

**CLARIFIER WASTE TREATABILITY STUDY
PHASE 1 – INFORMATION GATHERING**

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LIST OF ATTACHMENTS

Attachment 1	<i>Index of Phosphorus Files</i>
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1.0 INTRODUCTION

A clarifier at the former Rhodia, Inc. phosphorus manufacturing facility in Sliver Bow, Montana contains solidified phosphorus-rich waste. The clarifier is 100 feet in diameter, open-topped, with reinforced concrete walls and base. The clarifier walls extend above the ground approximately 0.5 feet on the south side and approximately 4.5 feet on the north, northeast and northwest sides, where the ground is somewhat lower. A metal railing approximately 3.5 feet tall is mounted on top of the west and southwest clarifier wall. The clarifier is approximately 12-feet deep, including the aboveground portion of the walls, and contains 8 to 9 feet of phosphorus rich waste, covered by more than 2 feet of water (the water cap). The waste consists of elemental phosphorus (about 20% [v/v]), water and solids such as phosphate dust, coke dust, and silica dust. The clarifier contains an estimated 500,000 gallons of crude phosphorus solids.

Rhodia retained Franklin Engineering Group to compile data regarding candidate treatment processes for phosphorus wastes, and catalog the processes according to treatment technology. This report presents these findings and includes descriptions of:

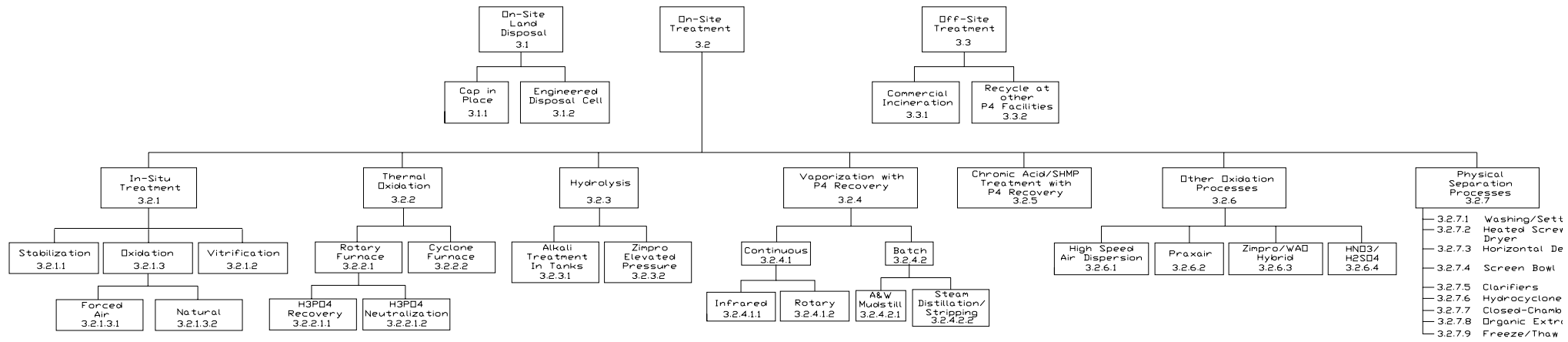
- Basic technology of each process
- Residuals generated by the process
- Maturity of the process, i.e. theoretical, bench-scale, pilot-tested, production history, etc.

Franklin's research included:

- An internet literature search
- Discussions with regulatory agencies throughout the US that dealt with operational and decommissioned phosphorus manufacturing facilities
- Information compiled by and for other decommissioned facilities
- Patents relevant to phosphorus disposal and/or treatment

This research was supplemented by Franklin's own experience at three phosphorus manufacturing or disposal facilities. An index for Franklin's phosphorus treatment and recovery files is included as Attachment 1.

Figure 1
Technology Alternatives



2.0 OVERVIEW OF TREATMENT TECHNOLOGY ALTERNATIVES AND ANCILLARY REQUIREMENTS

The candidate processes are depicted by Figure 1, Technology Alternatives. For the purposes of this report, the candidate processes are grouped into three categories:

- On-site land disposal
- On-site treatment
- Off-site treatment

The numbers in the blocks in Figure 1 refer to the applicable section number in this document. Franklin's research was focused on those technologies that have been proven in pilot-scale or production systems, or proposed by creditable sources. Our literature search, and field experience, did reveal several other processes or unit operations that may be applicable, albeit unproven, to recovery of the elemental phosphorus in the clarifier sludge. These processes are addressed in section 3.2.7: Physical Separation Processes.

Franklin participated in an extensive pilot testing program for treatment of phosphorus-rich sediments at a facility in Middle Tennessee, and we applied this experience, along with the results of other independent researchers, to the ranking used in this report.

There are several ancillary requirements such as regulatory, safety, material handling, and residuals disposal issues that must be considered when reviewing the applicability of any of these treatment and disposal technologies. Each of these topics is addressed below.

2.1 Regulatory and Safety Issues

Volume 1 of Rhodia's Waste Plan describes the ignitability, reactivity, toxicity, and radioactivity of the clarifier material. Although Rhodia disagrees, they understand that the EPA wants the clarifier material to be characterized as a D001 ignitable hazardous waste and a D003 reactive (for phosphine gas generation at toxic levels) hazardous waste for purposes of the Waste Plan evaluation, and the related survey of off-site TSDs. After performing mass balance calculations and conducting extensive sample analysis, Rhodia is confident the material does not exhibit the toxicity characteristic. Rhodia has also performed radiation surveys showing there is no indication that the clarifier material would have a gamma radiation level any higher than 95 $\mu\text{R/hr}$.

As part of the treatment option evaluation, the following regulatory and safety issues have been identified and should be considered:

- Unless EPA and MDEQ decide to waive requirements, many of the on-site treatment options would require RCRA hazardous waste treatment permits, Clean Air Act (CAA) permits for the gaseous emissions, and/or Clean Water Act (CWA) permits for the wastewater discharge. Treatment residuals may need to meet limits set in these permits, e.g. CWA discharge limits or CAA emission limits. Land-disposed residuals will also need to meet the RCRA land disposal restriction standards in 40 CFR § 268.40.
- Montana Statute 75-2-215 and Admin. Rule of Mont. 17.8.316 also place requirements on incinerators, boilers and industrial furnaces that exceed federal requirements. No such units are currently being operated in Montana. Several of the treatment and/or recovery systems described in this report may fall into this regulatory category.
- Since the crude phosphorus sludge was determined in a plea agreement to be handled as a RCRA hazardous waste, it can only be treated off-site at a RCRA-permitted facility. Even if the sludge is recycled, the recycling facility would need to have a RCRA permit unless EPA and MDEQ determine that the crude phosphorous sludge is excluded from the definition of solid waste when recycled.
- Handling of any material containing elemental phosphorus presents certain hazards. It is relatively benign when handled under water, but loss of effective water cover can expose operations and maintenance personnel to the risk of fire and respiratory hazards. Pumping systems are subject to pluggage and mechanical failure, and once the phosphorus freezes in a pump or piping system, it can be difficult to clean the system with the certainty necessary to allow safe maintenance. Small amounts of burning phosphorus can form a thin crust that blocks access to oxygen in air, but it can still burst into flame long after the spill.

2.2 Material Handling Issues

The clarifier contains an estimated 500,000 gallons of crude phosphorus solids covered by a water cap. The water cap prevents the atmosphere from contacting and reacting with the elemental phosphorus. Water losses occur as a result of leaks in the clarifier and evaporation. The water cap is maintained by an automatic water addition system. The automatic water addition system adds water when the level falls below the setpoint. The instruments are set to maintain the year-round water level at more than 2 feet above the level of crude phosphorus in the clarifier.

With the exception of the cap-in-place option, all of the on-site and off-site treatment processes ultimately require removal of the phosphorus-rich sludge from the clarifier. There are several methods for removing the material, and they can be grouped into one of two categories by the method of excavation: mechanical or hydraulic. Each method is described below.

2.2.1 Mechanical Excavation

Conventional earthworking equipment such as tracked excavators, back hoes, and clam shells, can be used to excavate the solidified sludge and transfer it to a shipping container or processing system. With careful operation, the phosphorus can be transferred with a water cover in the bucket to minimize mass burning, but there will be still be significant smoking from the occasional spill or residue that is above the water cover. The smoke consists of fine P_2O_5 particulate that produces a dense plume when even small amounts of material burn in contact with air. To capture this smoke, the clarifier and excavation system would need to be enclosed in a temporary structure. The enclosure would be operated at a slight negative pressure with the off gas treated in an air pollution control system. Air pollution control systems are described in section 2.3.2.

At a minimum, the smoke concentration inside the enclosure would require the equipment operators to wear respirators designed to treat fine particulate and inorganic acids. Phosphine monitoring may be required.

Mechanical excavation has one significant advantage over hydraulic excavation: large pieces of debris and frozen solids can be moved without size reduction. The hydraulic processes described below incorporate size reduction, i.e. melting or cutting, because the solidified material is ultimately transferred in a pipeline.

2.2.2 Hydraulic Excavation

This method of removal involves mixing of the phosphorus-rich sludge with water at the point of excavation, and transportation of the resultant slurry in a pipeline. Since the material is solid at ambient temperatures, it must be either chopped up or melted to allow pumping. Both the Glenn Springs (Occidental Chemical) and FMC processes utilized the former method; it is referred to as cutter-suction dredging. In the case of the Glenn Springs site, the dredge cutter and pump are mounted on the arm of a long-reach excavator. The FMC project was designed around a more conventional dredge, albeit small and remote controlled.

The cutters of both dredges were designed to produce solids consistent with the size of the pipeline to the treatment process. This pipeline size was dictated by the hydraulic capacity of the treatment system. The Glenn Springs system operates at approximately 1,800 gallons per minute on an 8" pipeline, with solids no larger than 3" in diameter. The FMC project was designed for approximately 400 gallons per minute in a 4" pipeline with ½" solids. Solids concentrations range from 2% to 15% by weight. For both of the projects, solids are removed from the slurry with a complex treatment system and the water returned to the excavation site for reuse. The

solids range in size from the largest mass that will pass through the cutter to fine clay size particles. Large solids can be removed from the slurry by gravity sedimentation, but the fine solids require more complex process such as polymer flocculation, basic neutralization, and filter press recovery. After separation, the phosphorus can be recovered, converted, or neutralized with one of the processes described in section 3.0.

Elemental phosphorus melts at approximately 105°F. An alternative to cutter-suction dredging relies on localized heating to soften the phosphorus-rich sediments for pumping. Some operators have used this property to ultimately concentrate or “upgrade” the phosphorus content with a process referred to at one plant as “washing”. This practice is described in section 3.2.7.1 but the actual method of removal has been referred to at different plants as the “mobile sump” or “cookie cutter” method. Heat is typically supplied by the injection of live steam or through a steam-jacketed cylinder surrounding the pump suction.

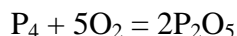
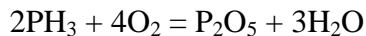
Hydraulic excavation offers the potential of reduced smoking, but it is not entirely eliminated. End-of-shift shutdowns, occasional blockages, and system maintenance will require exposing the cutter head to the air, and the residue will burn and smoke. All hydraulic dredging systems are sensitive to debris. If the object cannot be reduced in size by melting or cutting, it will not only remain in the clarifier, but it may be an impediment to further excavation. Hydraulic dredging projects also require a good deal of dilution water to maintain suspension velocity and prevent saltation. This water is usually introduced at the point of suction. In the case of “cold” hydraulic dredging, an underwater cutter is required to excavate the compacted solids. Dilution water is introduced at the cutter head. Even when the phosphorus is in the molten state, it is difficult to suspend the fine grain solids, so phosphorus-bearing sludge is frequently agitated with a high-velocity water jet to loosen it. A typical environmental dredging project will operate with about 10 weight % slurry. Additional make-up water would be required if hydraulic dredging is selected for use with any of the treatment options identified in section 3. Some of this water could be recycled, but it would ultimately have to be treated prior to discharge. Treatment of “phossy water” is addressed in section 2.3.3

2.3 Residuals

All of the processes described in the report generate residuals. These streams include solids, gasses, and liquids including pure P_4 . For consistency, the treatment and/or disposition of residuals from all of these processes are described below.

