

TECHNICAL REPORT

DIOXIN CONTAINMENT AND DESTRUCTION
IN THE PHENOXY HERBICIDE 2,4,5 T PROCESS

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THE PRESENT PROCESS

Trichlorophenol Process

The manufacture of 2,4,5-T acid begins with reaction to form the sodium salt of trichlorophenol by dechlorinating tetrachlorobenzene in methanol solution under alkaline conditons.

Trichlorophenol Process Safety Considerations

The engineering control of the trichlorophenol reaction is vital to the entire process for two reasons:

1. Dioxins are formed as a trace ^{contaminant?} containment in this reaction (this reaction is the only process step wherein dioxins are generated).
2. The reaction is highly exothermic.

The reaction is conducted in nickel clad, jacketed and agitated vessels designed for high pressure operation. Reaction is initiated by heating the reactants by applying steam to the reactor jacket. After reaction initiation, the steam heating is stopped and reaction is controlled by manually adding cooling water to the jacket. As a safety measure, cooling water will automatically flow through the reactor jacket if excess pressure is detected by instrumentation.

In order to make the system as fail-safe as possible to engineer, there are four pressure relief systems discharging into containment devices on each reactor. These systems guard against the unlikely; for example, the failure of the cooling water system during the reaction exotherm. Equipment, personnel, and the environment are protected from a "runaway" reaction by the following:

1. a spring loaded relief valve which discharges to a scrubber when the maximum allowable working pressure is exceeded;
2. two automatic valves which open and discharge to the scrubber if pressure is 5% in excess of maximum allowable working pressure;
3. a rupture disc which will discharge to a catch tank containing a heel of water, if the reactor pressure is 10% in excess of maximum allowable working pressure.

Consultant Verification of TCP Safety

In order to independently verify that the system for protection of personnel, the environment, and equipment is adequate, independent consultants were retained to examine the mechanical

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reliability and functional suitability of relief equipment and examine Vertac design calculations on the capacity and capability of equipment to function and contain reactor contents under conditions of complete failure of reaction control equipment. The consultants reports are attached as Appendix I. Complete design calculations are available for review by personnel of the Arkansas Department of Pollution Control and Ecology should further verification be desirable.

Methanol Recovery

After the trichlorophenol reaction, vessel contents are pumped to another vessel where water is added, by-product dimethyl ether is stripped off and scrubbed out by water, and methanol is stripped off for recovery.

Toluene Wash and Dioxins Concentration

After methanol recovery, the aqueous solution of the sodium salt of trichlorophenol is pumped to an additional vessel where toluene is added. The source of the toluene is both fresh and recycled toluene. As will be discussed below, toluene is used elsewhere in the process as a solvent or wash; however, ultimately all toluene is recycled to this step where high boiling point material remains behind in the "toluene still bottoms". The entire amount of the trace dioxins generated during the initial reaction and by-product 2,4,5 trichloroanisole are dissolved within the toluene phase.

The toluene phase is decanted to a still pot where toluene is distilled off for recycle. The "toluene still bottoms" have been previously stored in drums which are now overpacked in more substantial drums. Henceforth, as in discussed below under By-Product Anisole and Dioxin Containment, the "toluene still bottoms" will be handled differently, in essence totally contained.

2,4,5-T Acid Reaction and Processing

The aqueous solution containing the solution salt of trichlorophenol is pumped to a vessel. Toluene, NaOH and monochloroacetic acid are added and reaction occurs; after reaction, HCL is added to form the 2,4,5-T acid. Additional water is then added to dissolve the by-product salt brine which is then phase separated from the organics. Any remaining water and salt in the organic phase is removed in an evaporation step followed by filtration. The by-product salt brines are subsequently washed with toluene to remove residual organics prior to discharge as effluent to the Jacksonville Treatment Plant. The organic phase is cooled where upon 2,4,5-T acid crystals form and are separated from solvent in a centrifuge. The centrifuged product is subsequently dried.

DIOXIN DESTRUCTION

By-Product Anisole and Dioxin Containment

As previously discussed, dioxins are concentrated in "toluene still bottoms" or "by-product anisole".

