42456.92	110.20697
2/6	392.816	523.5144	536.44	15.8171	0.43203	1514.9012	0.00056	0.00285	6.97356	0.12102	49419.31	144.77191
2/7	399.1132	506.4952	596.68	15.8171	0.30152	1743.4042	0.00042	0.00179	22.05741	0.1473	65067.11	281.04346
2/8	405.6069	525.9653	656.92	15.8171	0.22947	1891.9899	0.00036	0.00137	21.3899	0.13142	75988.00	326.49146
2/9	415.7831	565.0259	717.16	15.8171	0.19079	2003.2764	0.00034	0.00118	13.64954	0.10598	81843.29	306.48459
2/10	431.8655	615.6426	777.4	15.8171	0.16276	2112.2946	0.00032	0.00105	8.63677	0.08607	85215.19	278.82575
3/1	439.6661	491.6111	861.08	3.7469	0.14107	2225.137	0.00032	0.00097	5.85946	0.07213	86464.26	253.83675
3/2	448.4851	503.4102	944.76	3.7469	0.13427	2268.07	0.00032	0.00095	5.18291	0.06822	86433.16	245.54656
3/3	458.3347	516.0766	1028.44	3.7469	0.12808	2311.2658	0.00032	0.00093	4.64053	0.06489	86165.02	237.81544
3/4	469.2089	529.571	1112.12	3.7469	0.12243	2354.7102	0.00032	0.00092	4.20332	0.06207	85686.17	230.6047
3/5	481.0836	543.8436	1195.8	3.7469	0.11726	2398.3867	0.00032	0.00091	3.84918	0.0597	85023.92	223.87771
3/6	493.9187	558.8371	1279.48	3.7469	0.11251	2442.2769	0.00033	0.0009	3.56114	0.05772	84205.85	217.60077
3/7	507.6613	574.4903	1363.16	3.7469	0.10815	2486.3607	0.00033	0.0009	3.326	0.05607	83258.96	211.74263
3/8	522.2484	590.7411	1446.84	3.7469	0.10412	2530.617	0.00033	0.0009	3.13344	0.05471	82208.98	206.27398
3/9	537.611	607.5294	1530.52	3.7469	0.1004	2575.024	0.00034	0.00091	2.97526	0.05359	81079.74	201.16713
3/10	553.6772	624.7984	1614.2	3.7469	0.09695	2619.5599	0.00034	0.00092	2.84495	0.05268	79892.69	196.39591

Fluid Temperature (C)

Figure A1. Fluid Temperature

Figure A2. Wall Temperature

Figure A3. Heat Flux

Figure A4. Density

Figure A5. Reynolds Number

Figure A6. Heat Transfer Coefficient

VI. Total Heat Lost

The reactor self-heating from the heat of combustion of the CS agent and the heat lost from the reactor to the environment are calculated in this section.

The heat of combustion for the CS agent is 5.01 kcal/g. At 5 wt % concentration

$$\begin{aligned}\dot{m}_{CS} &= \dot{m}_{\text{total}} \times 5\% \\ &= 0.0526 \text{ kg/s} \times 5\% \\ &= 2.63 \text{ g/s}\end{aligned}$$

The heat of combustion is then,

$$\begin{aligned}Q_{\text{com}} &= 5.01 \text{ kcal/g} \times 2.63 \text{ g/s} \\ &= 13.18 \text{ kcal/s} \quad 4.1868 \text{ kJ/kcal} \\ Q_{\text{com}} &= 55.2 \text{ kW}\end{aligned}$$

The total heat loss from the reactor is calculated as follows:

Assuming 1" thick Durablanket-S is used, the thermal conductivity of the Durablanket-S at average temperature (250-300 °C) is 0.058 W/m°C.

The thermal resistances are, (Ref: Heat Transfer by Holman)

$$R_f = \frac{1}{h_f 2\pi r_f L}$$

$$R_w = \frac{\ln(r_w/r_f)}{2\pi k_w L}$$

$$R_i = \frac{\ln(r_i/r_w)}{2\pi k_i L}$$

$$R_s = \frac{1}{(h_c + h_r) 2\pi r_i L}$$

where, r_f = inner radius of the pipe
 r_w = outer radius of the pipe
 r_i = radius of the insulation

h_f = heat transfer coefficient of the fluid
 k_w = thermal conductivity of the wall
 k_i = thermal conductivity of the insulation
 h_c = heat transfer coefficient of the air by convection
 h_r = heat transfer coefficient of the air by radiation

The total heat loss is then,

$$Q_L = \frac{\Delta T}{R_T}$$

where $R_T = R_f + R_w + R_i + R_s$

since also, $Q_c = A \Delta T h$
 $= (2\pi r_i L)(T_s - T_a)(h_c + h_r)$

$$Q_L = Q_c$$

$$\Rightarrow \frac{\Delta T}{R_T} = (2\pi r_i L)(T_s - T_a)(h_c + h_r)$$

For $L = L_r = 12.69 \text{ m}$

Temperature of fluid, $T_f = 550^\circ\text{C}$ (no heat input)