2.3.1 Off-Gas with P_4 and PH_3

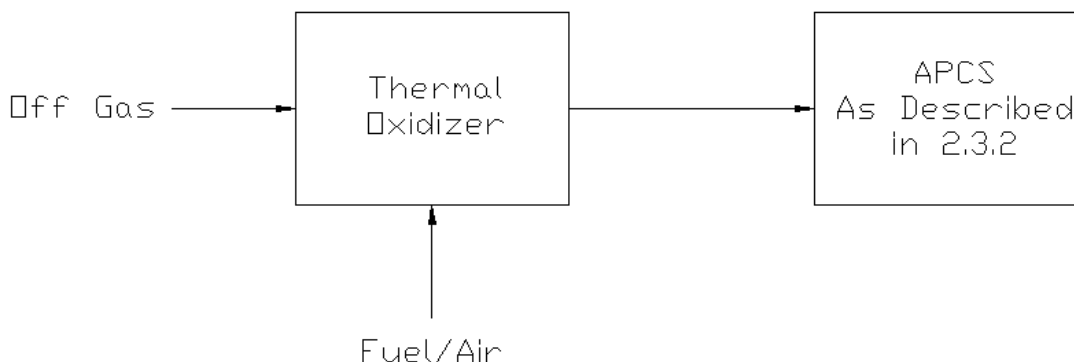
Gases containing P_4 and PH_3 are treated in a thermal oxidizer, which combusts the P_4 and PH_3 . The combustion reactions are depicted by the following equations:



A temperature of about 1400 °F is maintained in the thermal oxidizer by using natural gas as a supplemental fuel. Natural gas firing is required to control the thermal oxidizer at a minimum temperature in order to assure that the PH₃ is destroyed. The hot combustion gases are then routed to air pollution control equipment to remove the P₂O₅.

A typical air pollution control system would consist of a rapid quench chamber, high energy venturi scrubber, induced draft fan, and stack as described in section 2.3.2. Water treatment for this system is described in section 2.3.4, and solids disposal is described in section 2.3.5.

Flow Diagram:



2.3.2 Off-Gas with P₂O₅/ and H₃PO₄

Gases containing P₂O₅ and H₃PO₄ are typically treated with an air pollution control system consisting of a rapid quench chamber, high energy venturi scrubber, induced draft fan, and stack. The hot gases would flow to the rapid quench chamber where water sprays would be used to quench (cool) the hot gases to temperatures in the range of 180 °F. Fresh water would be sprayed through nozzles at the top followed by water sprays containing recirculated water at lower levels in the tower. The hot gases would enter the top of the quench chamber and flow downward where they would come in contact with water droplets formed by the fresh water spray. By contacting the hot combustion gases with the fresh water first, formation of secondary particulate is minimized. If the hot gases initially came into contact with the recirculated water, there would be the potential for secondary particulate formation where the water evaporated and the dissolved solids were released as fine solid particulate. The quench chamber would remove some of the P₂O₅ and H₃PO₄ but the majority of the removal would occur in the scrubber.

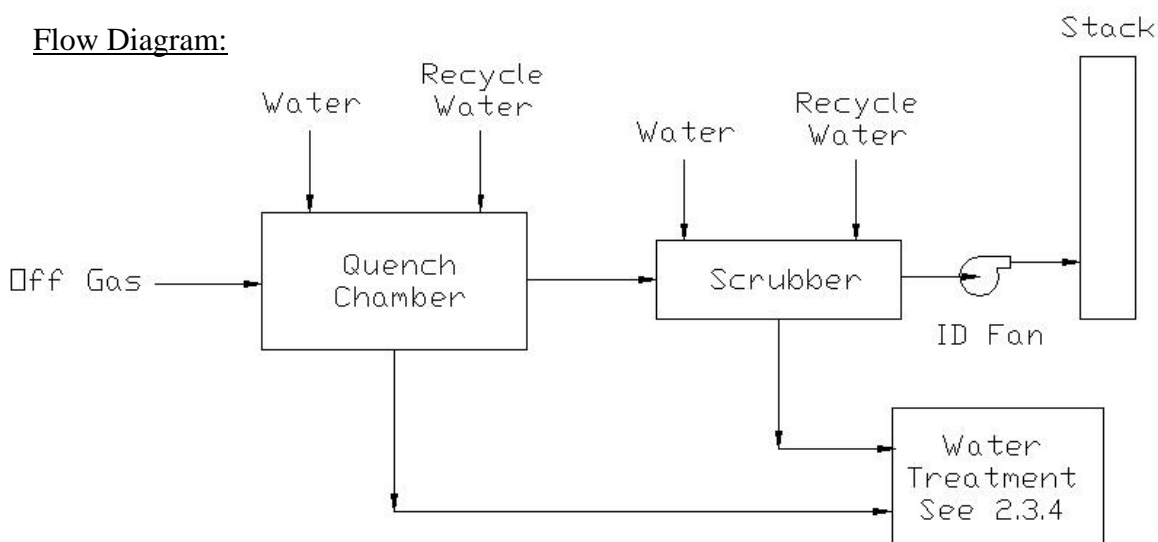
Water from the quench chamber is sent to the waste water treatment plant described in section 2.3.4. Part of the treated water is recirculated to the quench chamber in order to reduce water usage, but this causes dissolved solids to build up in this water. Dissolved solid content is controlled by regulating the amount of water that is returned in the recirculation loop and therefore, the amount of freshwater that is added.

After the hot combustion gases have been quenched, the gases are then routed to a high-energy venturi scrubber for P_2O_5 and H_3PO_4 removal. The scrubber is typically designed for a pressure drop of 50-60 inches of water in order to remove the submicron P_2O_5 particulate and H_3PO_4 . Water is used as the scrubbing liquid. The P_2O_5 reacts with the scrubber water to form phosphoric acid. Again, part of the water is typically recirculated in order to minimize water use after first going to the wastewater treatment plant. Dissolved and suspended solids concentration is controlled by regulating the amount of recirculated water as high solids content can affect the overall performance of the scrubber.

The gas exits the high-energy venturi scrubber and passes through a mist eliminator to remove entrained water droplets. The mist eliminator can be a cyclone, or a vessel that contains a mist eliminator element such as a wire mesh pad or chevron vane mist eliminator.

Finally, the scrubbed combustion gas pass through an induced draft fan. This fan is necessary in order to produce the large pressure drop required across the scrubber. The gas then is routed to a stack for discharge to the atmosphere.

Flow Diagram:

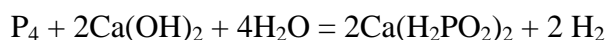


2.3.3 Phosphy Water/Hydrolysis Treatment

Condensation of phosphorus vapor with direct contact cooling water generates “phosphy” water. Phosphy water contains small particles of elemental phosphorus along with dissolved oxides and suboxides of phosphorus, all of which cause the water to become acidic. Treatment of this water is very similar to the process described in section 3.2.3.1 except that the phosphy water tends to have a lower P₄ content and does not typically have as high a sludge content.

Treatment of this water can be accomplished by hydrolysis with an alkaline base such as hydrated lime (Ca(OH)₂). Treatment is typically performed in a batch mode in a stirred pressure vessel. After the phosphy water is pumped into this vessel, treatment starts by first bringing the water up to a temperature of about 160 °F. Hydrated lime solution is then slowly added to the vessel until a pH in the range of 10-11 is reached. As the pH rises, the hydrolysis reaction generates large amounts of gas. This evolution of gas raises the pressure in the vessel and the gas is released on pressure control to downstream equipment. The addition of lime is controlled by pressure in the vessel and is stopped when the pressure reaches a high value. With decreasing pressure, the lime addition is started again. Lime addition is continued in this manner until the pH remains constant for an extended period of time and the pressure remains at or near atmospheric, which indicates that the reactions have been completed. The treated water is then ready for discharge from the vessel.

The reaction between the hydrated lime and P₄ is described by the following reactions:

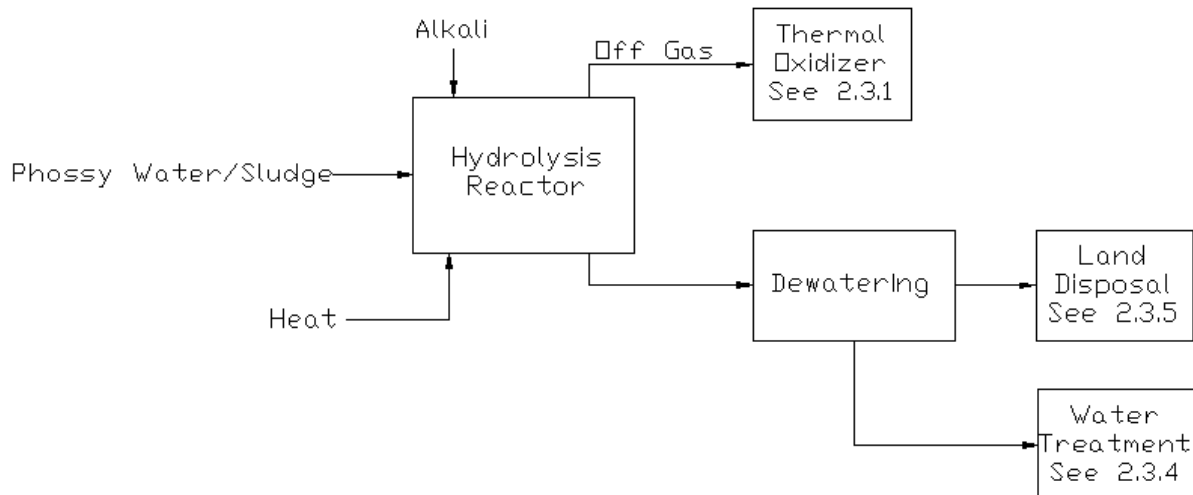


However, these reactions do not fully describe the chemistry that occurs. It is known that for each 3.5 pounds of P₄, approximately 1.0 pound of PH₃ is formed. Similarly, approximately 0.02 pounds of H₂ is formed for every pound of PH₃ formed.

The liquid is then pumped to a pressure leaf filter where the precipitated solids and excess hydrated lime are removed from the liquid. The recovered solids are then sent to a landfill for disposal and the filtrate is sent to a water treatment plant. A typical plant for treating water from a phosphorus plant is described in section 2.3.4.

The evolved gases from the hydrolysis reaction are treated in a thermal oxidizer, as described in section 2.3.1. The hot combustion gas is then treated in an air pollution control system as described in section 2.3.2.

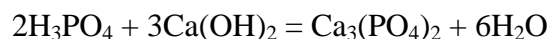
Flow Diagram:



2.3.4 Scrubber Water/Wastewater Treatment

Scrubber water is sent to a waste water treatment system. This system will typically consist of neutralization, clarification, and sand filtration.