We plan to install a heavy walled 10,000 gallon carbon steel vessel for the containment of by-products from resumed operations. The storage vessel will be equipped with level and temperature monitoring instruments as well as an emission control device. The storage vessel will be installed in a secured and dedicated concrete diked area with no effluent drainage. The one containment vessel will allow accumulation of "toluene still bottoms" during one year of operation. "Toluene still bottoms" will be pumped from the toluene still to the by-product containment tank in steam traced and insulated process piping. Breathing vents from the containment tank will be piped to a conservation vent and then to an activated carbon bed. Temperature and level monitoring devices suitable for high freeze point materials will be installed. Adequate controls will be installed on the steam to the process piping and the storage tank to prevent freeze-ups or overheated material.

By-Product Anisole Recovery and Dioxin Destruction

We have applied for a patent on this process and consider it highly proprietary. Disclosure of the technical information would be harmful to the Corporation; for this reason, we have not included the technical details in the body of this report, but rather have included them in Appendix II, which is attached and labeled confidential.

During the time that we operate the 2,4,5-T acid process and accumulate "toluene still bottoms" we will complete the development and engineering of the destruction process. We believe that this technology is of importance beyond the Corporation and as such hope to obtain a Federally funded and State administered grant.

Long Term Disposition of Materials Generated in the Past

We are committed to responsible containment of past materials on the site of plants that we operate. It may develop that public opinion and Federal funding will make desirable the detoxification of dioxin contaminated materials generated in the past, even though the material is contained within a dedicated and monitored site. We hope to obtain a Federally funded State administered R and D grant to develop the highly difficult technical, safety and material handling aspects of disturbing abandoned material. Our efforts are preliminary at this point, however, this technology can be developed only after complete development and design of the destruction process.

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WASTE WATER STUDIES

As noted in the discussion under Dioxin Destruction the main dioxin containing plan is to contain and destroy the dioxin. The final product can contain up to 0.1 ppm dioxin; therefore, the complete dioxin containment plan must include treatment of waste water to stop dioxin from leaving the boundary line via that route because spills of product into the waste water stream are possible. The waste water presently comes from 3 process areas:

- 1-recovery area
- 2-esterification area
- 3-formulation area

The waste water plan consists of phase separators in the water flowing from each of the 3 process areas followed by an alternative to the present neutralization pond.

Recovery Area

Process wastewater from the recovery area includes the dechlorination area sump, the brine washer discharge, the salt filter backwash, water removed by the evaporator, and various miscellaneous flows from pump seals, tank cleanup and process area stormwater. All wastewater in this area goes through a collector sump which overflows to the industrial sewer. Losses to the sump include suspended solids, nonsoluble organic liquids and some soluble organics. Phase separation of the wastewater to recover heavier than water (mostly solids), and lighter than water (toluene and phenols) organics will greatly reduce the loading to the neutralization system. Studies are underway to develop data necessary for design of an effective phase separation system for this wastewater stream.

Esterification Area

Process wastewater from the esterification area is comprised mostly of water used in cleaning process equipment between product changes from 2,4-D to 2,4,5-T, etc. Emulsifiers are presently used to assist in cleaning the equipment making phase separation impractical. Investigation is underway to determine if process changes can be made so that emulsifiers will no longer be required to clean the equipment. Another possibility being investigated is the use of chemical agents such alum to break the emulsion. This would allow Vertac to employ phase separation to greatly reduce the organic loading from this operating area to the neutralization system.

Formulation Area

A third process area that contributes wastewater from the manufacture of 2,4,5-T and 2,4-D herbicides is the formulation area. The waste water in the formulation sump contains emulsifiers and therefore phase separation is only possible after making changes

similar to those discussed under esterification. Studies are underway to determine what changes can be made to reduce the losses from this area.

Neutralization Pond Alternatives

Process wastewater is presently neutralized by limestone followed by hydrated $\text{Ca}(\text{OH})_2$. Solids do fall out in the present pond; however, the pond is not complete protection. It has been determined in the laboratory that neutralization, coagulation and flocculation followed by filtration of the supernatant to remove all the solids will insure that no dioxins present in trace amounts because of spills will remain in the wastewater. Work is underway to develop the data necessary to completely design the system.