Using 550°C maximum wall temperature for Inconel 625,

$$K_w = 10 \text{ Btu/ft-hr-}^\circ\text{C} \times 1.7307 = 17.307 \text{ W/m-}^\circ\text{C}$$

$$h_{f550} = 524.62 \text{ W/m}^2\text{-}^\circ\text{C} \quad (\text{from heat flux calculation})$$

Thermal resistance:

$$\begin{aligned} R_w &= \ln(r_w/r_f)/2\pi k_w L_r = 0.00028 \text{ }^\circ\text{C/W} \\ R_i &= \ln(r_i/r_w)/2\pi k_i L_r = 0.15136 \text{ }^\circ\text{C/W} \\ R_f &= 1/(h_f 2\pi r_f L_r) = 0.0014 \text{ }^\circ\text{C/W} \\ R_s &= 1/(h_c + h_r)(2\pi r_i L_r) = 0.24856 \text{ }^\circ\text{C/W} \end{aligned}$$

$$\begin{aligned} \text{Where } h_c &= 1.32 (\Delta T/d)^{1/4} = 2.34199 (T_s - 20)^{1/4} \text{ W/m}^2\text{-}^\circ\text{C} \\ h_r &= 5.67 \times 10^{-8} (T_s^2 + T_o^2)(T_s + T_o) \text{ W/m}^2\text{-}^\circ\text{C} \end{aligned}$$

$$R_{\text{total}} = R_w + R_i + R_f + R_s = 0.15304 + R_s$$

$$\begin{aligned} Q_t &= \Delta T/R_t = (550 - 20)/R_t \text{ W} \\ Q_c &= \text{Area } (T_s - T_o)(h_c + h_r) = 4.02313 (T_s - 20)(h_c + h_r) \text{ W} \end{aligned}$$

By iteration,

$T_s(^\circ\text{C})$ (Guess)	h_c	h_r ($\text{W/m}^2\text{-}^\circ\text{C}$)	$h_c + h_r$	R_s ($^\circ\text{C/W}$)	R_t ($^\circ\text{C/W}$)	Q_t (W)	Q_c (W)	ΔQ
300	9.58022	20.3569	29.9371	0.0083	0.1613	3284.95	33723.38826	30438.4407
100	7.0042	8.50704	15.5112	0.01602	0.1691	3134.91	4992.29488	1857.38455
80	6.51814	7.71938	14.2375	0.01746	0.1705	3108.55	3436.761563	328.210641
70	6.22771	7.34873	13.5764	0.01831	0.1713	3093.13	2730.987059	-362.141476
75	6.37788	7.53216	13.91	0.01787	0.1709	3101.08	3077.90279	-23.1724373
75.3	6.38656	7.54328	13.9298	0.01784	0.1709	3101.54	3099.097623	-2.4386637

The heat loss in this section is: **3100 W**

For $L = L_1 = 1.75 \text{ m}$

The maximum heat loss occurs at maximum temperature in wall, $T_w = 625^\circ\text{C}$

$$K_w = 11 \text{ Btu/ft-hr} \times 1.7307 = 19.0377 \text{ W/m-}^\circ\text{C}$$

$$\begin{aligned} R_w &= \ln(r_w/r_f)/2\pi k_w L_r = 0.00184 \text{ }^\circ\text{C/W} \\ R_i &= \ln(r_i/r_w)/2\pi k_i L_r = 1.09757 \text{ }^\circ\text{C/W} \\ R_s &= 1/(h_c + h_r)(2\pi r_i L_r) = 1.80244 \text{ }^\circ\text{C/W} \end{aligned}$$

Where $hc = 1.32 (\Delta T/d)^{(1/4)} = 2.34199 (Ts-20)^{(1/4)} \text{ W/m}^2\text{-}^\circ\text{C}$
 $hr = 5.67\text{E-}8 (Ts^2+To^2)(Ts+To) \text{ W/m}^2\text{-}^\circ\text{C}$

$R_{total} = R_w + R_i + R_s = 1.0994 + R_s$

$Q_t = \Delta T/R_t = (625 - 20)/R_t \text{ W}$
 $Q_c = \text{Area } (Ts - To)(hc+hr) = 0.5548 (Ts-To)(hc+hr) \text{ W}$

By iteration,

Ts(°C) (Guess)	hc	hr (W/m ² -°C)	hc+hr	Rs (°C/W)	Rt (°C/W)	Qt (W)	Qc (W)	ΔQ
300	9.58022	20.3569	29.9371	0.06021	1.1596	521.726	4650.585458	4128.85939
100	7.0042	8.50704	15.5112	0.1162	1.2156	497.694	688.4567407	190.762924
80	6.51814	7.71938	14.2375	0.1266	1.226	493.474	473.9426899	-19.5310252
82	6.57179	7.79534	14.3671	0.12546	1.2249	493.934	494.1991575	0.26531536