Water from the scrubbing system will typically contain phosphoric acid. The acidic wastewater will first be neutralized with an alkaline base such as hydrated lime. The hydrated lime will react with the phosphoric acid according to the following reaction:



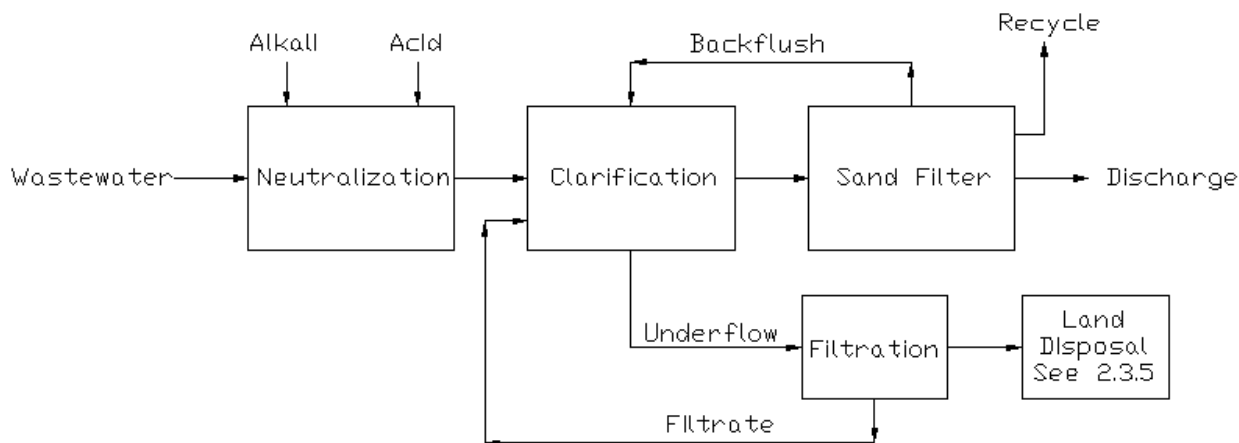
Water from sources with a high pH (such as from hydrolysis) can be fed to this system. In this case, acid would be added if necessary to lower the pH.

After neutralization, the water will flow to a clarifier where the solids will be separated from the main water stream. Overflow from the clarifier will flow to a sand filter for final polishing before discharge. The underflow will flow to a filter press for solids removal and then the water will be routed back to the clarifier.

The filtered solids would then be transported to a hazardous waste landfill.

The treated water would then be discharged or disposed of at an off-site facility.

Flow Diagram:



2.3.5 *P₄*-free Solids

This material consists of ash and inert material that is free of P_4 . Even though this material is free of P_4 , it must be transported to a hazardous waste landfill for disposal unless an exemption from the derived from rule can be obtained.

Some of the thermal treatment processes described in this report produces solid metaphosphoric, orthophosphoric, and/or pyrophoric acid. The regulatory status of these compounds should be investigated if thermal treatment is selected.

3.0 TREATMENT TECHNOLOGY DESCRIPTIONS

3.1 On-site Land Disposal

3.1.1 *Cap in Place*

This process description was taken from the Rhodia Waste Plan. The cost information was removed, and the Rhodia text was edited for brevity to match the other technologies investigated in this report.

Process Description:

Under this option, a cap would be installed over the clarifier to meet or exceed the design that EPA Region 10 recently approved for closure of Ponds 8S and 15S at the FMC/Astaris facility. The Astaris-type cap will provide about 16 feet of cover material over the crude phosphorus in the clarifier. The cap includes a 60 mil flexible membrane liner, a geosynthetic clay liner, and a biotic protection layer. When all phases of the cap are completed and adequately sloped to promote proper run-off, the Astaris-type cap will necessarily extend beyond the clarifier and cover other nearby production areas, including a currently-capped burial area, which contains the same type of crude phosphorus material as the clarifier. As a result, this larger cap will provide additional environmental benefit beyond the clarifier material.¹ The Astaris-type cap would be inspected twice a year (after the spring snow melt and before significant snow in the fall) and after precipitation events that exceed the 25-year, 24-hour storm design criteria. The cover would be maintained (e.g., mowing and inspection), and repairs would be made whenever necessary to correct the effects of settling, erosion or other relevant events. A 10-foot fence and signage, which would warn not to dig or trespass and identify the hazards and a contact telephone number, would be maintained around the cap and repaired and replaced whenever necessary. Rhodia would maintain the cap, fencing and signage for as long as it owns the property, and require its successors, through a combination of contractual obligations and institutional controls, similarly to maintain the cap, fence and signage.

¹ Prior to construction of the cap, additional sampling will be conducted in the areas beyond the clarifier and the burial area that will be under the cap. The objective of this sampling is to characterize the constituents of concern in the soil in this area. After this sampling is completed, Rhodia would construct all phases of the cap, or if EPA and MDEQ prefer, would construct the cap in phases that are consistent with timelines that may otherwise be established for remediation of other plant areas beyond the clarifier that may require a cap. For example, Rhodia could first install all of the subgrade up to the flexible membrane liner, and, at a later time, install the liner and complete the remainder of the cap when instructed to do so by the Region.

A groundwater monitoring program would be implemented around the cap that meets the substantive requirements of RCRA post-closure groundwater monitoring at 40 CFR § 265.90 through § 265.94. The groundwater monitoring wells would be maintained and repaired, as necessary.

Rhodia expects that 30 years of groundwater monitoring will be more than adequate to establish groundwater quality trends and demonstrate the protectiveness of the cap. Current data show that elemental phosphorus in the groundwater degrades to non-toxic compounds and concentrations within 30 feet of the clarifier, as would be expected based on the chemistry of this element. Modeling discussed in the Rhodia Waste Plan (pages 76-78) shows that once the clarifier is capped with an enhanced cap, the incremental risk level to humans of cancer from the potential leaching from the capped clarifier is 10^7 (1 in 10 million) for arsenic and 10^9 (1 in 1 billion) or lower for other heavy metals. These risks are well below EPA's typical 10^4 to 10^6 drinking water standards. In light of this, and so as not to inflate the expected cost of this groundwater measure, Rhodia has estimated the groundwater monitoring and maintenance costs over a 30 year period. The RCRA regulations allow the Regional Administrator or state authority to require longer term groundwater monitoring, and Rhodia would undertake such longer-term monitoring, if it is determined to be necessary.

Rhodia would also monitor, and as necessary, collect and treat with a carbon system any phosphine gas that is generated from under the cap. A system of pipes will be installed under the cap to collect any gas, and it will be sealed to prevent emissions to the atmosphere and air entering the subgrade. This proposal includes BAH's recommendation to include in the cost estimate the expected costs for a carbon treatment system, which is the same type of system Region 10 approved for FMC at Pocatello. The phosphine monitoring and collection systems would also be inspected routinely and maintained as necessary. Since little phosphine generation is expected based both on the subsurface conditions (neutral pH, about 60°F, and no agitation) and FMC's experience with not seeing appreciable phosphine in the monitoring systems under its completed caps, Rhodia has estimated phosphine collection and treatment for five years to avoid overstatement of those costs. Rhodia would monitor for ten years, i.e., five more years after collection and treatment, to establish that longer term collection and treatment is not necessary. If a longer period of collection and treatment is determined to be necessary, Rhodia would continue to operate and maintain the phosphine system.

The RCRA §7003 order could obligate Rhodia and its successors to undertake the post-closure care (monitoring, maintenance, repair, inspections, reporting, etc.) and to maintain the financial assurances noted above. Since financial assurances are based on the costs of third-parties doing the work, and since the Region and/or state would be the designated beneficiaries of the financial assurance mechanism, e.g., letters of credit, trust or insurance, there will be ample money available to the Region and/or state to ensure that any necessary maintenance tasks are completed in the unlikely event that Rhodia or its successors were to become insolvent.

Institutional Controls

Institutional controls would also be put into place to protect the cap from unauthorized disturbance, to ensure that groundwater associated with the capped area is not consumed, and to require cap maintenance. As discussed in EPA's institutional controls guidance documents, these institutional controls would be "layered" to provide redundant assurances that the capped material will not pose a future risk. All of the institutional controls are based on Montana law authorizing the controls, and in most cases, on specific situations where the controls have been used at similar sites in Montana. The specific types of controls and the precedent for them are briefly noted below:

- **Governmental Controls** – Rhodia would work with the Silver Bow County and/or state authorities to develop and have adopted prohibitions on disturbance of the capped area and the drilling of drinking water wells in the upper aquifer downgradient from the clarifier up to the Streamside Tailing Operable Unit. For example, authority for adoption of such prohibitions appears at Mont. Code Ann. 85-2-506.
- **Private Property Law Restrictions** – Rhodia would place on the title and other land use records land use restrictions that prevent disturbance of the capped area and use of contaminated groundwater for drinking water purposes. In addition, Rhodia would ensure that the title would provide for an easement that would allow access to Rhodia, its successors, and third-parties, including governmental agencies, to conduct the monitoring and maintenance of the cap, the groundwater wells, and the phosphine system. A covenant would also be placed on the land requiring perpetual care and maintenance of the cap, fence and signage by Rhodia and future owners. Montana Code Annotated § 75-10-727 expressly authorizes the establishment of these covenants and easements in the land records, and they can be established at any time, i.e., they need not be associated with a property conveyance.

- Informational Devices – Rhodia would also place in the land records a notice identifying the fact that the clarifier material has been capped in place, that the cap should not be disturbed, and that groundwater downgradient from the capped area should not be consumed so long as it exceeds drinking water standards.
- Enforcement Tools – The RCRA §7003 order could require Rhodia to have included in the appropriate land records the covenants, easement, and notices noted above, and to use best efforts to obtain enactment by the County and/or the state of the governmental controls noted above. In addition, Rhodia and its successors could be ordered to provide notice to EPA Region 8 and MDEQ of any land transfer involving the capped clarifier area.

Note that similar types of institutional controls have been established at the Montana Pole and Treating Plant Superfund site in Butte (see September 3, 1993 ROD), in the Streamside Tailings Operable Unit Consent Decree (see subparagraph 40.a. and b.), and at the Anaconda Company Smelter (see 1994 ROD and Land Use Master Plan).

Byproducts/Residuals:

Any phosphine collected from beneath the cap membrane will be collected and treated with a carbon system similar to that approved by Region 10 for the FMC facility at Pocatello.

3.1.2 *Engineered Land Disposal Cell*

Process Description:

In this process, the contents of the clarifier would be transferred to an engineered cell with an appropriately designed liner and cap system. The issues associated with transferring this material are discussed in sections 2.1 and 2.2. With either mechanical or hydraulic transport, the disposal cell would remain full of water until the transfer was complete. The water would be pumped off and treated as part of the capping process.

The capping plan described in section 3.1.1 included the clarifier in a larger plan to cap the surrounding area. This plan for transfer to an engineered disposal cell would have merit if there was a need or advantage to decoupling the remediation of the clarifier from that of the surrounding facility, and the cell was designed with an approved inter-containment leak detection system that would eliminate the need for groundwater monitoring.

Byproducts/Residuals:

The phosphorus would remain on-site, protected by an engineered cap and liner.

Gas: Any phosphine collected from beneath the cap membrane will be collected and treated with a carbon system similar to that approved by Region 10 for the FMC facility at Pocatello.

Liquids: A considerable amount of phosphy water would be generated during the transfer process. The water could be treated on-site with the hydrolysis system described in section 2.3.3, or shipped off-site for disposal at a permitted commercial facility.

Solids: Solids from the phosphy water hydrolysis system would be concentrated with a filter press and landfilled on site, as at other similar facilities.

State of Development:

Engineered disposal cells are in use at the FMC facility in Pocatello Idaho.