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SAFETY RELIEF CALCULATIONS AND REVIEW
OF THE 2,4,5-TRICHLOROPHENOL AUTOCLAVES

A REVIEW OF THE SAFETY RELIEF CALCULATIONS AND PROCEDURES FOR THE 2,4,5-TRICHLOROPHENOL AUTOCLAVES WAS CONDUCTED BY VERTAC. THE VERTAC, INC., JACKSONVILLE PLANT, IS PREPARED TO REVIEW THESE SAFETY RELIEF CALCULATIONS AS DEEMED NECESSARY BY THE DEPARTMENT. VERTAC HAS RETAINED AN INSTRUMENTATION CONSULTANT, MR. STEVE POCSIK, TO REVIEW AND COMMENT ON THE 2,4,5-TRICHLOROPHENOL AUTOCLAVE INSTRUMENTATION. MR. POCSIK'S INSTRUMENTATION INSPECTION EVALUATION REPORT FOLLOWS:

1. CALCULATIONS INDICATE THAT EXISTING CONTROL AND RELIEF DEVICES ARE AMPLY ADEQUATE TO SAFELY HANDLE ANY FORESEEABLE PROCESS UPSET.

2. EXAMINATION AND INSPECTION OF ALL INSTRUMENTS AND ALL CONTROL AND RELIEF DEVICES INDICATE THAT THEY APPEAR TO BE IN OPERATING CONDITION AND THEREFORE THERE IS NO REASON WHY THE 2,4,5-T PLANT COULD NOT RESUME NORMAL OPERATION.

3. RECOMMENDATIONS (IMMEDIATE)

(A) START A REGULAR PERIODIC PROGRAM (SUGGEST MONTHLY) FOR EXAMINATION AND TESTING OF ALL SPRING-LOADED RELIEF VALVES. MAINTAIN WRITTEN RECORD OF TEST DATA.

(B) START A REGULAR PERIODIC PROGRAM (SUGGEST MONTHLY) FOR EXAMINATION/INSPECTION OF ALL RUPTURE DISC. THIS SHOULD INCLUDE WRITTEN RECORD OF ALL FINDINGS AND/OR REPLACEMENTS.

(C) START A REGULAR PROGRAM (SUGGEST MONTHLY) FOR TESTING THE FUNCTION AND PROPER OPERATION OF THE AUTOMATIC KNOCK-BACK PRESSURE CONTROLS. TEST RESULTS SHOULD BE RECORDED IN A LOG.

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(D) START A PROGRAM (SUGGEST SEMI-ANNUAL) FOR COMPLETE CALIBRATION CHECK OF THE EXISTING PRESSURE AND TEMPERATURE RECORDING INSTRUMENTS. KEEP A LOG OF ALL CALIBRATIONS.

4. RECOMMENDATIONS (LONG-RANGE FOR GENERAL UPGRADE OF THE FACILITIES)

(A) REPLACE PRESSURE INSTRUMENTS WITH CHEMICAL SEALED PNEUMATIC PRESSURE TRANSMITTERS/PNEUMATIC RECEIVER RECORDERS. ADD ALARMS (AUDIBLE AND VISUAL) FOR HIGH PRESSURE. INSTALL LARGE DIAL PNEUMATIC INDICATING RECEIVER GAUGES FOR PRESSURE.

(B) REPLACE TEMPERATURE INSTRUMENTS WITH DUAL THERMO-COUPLES (ONE FOR DIGITAL TEMPERATURE INDICATION FOR EACH REACTOR: ONE FOR USE WITH MV/P* TRANSDUCER FOR OPERATIONS WITH TEMPERATURE RECORDER (MV/P SHOULD INCLUDE BATTERY BACKUP FOR POWER SUPPLY)).

(C) REPLACE ALL PRESENT ELECTRIC OPERATED STEAM AND WATER CONTROL VALVES WITH MANUALLY CONTROLLED, PNEUMATIC PISTON OPERATED VALVES. VALVES TO BE PROPERLY SPECIFIED FOR FAIL-SAFE OPERATION.

(D) REPLACE ELECTRIC OPERATORS ON THE TWO-INCH MANUAL VENT VALVES WITH PNEUMATIC OPERATORS ARRANGED FOR FAIL-SAFE OPERATION.

(E) CONSIDER RELOCATION OF CONTROL ROOM AND A NEW INSTRUMENT PANEL.

(F) ADD SPEED SWITCH AND AUDIBLE/VISUAL ALARM ON AGITATOR SHAFT.

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* MILLIVOLT ELECTRICAL TO PNEUMATIC