The heat loss in this section is: **500 W**

For L = L2 = **6.024 m**

The maximum heat loss occurs at maximum temperature in wall, Tw = 625 °C

$K_w = 11 \text{ Btu/ft-hr} \times 1.7307 = 19.0377 \text{ W/m-}^\circ\text{C}$

$R_w = \ln(rw/rf)/2\pi k_w L_r = 0.00053 \text{ }^\circ\text{C/W}$
 $R_i = \ln(ri/rw)/2\pi k_i L_r = 0.31885 \text{ }^\circ\text{C/W}$
 $R_s = 1/(hc+hr)(2\pi r_i L_r) = 0.52362 \text{ }^\circ\text{C/W}$

Where $hc = 1.32 (\Delta T/d)^{(1/4)} = 2.34199 (Ts-20)^{(1/4)} \text{ W/m}^2\text{-}^\circ\text{C}$
 $hr = 5.67\text{E-}8 (Ts^2+To^2)(Ts+To) \text{ W/m}^2\text{-}^\circ\text{C}$

$R_{total} = R_w + R_i + R_s = 0.31938 + R_s$

$Q_t = \Delta T/R_t = (625 - 20)/R_t \text{ W}$
 $Q_c = \text{Area } (Ts - To)(hc+hr) = 1.9098 (Ts-To)(hc+hr) \text{ W}$

By iteration,

Ts(°C) (Guess)	hc	hr (W/m ² -°C)	hc+hr	Rs (°C/W)	Rt (°C/W)	Qt (W)	Qc (W)	ΔQ
300	9.58022	20.3569	29.9371	0.01749	0.3369	1795.93	16008.64388	14212.7137
100	7.0042	8.50704	15.5112	0.03376	0.3531	1713.2	2369.864804	656.660489
80	6.51814	7.71938	14.2375	0.03678	0.3562	1698.68	1631.446151	-67.231369
82	6.57179	7.79534	14.3671	0.03645	0.3558	1700.26	1701.1747	0.91329128

The heat loss in this section is: **1700 W**

For $L = L_3 = 8.368 \text{ m}$

The maximum heat loss occurs at maximum temperature in wall, $T_w = 625^\circ\text{C}$

$$K_w = 11 \text{ Btu/ft-hr} \times 1.7307 = 19.0377 \text{ W/m-}^\circ\text{C}$$

$$\begin{aligned} R_w &= \ln(r_w/r_f)/2\pi k_w L_r = 0.00038 \text{ }^\circ\text{C/W} \\ R_i &= \ln(r_i/r_w)/2\pi k_i L_r = 0.22953 \text{ }^\circ\text{C/W} \\ R_s &= 1/(h_c+h_r)(2\pi r_i L_r) = 0.37694 \text{ }^\circ\text{C/W} \end{aligned}$$

$$\begin{aligned} \text{Where } h_c &= 1.32 (\Delta T/d)^{1/4} = 2.34199 (T_s-20)^{1/4} \text{ W/m}^2\text{-}^\circ\text{C} \\ h_r &= 5.67\text{E-}8 (T_s^2+T_o^2)(T_s+T_o) \text{ W/m}^2\text{-}^\circ\text{C} \end{aligned}$$

$$R_{\text{total}} = R_w + R_i + R_s = 0.22992 + R_s$$

$$\begin{aligned} Q_t &= \Delta T/R_t = (625 - 20)/R_t \text{ W} \\ Q_c &= \text{Area } (T_s - T_o)(h_c+h_r) = 2.65292 (T_s-T_o)(h_c+h_r) \text{ W} \end{aligned}$$

By iteration,

$T_s(^\circ\text{C})$ (Guess)	h_c	h_r (W/m ² -°C)	h_c+h_r	R_s (°C/W)	R_t (°C/W)	Q_t (W)	Q_c (W)	ΔQ
300	9.58022	20.3569	29.9371	0.01259	0.2425	2494.74	22237.77092	19743.0259
100	7.0042	8.50704	15.5112	0.0243	0.2542	2379.83	3292.003432	912.1738
80	6.51814	7.71938	14.2375	0.02648	0.2564	2359.65	2266.258531	-93.3917822
82	6.57179	7.79534	14.3671	0.02624	0.2562	2361.85	2363.119171	1.26866226

The heat loss in this section is: **2400 W**

The total heat loss is :

$$Q_t = 3100 + 500 + 1700 + 2400 = 7700 \text{ W}$$

Recall that, $Q_{\text{com}} = 55.2 \text{ kW}$

$$Q_t \ll Q_{\text{com}}$$

Therefore, no additional energy required.

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