3.2 On-site Treatment

3.2.1 In-Situ Treatment

3.2.1.1 Stabilization

Process Description

Stabilization involves the addition of a cementitious material to effect a pozzolanic reaction that reduces the mobility of the contaminants in the waste material. It is widely used for wastes containing metals prior to landfilling. In addition to the chemical changes, stabilization increases the mechanical strength of the waste material. This property is also desirable for landfilling, and it is referred to as solidification. The reagents used for stabilization are alkaline in nature, and phosphine and hydrogen gas will be generated when they are mixed with phosphorus. In addition, the phosphorus-rich sludge would need to be either melted or finely ground for efficient mixing with the stabilizing agent. This technology has little application with elemental phosphorus.

3.2.1.2 Vitrification

Process Description:

In-situ vitrification (ISV) involves heating of the waste to a sufficient temperature, usually 2,500 °F to 3,600 °F, that the material fuses into a glassine monolith.

Byproducts/Residuals:

Gases: Water and phosphorus from the sludge would evaporate prior to the clarifier reaching the fusion temperature. The vapors would need to be collected and condensed with a system similar to those described in section 3.2.4.

Liquids: Condensed water would have slight amounts of P_4 and would need to be treated with the neutralization process described in section 2.3.4. Condensed phosphorus could theoretically be recovered in a system similar to that used with the batch still described in section 3.2.4.2.1.

Solids: In theory, the waste will be solidified in a monolith.

State of Development:

The process is sensitive to the moisture content, chemistry and conductivity of the waste. There is no record of successful laboratory or pilot testing on phosphorus-bearing sludge in our files.

3.2.1.3 Oxidation

3.2.1.3.1 Forced Air Oxidation

Process Description:

This process would involve melting the clarifier sludge in place, and injecting air to oxidize the phosphorus underwater. The chemistry is similar to the ex-situ air dispersion oxidation process described in section 3.2.6.1. Other oxidizers could be used, but the theory remains the same. The phosphoric acid generated during the oxidation process would be removed and neutralized with an external treatment system. The clarifier would need to be enclosed to contain the P_2O_5 emissions, and the off-gas would need to be treated prior to discharge. The requisite off-gas treatment process is described in section 2.3.2. A mechanical agitator would be required to enhance the oxidation process. The concentration of gases inside the enclosure may reach explosive concentrations and necessitate special equipment designs and handling practices including the possibility of remote control equipment. The acid removal rate would need to be sufficient to prevent damage to the concrete shell of the clarifier.

Byproducts/Residuals:

Liquids: A dilute hot acid stream would be produced by the underwater oxidation reaction, and a water treatment system would be required to neutralize this stream. See section 2.3.4.

Gases: Off gases from the clarifier would have to be treated in a scrubber, and possibly a thermal oxidizer if phosphine gas is present. See section 2.3.2 and 2.3.1.

Solids: The residual sludge in the clarifier would contain some amount of phosphorus, but it may be low enough that it can be land-disposed. Sludge would also be produced by the acid neutralization process and the scrubber water treatment system as described in section 2.3.4.

State of Development:

No history of successful pilot or production scale in-situ forced air phosphorus oxidation demonstrations has been found.

3.2.1.3.2 Natural Oxidation

Process Description:

This process involves oxidation of phosphorus-rich sludge as a result of drying from natural evaporation. It is generally referred to in almost every publication dealing with elemental phosphorus remediation, but none proposes a material handling or emissions collection system that would meet contemporary standards for protection of human health and the environment.

Byproducts/Residuals:

Liquids: Water from the sludge would evaporate into the atmosphere.

Gases: Smoke from the burning sludge would disperse into the atmosphere.

Solids: The amount of phosphorus in the dry sludge residue would be a function of how well the sludge was turned during the drying process. If allowed to smolder without turning, the burning phosphorus will form a crust and the underlying material will not receive enough oxygen to burn.

State of Development:

The only record of effective air drying of sludge involved low concentrations of phosphorus. This project did not utilize an emissions collection system and excessive smoking became an issue. No history of successful pilot or production scale demonstrations with an emissions collection system has been found.

3.2.2 Thermal Oxidation

This section describes three systems for burning phosphorus-rich sludge in high temperature systems. All of these systems require that the compacted clarifier sludge be converted to a pumpable form for consistent feed to the combustion chamber. This preparation could include melting and pumping at elevated temperatures, or mechanical size reduction for pumping at ambient temperatures. With all of these systems, there is a significant cost associated with evaporating the water in the sludge. Most, if not all, high temperature systems included a

dewatering process upstream of the thermal treatment process. Low temperature oxidation systems are described in section 3.2.6.

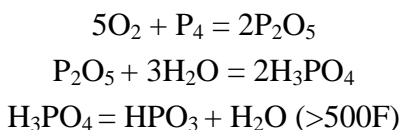
3.2.2.1 Rotary Furnace

Rotary furnace treatment options include systems with phosphoric acid recovery and phosphoric acid neutralization.

3.2.2.1.1 Thermal Oxidation Rotary Furnace with H_3PO_4 Recovery

Process Description:

Thickened P_4 sludge is fed to a transportable direct-fired rotary kiln similar to that used for on-site incineration of organic wastes. Auxiliary fuel and combustion air are needed to provide the necessary heat input at low P_4 levels. After the water contained in the sludge is evaporated, phosphorus reacts with oxygen in the combustion gas according to the following equation:



Some metaphosphoric acid (HPO_3) is also formed during this process. The P_2O_5 exits the dryer as a vapor in the gas stream, which is quenched and then scrubbed. When the gas is scrubbed with water, phosphoric acid (H_3PO_4) is formed and collected. The quench/scrubber water balance must be controlled such that the H_3PO_4 is concentrated, and a filtration step is required to produce a useful product.

Byproducts/Residuals:

Product: H_3PO_4 is generated when P_2O_5 contacts the quench/scrubber solution. As the scrubber solution circulates, H_3PO_4 is concentrated in the scrubber sump. This solution is collected, filtered and sold.

Solids: Ash from the rotary furnace consists mostly of the inerts contained in the crude sludge. The ash stream can also contain metaphosphoric acid formed in the oxidizer, and potentially ortho and pyrophosphoric acid. Section 2.3.5 describes disposal of the inert material, but the possibility of these other compounds should be considered when selecting the method of treatment and disposal facility.

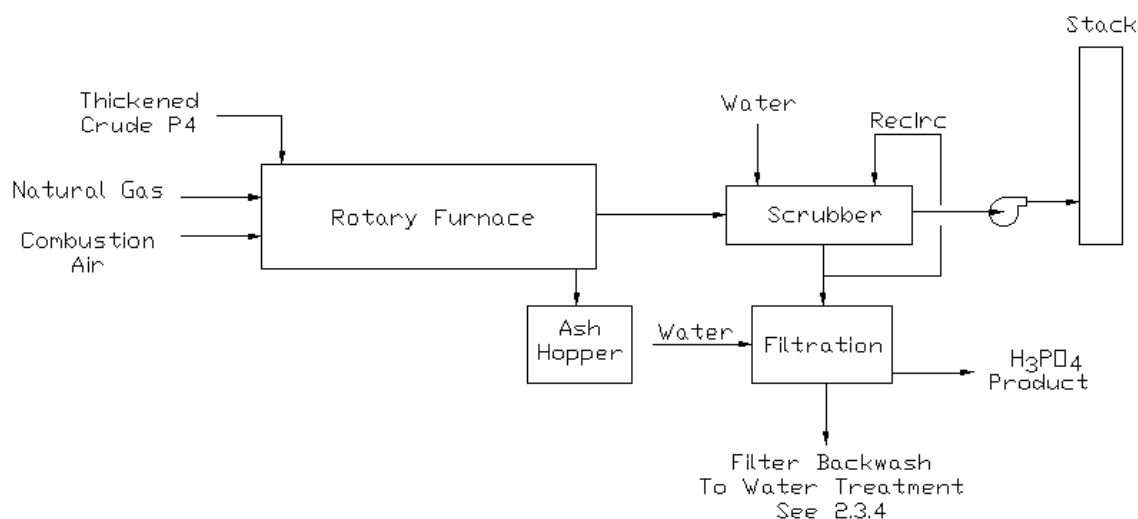
Liquids: The wastewater generated from this process is the primarily the filter backwash solution which contains suspended solids and H_3PO_4 . This solution is neutralized in a water treatment system, described in section 2.3.4.

Gases: Stack emissions consist of a saturated CO_2 and air stream which results from natural gas combustion in the oxidizer and excess air supplied for the thermal oxidation process. Small quantities of P_2O_5 or H_3PO_4 mist are emitted, depending on scrubber efficiency.

State of Development:

Manufacture of phosphoric acid from elemental phosphorus is a well proven process. Production scale fixed-base phosphoric acid burning furnaces are operated by Crane Army Ammunition plant in Crane, Indiana, and Samancor in South Africa. The Crane system is designed to process pure phosphorus and is unsuitable for phosphorus-bearing sludge. No history of transportable acid burning systems has been found.

Flow Diagram:



3.2.2.1.2 Thermal Oxidation Rotary Furnace with H_3PO_4 Neutralization

Process Description:

Thickened P_4 sludge is fed to the same type of rotary dryer system described above, but in this process the acid is neutralized and not shipped off site.

Byproducts/Residuals

Solids: Ash generated by the rotary furnace consists mostly of the inerts from the crude sludge. The ash stream can also contain metaphosphoric acid formed in the oxidizer, and potentially ortho and pyrophosphoric acid. Inert material disposal is addressed in section 2.3.5, but the

possibility of these other compounds should be considered.

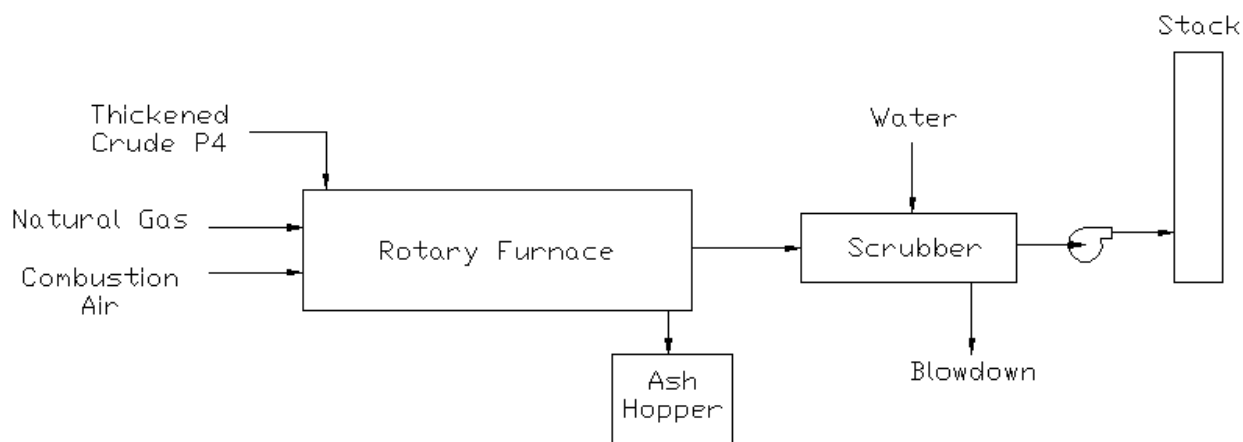
Liquids: The wastewater generated from this process is the scrubber blowdown solution, which contains suspended solids and H_3PO_4 . The H_3PO_4 is generated when P_2O_5 contacts the scrubber solution. This solution is acidic and it is neutralized with lime or caustic as described in section 2.3.4.

Gases: Stack emissions consist of a saturated CO_2 and air stream which results from natural gas combustion in the oxidizer and excess air supplied for the thermal oxidation process. Small quantities of P_2O_5 or H_3PO_4 mist are emitted, depending on scrubber efficiency.

State of Development:

This process has been in full-scale operation at the GSHI facility in Columbia, Tennessee since about 2000.

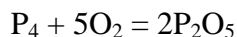
Flow Diagram:

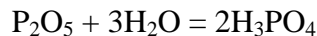


3.2.2.2 Cyclone Furnace

Process Description:

Sludge is burned in a 2-zone conical or cyclone burner with 25-40 % excess air. The process is limited in that the sludge P_4 content must be greater than 20 wt%, and preferably should be in the range of 40-70 wt%. The cyclone burners reportedly cannot handle less than 35 wt% P_4 and the 2-stage conical burner cannot handle less than 20 wt%. Burner operating temperatures range from 1742-3272 °F with temperatures greater than 2552 °F required to minimize lower oxide formation. Dirt in the sludge typically melts into a phosphate slag which is tapped out and solidified. The P_2O_5 that is produced during the combustion process is hydrated and scrubbed to make phosphoric acid. The reactions can be depicted by the following equations:





Equipment for the cyclone burner consist of a heat exchanger, cyclone burner, separator, scrubber, sumps, and pumps for liquid streams.

Byproducts/Residuals:

Product: Impure H_3PO_4

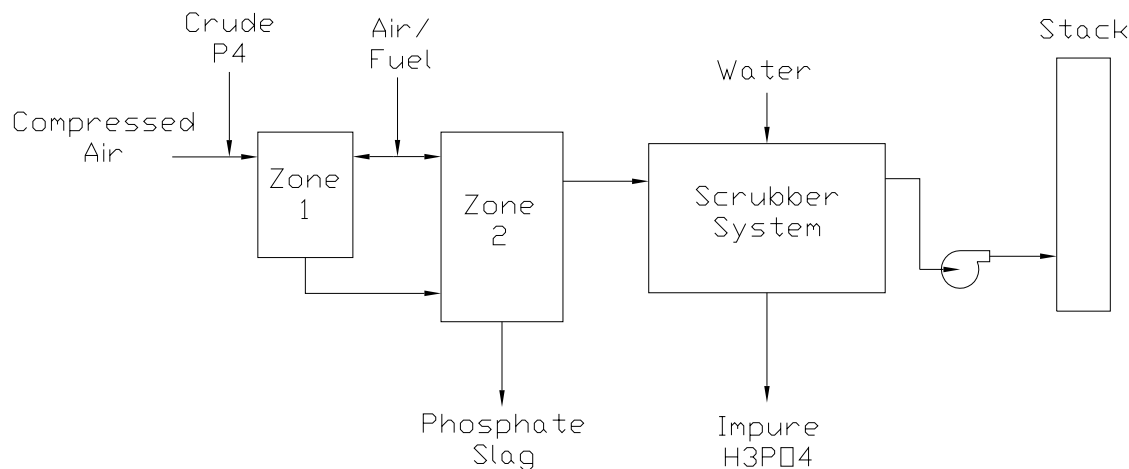
Solids: A glassy phosphate slag is generated during oxidation. This material must be tapped and drained periodically. Disposal of this material is discussed in section 2.3.5.

Gases: Small quantities of P_2O_5 or H_3PO_4 mist are emitted, depending on scrubber efficiency.

State of Development:

This is proven technology for P_4 -rich streams and is presumably being used in Europe where the paper was published. The narrow range of acceptable phosphorus concentrations prevents this technology from being directly applicable to the Rhodia project.

Flow Diagram:



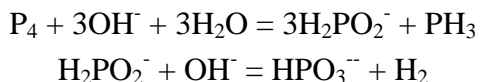
3.2.3 Hydrolysis

3.2.3.1 Alkali Treatment in Tanks

Process Description:

Phosphy water and sludge are transferred into a stirred batch reactor and heated to a temperature greater than 140 °F. A source of hydroxide ion (typically hydrated lime) is then added while continuing to stir the reactor contents. A pH of ~11 is maintained. Phosphorus reacts with the

hydroxide according to the following reactions to form hypophosphite ion (H_2PO_2^-) and phosphite ion (HPO_3^{--}), along with the gaseous components phosphine and hydrogen.



Phosphine and hydrogen gas produced by this process are typically combusted in a thermal oxidizer at temperatures above 1400°F to form water vapor and P_2O_5 . The P_2O_5 is then scrubbed with water, producing a phosphoric acid stream which can be neutralized or potentially sold as product, with appropriate concentration and cleanup.

Byproducts/Residuals

Solids: The solid residue in the hydrolysis reactor bottoms stream consists primarily of inerts (dirt), unreacted lime, and insoluble calcium phosphite (CaHPO_3).

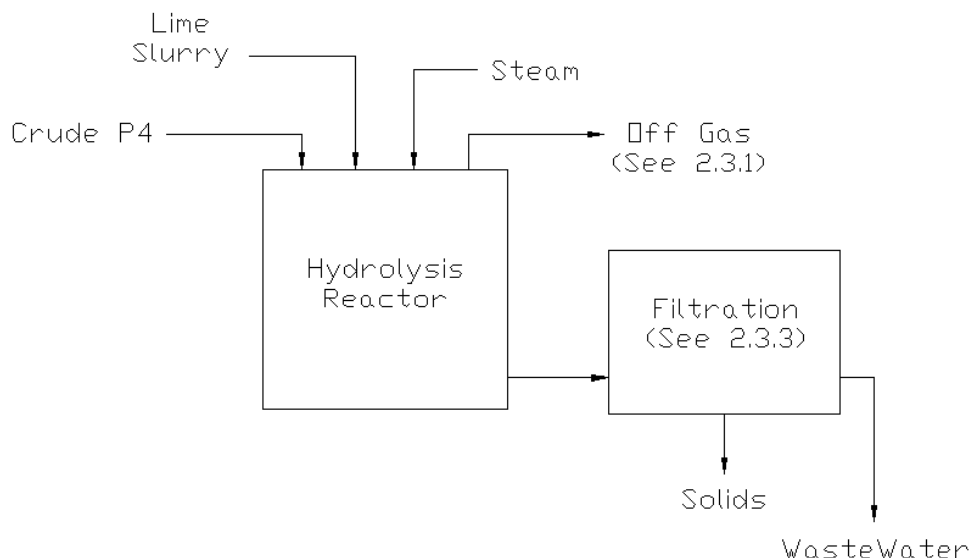
Liquids: The wastewater generated from this process contains suspended solids and soluble calcium hypophosphite, $\text{Ca}(\text{H}_2\text{PO}_2)_2$. Treatment of this water would be similar to that described in section 2.3.4.

Gases: Gases produced during hydrolysis include phosphine (PH_3), hydrogen (H_2), and water vapor. N_2 used for blanketing the hydrolysis reactor is also included in the gas stream. Refer to section 2.3.1 for a description of the off-gas treatment system.

State of Development

This process has been in full-scale operation for treating a waste stream with low concentrations of P_4 at the GSHI facility in Columbia, Tennessee since about 2000. Because this process is based on pumping the phosphorus sludge into the reactor, there must be some method of size reduction that produces sub-1/2" solids. It may be covered, in whole or in part, by US patent 4402833.

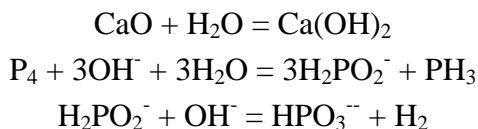
Flow Diagram:



3.2.3.2 Zimpro Elevated Pressure Hydrolysis

Process Description:

P₄ sludge is pumped to an in-line static mixer where it is blended with lime slurry before entering the anoxic reactor. This reactor operates at a pressure of approximately 600 psig and a temperature of about 464 °F. The reactor is a vertical up-flow column designed for a residence time of about one hour. Phosphorus reacts with the hydroxide, according to the reactions below, to form hypophosphite ion (H₂PO₂⁻) and phosphite ion (HPO₃⁻), along with the gaseous components phosphine and hydrogen.



The overhead gas stream produced in the reactor contains phosphine, hydrogen, and water. This stream is routed through a cooler before being throttled to about 50 psig across a control valve and fed to a separator where the gas and liquid phases are separated. The gas is routed to an on-site burner for thermal treatment. The water and reactor blowdown streams are sent to a wastewater treatment system for disposal.

Byproducts / Residuals

Solids: The solid residue from the reactor consists primarily of inerts (dirt), unreacted lime, and insoluble calcium phosphite (CaHPO₃). Disposal of this material would be as described in section 2.3.3.

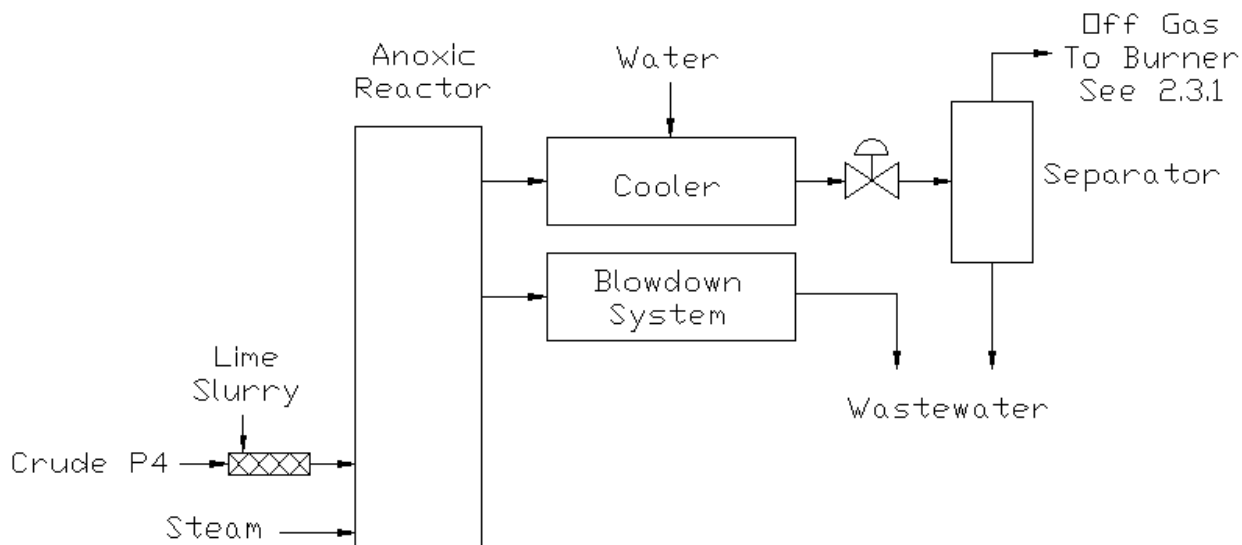
Liquids: The wastewater generated from this process contains suspended solids and soluble calcium hypophosphite, $\text{Ca}(\text{H}_2\text{PO}_2)_2$. Treatment of this material would be similar to that described in section 2.3.3.

Gases: Gases produced during hydrolysis include phosphine (PH_3), hydrogen (H_2), and water vapor. Refer to section 2.3.1 for a description of treatment.

State of Development

This process was based on pilot tests performed at US Filter/Zimpro facilities for FMC (Idaho). A full scale commercial unit was installed at FMC but never operated. As with the systems described elsewhere in this report, this process is usable only if the sludge is processed to include only fine-grain particles.

Flow Diagram



3.2.4 Vaporization with P_4 Recovery

3.2.4.1 Continuous Vaporization

This section describes systems in which the clarifier sludge is continuously fed into a heated chamber to vaporize the elemental phosphorus. Two batch vaporization systems are described in section 3.2.4.2.

3.2.4.1.1 Infrared Vaporization

Process Description:

The batch IR vaporization process developed by McLaren/Hart used a combination of infrared heating and air stripping to treat soil containing phosphorus. Although the title of the system implies a vaporization process similar to that described in section 3.2.4.1.2, the available literature indicates the unit was operated in a low-temperature oxidizing mode when tested on phosphorus-bearing waste.

There is literature reference to a high-vacuum IR system that may vaporize phosphorus, but no details or operating history are available. If this system has any applicability for use with phosphorus, the chamber must be heated above 522 °F to evaporate the water and phosphorus. The gas would be conveyed to a quench chamber, or other device, where the P_4 is condensed for recovery. Some phosphorus will remain in the vapor phase after the condensation step and it must be removed by a thermal oxidizer and downstream P_2O_5 scrubber. Phosphine gas formed by the reaction of P_4 with water vapor must also be destroyed in the thermal oxidizer.

Byproduct/Residuals:

The residuals from a true vaporizer system are described below in section 3.2.4.1.2

State of Development:

A unit demonstrated in Ogden, UT was used to treat soil with low quantities of phosphorus. There is no evidence that the system has been further developed since the demonstration.

Flow Diagram:

Not Available

3.2.4.1.2 Rotary Vaporization

Process Description:

In this continuous process, dewatered sludge is fed to a heated rotary drum where the water and P_4 are evaporated. The drum is indirectly heated through its stainless steel shell to vaporize the P_4 . Temperatures in excess of 522 °F must be reached in order to completely vaporize the P_4 . A carrier or purge gas must be added in order to sweep the evaporated P_4 out of the drum, but the purge gas must be free of oxygen to prevent burning inside the drum. The gas is conveyed to a quench chamber where the P_4 is condensed for recovery. Some phosphorus will remain in the vapor phase after the condensation step. This phosphorus must be treated by a thermal oxidizer and downstream P_2O_5 scrubber. Phosphine gas formed by the reaction of P_4 with water vapor must also be destroyed in the thermal oxidizer.

Byproduct/Residuals:

Products: Vaporizers produce saleable phosphorus, but a high-efficiency filter is required to meet commercial standards.

Solids: Inert material is discharged from the vaporizer drums through dry or wet draft seals. The characteristics of this material varied considerably from system-to-system, but most operators reported that it contained only trace amounts of red and white phosphorus.

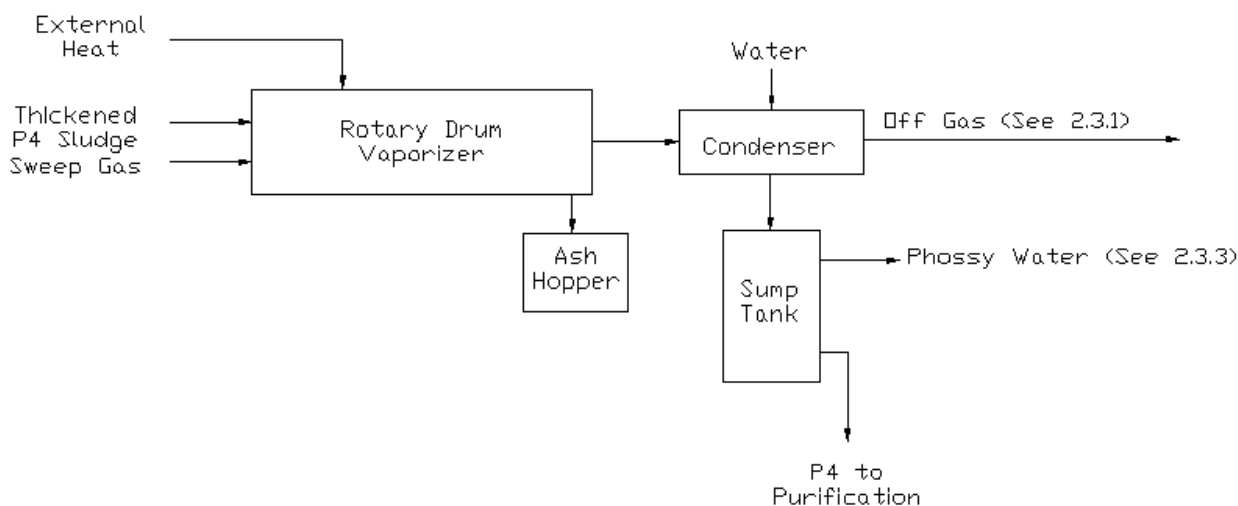
Liquids: The condenser generates phoshy water and the downstream scrubber system generates blowdown that could require additional treatment prior to discharge. Refer to sections 2.3.3 and 2.3.4 for a description of treatment for these two water streams

State of Development:

Rhodia, and its predecessor Stauffer, operated these systems at three facilities in the US and one in Mexico. Occidental operated two units at the Columbia, Tennessee facility. All of these plants referred to the systems as “roasters”, and all reported similar operational issues. These issues included problematic seals, resulting in occasional phosphine explosions; severe corrosion issues; and frequent plugging of the feed system.

It should be noted that in March 1997, Rhodia’s roaster process used for recovering P_4 from the clarifier material was shut down because the crude phosphorus could no longer be removed from the clarifier and fed into the roaster. The feed stream could not be maintained in a uniform slurry. The piping continuously plugged. Steady state feed conditions, which were critical to maintenance of operating temperature and pressure, could not be maintained. The other systems have also been scrapped.

Flow Diagram:



3.2.4.2 Batch Vaporization

3.2.4.2.1 A&W Mud Still

Process Description:

The Albright & Wilson (ERCO) still is a batch operation. P_4 -containing material is loaded into a 10'-0" diameter by 3'-0" tall steel skip and the skip is placed in the pot still where it is heated to greater than 1112 °F over a 20 to 30 hour time period in a lead bath. Water is evaporated first, and then the P_4 is vaporized. White P_4 is driven off at a temperature of about 522 °F, followed by red phosphorous at 1112 °F. A later improvement to the process involves adding air late in the cycle to burn off the red phosphorus. Vaporized P_4 is condensed for recovery. At the end of a batch, the remaining solids are dumped or vacuumed out of the skip. Current technology uses molten lead for both the gas seal and heat transfer medium.

Byproduct/Residuals:

Product: Purified P_4 is saleable after filtration.

Solids: The residual solids from the mud still consist of inert material. Disposal is described in section 2.3.5.

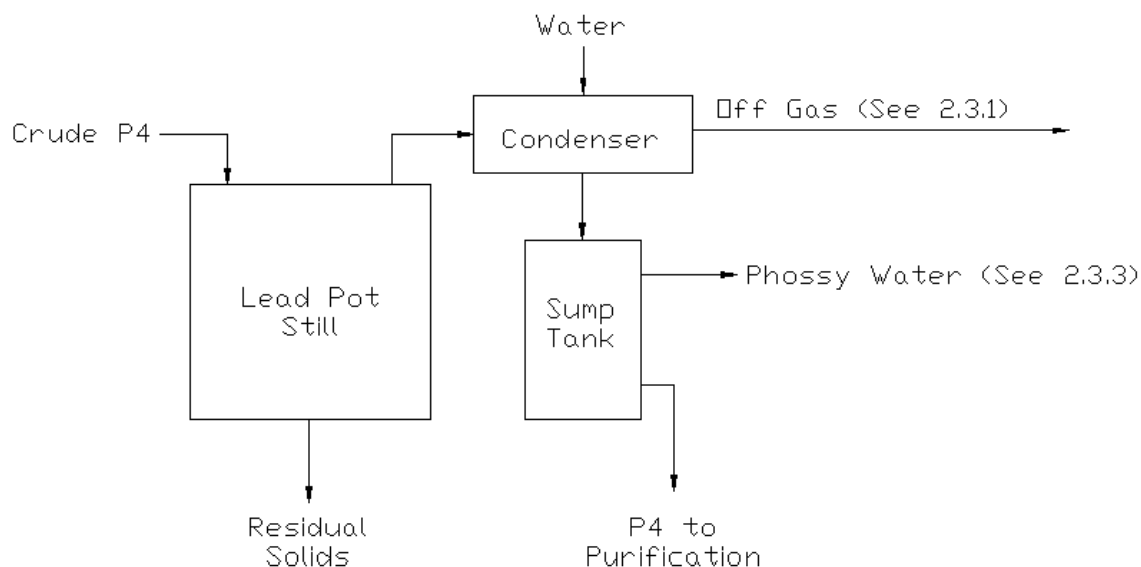
Liquids: Phossey water from direct-contact condensation must be treated as described in section 2.3.3.

Gases: Non-condensable gases including PH_3 , H_2 , and N_2 are treated in a thermal oxidizer and scrubbed for particulate removal as described in section 2.3.1 and 2.3.2.

State of Development:

This process was patented in 1978 and has been used at three facilities for P_4 sludge treatment. The Mud Still is unique among the other technology-based treatment and/or recovery systems in that it does not require size reduction past that required to fit the "chunks" of solidified sludge into the vessel.

Flow Diagram:



3.2.4.2.2 Steam Distillation/Stripping

Process Description:

Steam is bubbled through a slurry containing phosphorus in a pressurized system operating at 60-150 psig. P_4 vaporizes and is carried out by uncondensed steam. The steam and P_4 vapor are condensed and separated by phase. The process can be operated in a batch or continuous mode. In the batch mode, it is predicted that ~41 lb steam/lb of P_4 will be required. A steam usage rate of 20-30 lb steam/lb P_4 is predicted when operating in a countercurrent multistage mode utilizing superheated steam. The process is able to treat slurries with a wide range of P_4 concentrations and is believed to be capable of reducing the P_4 level to less than 50 ppm if a total residence time of 4 hours is allowed. The steam that is condensed along with the P_4 would contain some P_4 which would require additional treatment.

Byproduct/Residuals:

Product: Purified P_4 is saleable.

Solids: The residual solids consist of inert material. Disposal of this material is as described in section 2.3.5.

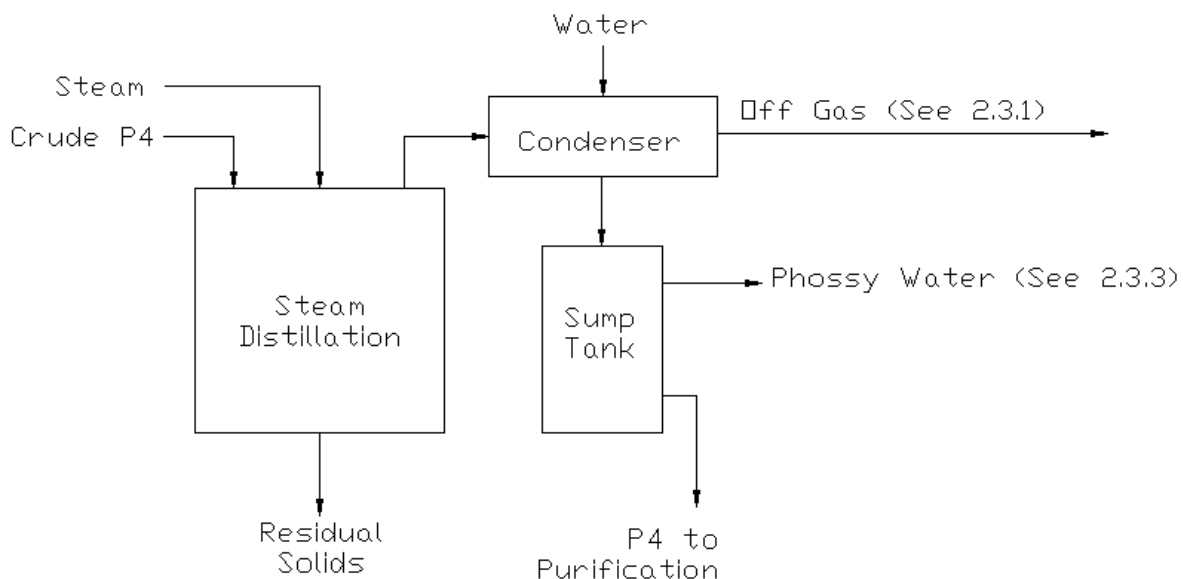
Liquids: Phossey water from condensation must be treated as described in section 2.3.3.

Gases: Non-condensable gases including PH_3 and H_2 are treated in a thermal oxidizer and subsequently scrubbed for particulate removal as described in section 2.3.1 and 2.3.2.

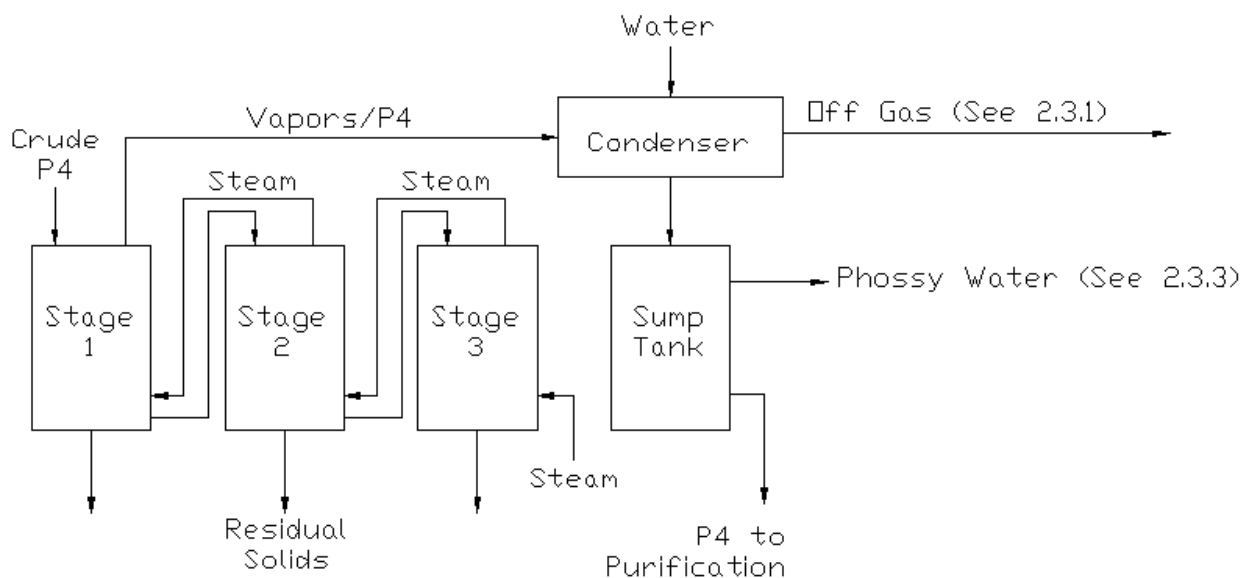
State of Development:

FMC ran a pilot plant in 1978. Hoechst used this technology with superheated steam to boil sludge to dryness. Acids were controlled by adding limestone. Presumably, the batch process could be used without the rigorous size reduction processes needed for other continuous processes. For unknown reasons, FMC did not select this technology for treating the clarifier sludge at the Pocatello facility.

Batch Process Flow Diagram:



Continuous Process Flow Diagram:



3.2.5 Chromic Acid Treatment with P_4 Recovery

Process Description:

Phosphorus sludge is heated to a temperature of 131-167 °F to melt the phosphorus. The heated sludge, chromic acid, and water are then added to a reactor and the contents are stirred to facilitate a phase separation of the dirt, phosphorus, and water. After settling, the phases are decanted and the phosphorus is recovered. The recovered phosphorus is then centrifuged and filtered. The dirt and water layers still contain some phosphorus, and they must be treated using hydrolysis followed by thermal oxidation of the phosphine and hydrogen off-gas.

Byproducts/Residuals:

Product: The elemental P_4 purity is typically 90-99 wt% with the balance being dirt. The P_4 is saleable after filtration.

Solids: The residual solids leaving the process consist of the inert material contained in the crude sludge. Also contained in this material are small quantities of P_4 and hexavalent chromium (Cr^{+6}), which can be treated using a reducing agents such as ferrous sulfate or sodium sulfite and hydrolysis.

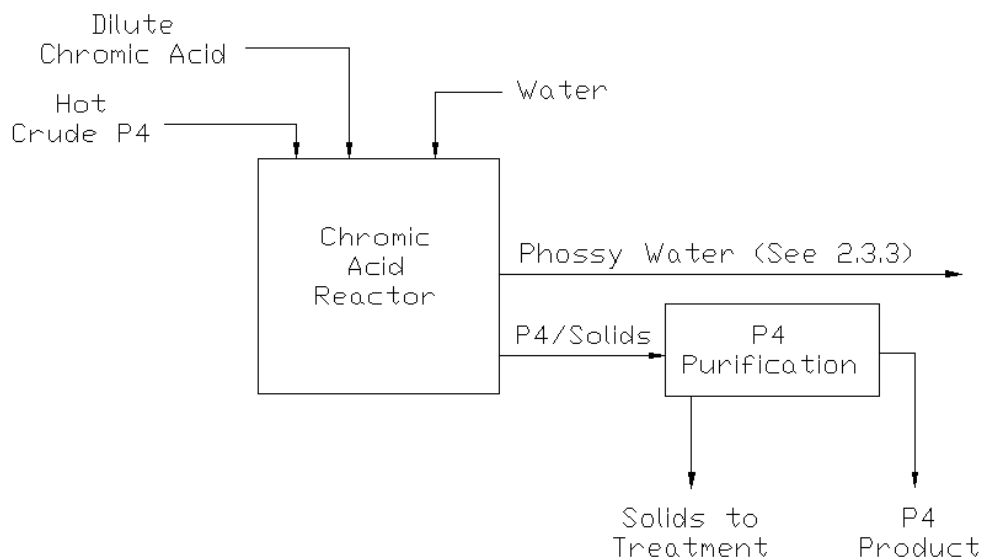
Liquids: The amount of wastewater produced equals the amount of water in the feed plus an extra 90 to 150 wt% (of feed mass) added to float the dirt away from the phosphorus. The wastewater will also have small amounts of hexavalent chromium and P_4 .

Gases: There are no gases generated during the chromic acid treatment process. The subsequent phosphy wastewater treatment is a hydrolysis process, however, which generates phosphine and hydrogen gas that require thermal oxidation and scrubbing.

State of Development:

This process was patented on 9/17/02 and has been in full scale operation at the GSHI facility in Columbia, TN since about 2000. The waste must either be melted or finely classified for feeding into the reactor. The system is covered by US Patent No. 6,451,276.

Flow Diagram:



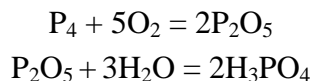
3.2.6 Other Oxidation Processes

This section describes processes where the phosphorus sludge is oxidized at relatively low temperatures. High-temperature oxidation processes are described above in section 3.2.2.

3.2.6.1 High-Speed Air Dispersion for Wet Oxidation

Process Description:

The phosphorus sludge is treated to achieve a uniformly sized feed for the high-speed air dispersion (HSAD) reactor. The reactor contents are mixed using a high shear agitator at speeds ranging from 4,000 to 21,000 rpm. Air is sparged into the mixing zone of the reactor where the air bubbles are sheared to approximately 1 micron. A quick exothermic reaction occurs between the dissolved O_2 and P_4 . The batch profile is characterized by a rapid increase in temperature and corresponding decrease in pH due to the following reactions:



Reaction fumes pass through a water condenser followed by a scrubber which utilizes a strong alkali, such as KOH or NaOH, for neutralization. After the reaction is complete, the remaining solids are thickened, washed, and prepared for landfill. The batch supernatant is a dilute H_3PO_4 solution which can either be prepared for commercial use or neutralized for land disposal.

Byproducts/Residuals

Product: Impure H_3PO_4 solution.

Solids: The solid residue remaining after the batch consists of the sludge-bound inerts (dirt). This material is washed to make it suitable for landfill disposal.

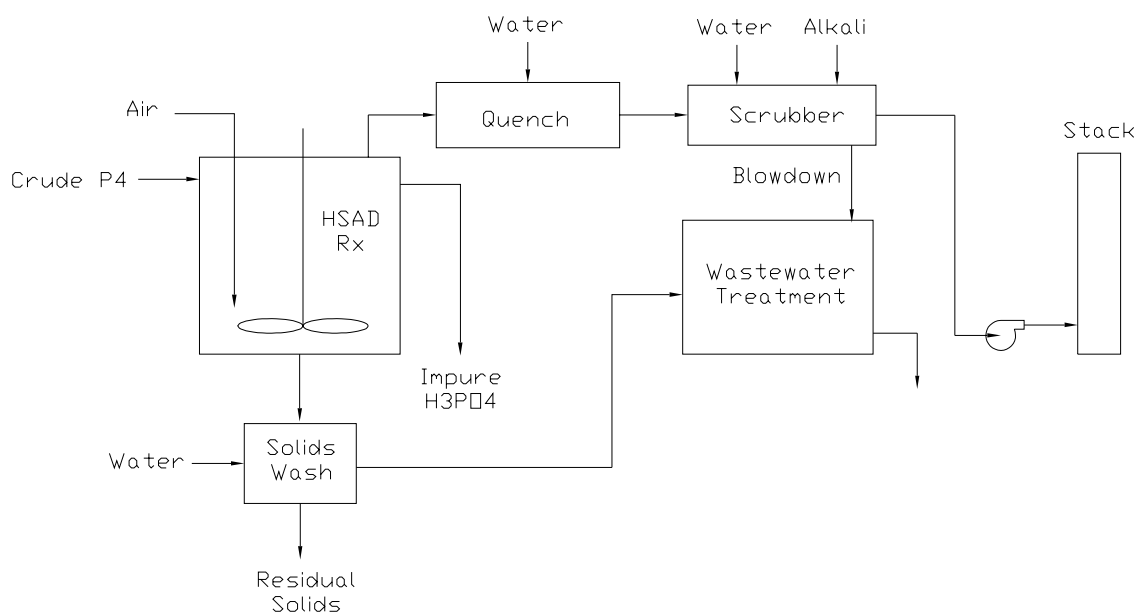
Liquids: Wastewater generated from this process includes the neutralized condenser and scrubber solutions and the solids wash solution. These streams will need to be processed in a water treatment system before disposal, such as that described in section 3.2.4.

Gases: Small quantities of P_2O_5 and H_3PO_4 mist are emitted, depending on scrubber efficiency.

State of Development

This process has been lab tested using P_4 sludge from FMC and TVA.

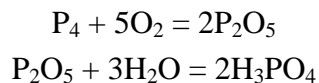
Flow Diagram:



3.2.6.2 Praxair Oxidation Process

Process Description:

A slurry of P_4 sludge is transferred to an agitated preheat tank where the contents are heated to 130 °F in order for the reaction to be sustained. The material is then transferred to a stirred batch reactor where oxygen is added. P_4 reacts with the oxygen to form phosphoric acid according to the following reactions:



The reactor is maintained at a temperature of about 200 °F and a pressure of 50 psig. Because the P₄ oxidation reaction is exothermic, heat must be removed from the reactor by the use of internal cooling coils. This reaction creates a corrosive environment; therefore, the reactor and wetted parts of the mixer should be constructed of Hastelloy C-2000 or some similar material. Phosphoric acid produced by this process would typically be neutralized and then sent to a filter for separation of the solids from the liquid.

Byproducts/Residuals

Solids: The solid residue in the oxidation reactor bottoms stream after the neutralization step consists primarily of inerts (dirt), unreacted lime, and insoluble calcium phosphate, Ca₃(PO₄)₂.

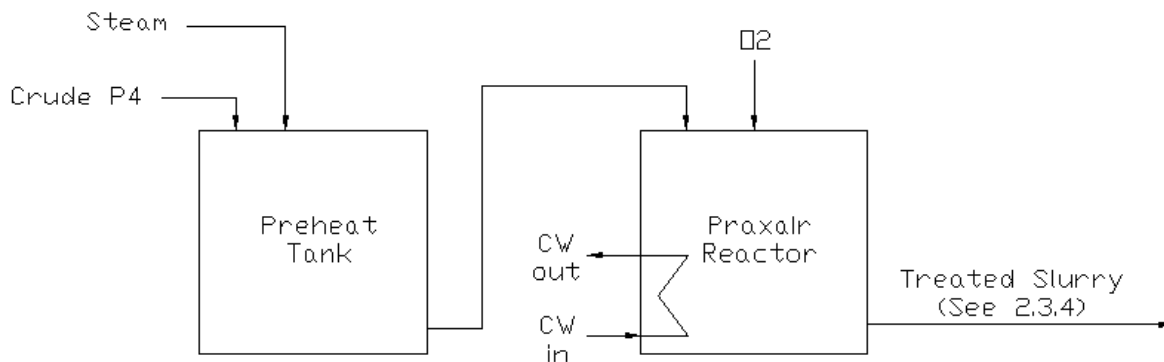
Liquids: The wastewater generated from this process contains suspended solids. Refer to section 2.3.4 for treatment details.

Gases: There are no gases produced during this process; however, the oxygen used in the process does require special consideration.

State of Development

This process was pilot tested in 1998 with process information provided by Praxair.

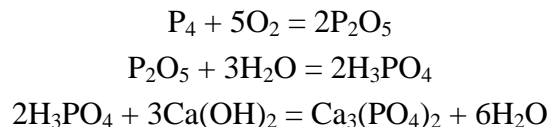
Flow Diagram:



3.2.6.3 Zimpro/Wet Air Oxidation Hybrid

Process Description:

P₄ sludge is pumped into a reactor which operates at a pressure of approximately 500 psig. High-pressure steam is injected to maintain an operating temperature of about 392 °F. Lime slurry is also pumped to the reactor to maintain pH, and a compressor supplies air at the required conditions. The reactor is a vertical column designed for 700 psig and constructed of Alloy C276. It is sized for a residence time of about one hour. The main reactions are as follows:



Some side reactions also occur. The oxidized liquid, oxidation product gases, and spent air are then routed to a process cooler. The cooled reactor effluent is throttled to about 50 psig across a control valve and fed to a separator where the gas and liquid phases are separated. The gas is routed to an onsite burner (thermal oxidizer), and the liquid is sent to a filter for solids separation. Water is then sent to wastewater treatment.

Byproducts/Residuals

Solids: The solid residue from the oxidation reactor consists primarily of inerts (dirt), unreacted lime, and insoluble calcium phosphate, $\text{Ca}_3(\text{PO}_4)_2$. Disposal would be as described in section 2.3.5.

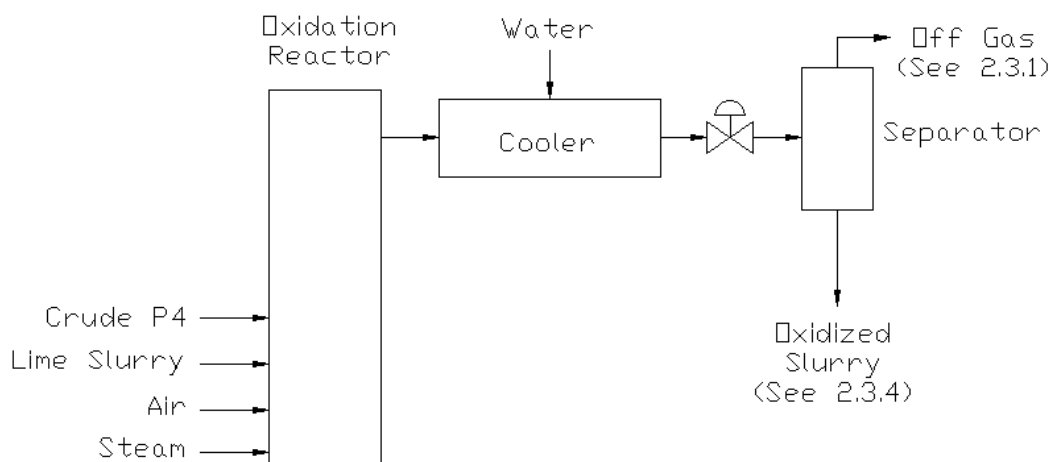
Liquids: The wastewater generated from this process will contain suspended solids, and probably some soluble forms of phosphorus salts. Treatment of this water would be the same as as described in 2.3.4 downstream of neutralization.

Gases: There are oxidation gases produced during this process; however, these gases are not well defined by the technology supplier. Refer to section 2.3.1 for description of a typical treatment process.

State of Development

This process was based on pilot tests performed at US Filter/Zimpro facilities and is not known to have been used in a commercial unit.

Flow Diagram



3.2.6.4 Nitric/Sulfuric Acid Oxidation

Process Description:

Sludge is transferred to a stirred batch reactor, mixed with the acid, and heated to 216-230 °F. The contents must be held at this temperature for several hours. A 1:1 mixture of nitric acid and sulfuric acid is used for this process. This mixture has been found to be most effective in converting the P_4 to orthophosphate acid which can then be reacted with ammonia to form ammonium phosphate, which can be used as a plant fertilizer. This process produces nitrogen oxide gases. Sludge from this process is granulated. It is reported that up to 97-99 % of the phosphorus can be converted to orthophosphate.

Byproducts/Residuals

Solids: The solid residue in the reactor bottoms stream consists primarily of inerts (dirt), and small amounts of unreacted white phosphorus.

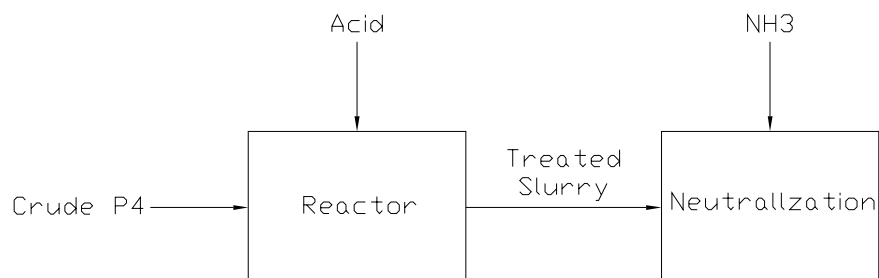
Liquids: The water stream generated by this process can be sold as a liquid fertilizer containing ammonium phosphate, ammonium nitrate, and ammonium sulfate; or the water could be evaporated to sell the ammonium salts as a solid.

Gases: Nitrogen oxide is produced during the oxidation process.

State of Development

This process has been demonstrated on a pilot scale by TVA at a pilot plant constructed in 1993. They reported successful operation with 30,000 pounds of P_4 sludge converted to phosphate fertilizer. Operational concerns were reported relating to the sludge granulation, and generation of large amounts of fertilizer and nitrogen oxide gases that would require further management or disposal. TVA stated that operation on a larger scale may not be manageable because of these concerns.

Flow Diagram:



3.2.7 Physical Separation Processes

Several other processes have been used, or tested, to separate elemental phosphorus from sludge similar to that in the Rhodia clarifier. Franklin's staff has either managed or participated in many such investigations. These technologies are described below:

3.2.7.1 Washing/Settling

This process utilizes a heated and agitated storage tank. Hot water is continuously pumped into the vessel, and light and/or fine-grain solids are carried out with the overflow water. By careful control of the agitator speed, intermediate-size solids are kept in suspension and phosphorus settles to the bottom of the tank. The phosphorus is then pumped to a filter where the residual fine grain inert solids are removed. After several washes, the intermediate solids are pumped to settling ponds. They still have phosphorus content in the range of 1% to 5% so this is not a complete solution for P₄ separation.

Washing was commonly used at one production facility that still had the utilities needed to support the process. These included steam boilers, leaf filters with pre-coat systems, waste water treatment systems to process the supernatant from the wash vessel, and disposal basins for contaminated residual solids.

3.2.7.2 Heated Screw/Porcupine Dryer/Quill Dryer

These devices are similar in appearance and operation. They resemble and function like a common screw conveyor, but apply heat to the material as it moves through the device by circulating a heating fluid through hollow screw flights or tubular mixers blades called quills.

When tested on phosphorus sludge, these devices were installed on an angle with the discharge point above the feed point. Phosphorus-rich sludge was pumped into the lower end, with the theory that phosphorus would melt and flow to a low point where it could be pumped out of the device. The temperature of the system would be above the melting point of phosphorus (105°F), but below the flash point of water. The screw housing could therefore remain full of water, and the water would be carried out of the screw with the inert solids.

These devices did liberate some phosphorus, but it was heavily laden with fine-grain solids. Phosphorus would accumulate in the housing but it could not be reliably removed by pumping. The seals on the rotating shaft would fail from the abrasive slurry and the hot molten phosphorus would immediately ignite. When shut down for maintenance, the screw/porcupine/quill housing was packed with phosphorus-rich sludge and very difficult to service.

3.2.7.3 Horizontal Decanter Centrifuges

The horizontal decanter centrifuge uses centrifugal force from spinning the slurry in a horizontal tube to separate the components of the slurry by density. The heavier material leaves the tube through one port, the water and lighter material leaves through a second port. These units have recently been tested on both hot and cold sludge, but there is no history of production use. The principal deterrent from using this process on clarifier sludge relates to the density of the inert solids in the sludge. The density of mineral-type solids is so close to that of phosphorus that the separation is incomplete. The “waste” from the centrifuge is still rich in phosphorus and will ignite if exposed to air, and the phosphorus-rich stream is still mostly inert solids, tightly bound to the phosphorus.

3.2.7.4 Screen Bowl Centrifuges/Filters

Vertical screen bowl centrifuges work much like a washing machine on the spin cycle. The hot phosphorus-rich slurry is pumped into the spinning bowl. The bowl is perforated and lined with fine-mesh screen which is, in turn, pre-coated with a porous “cake” that allows the phosphorus and water to pass through, but retains the inert solids. These devices use the centrifugal force of the spinning drum to force the liquids through the filtration cake: these are more akin to filters than they are to the horizontal decanter centrifuge. The surface of the spinning cake is continuously scraped with a stationary blade to remove the accumulation of inert solids. This extends the life of the pre-coat filtration cake. These devices have been successfully used on hot sludge with phosphorus contents well above 50%. When used on sludge with low phosphorus content, the cake is rapidly blinded by the inert solids, and the efficiency is very low. Additionally, the inert solids from the scraping process are still rich in phosphorus and must be treated by the phosphy water hydrolysis system described in section 2.3.3.

Another type of filter used in phosphorus processing is the pressure leaf filter. These devices use large, fine-mesh circular screens, mounted inside a pressure vessel and treated with pre-coat, to filter the phosphorus and water from the sludge. They are highly sensitive to high loadings of inert solids and are used only as a final polishing step downstream of the screen bowl centrifuge.

3.2.7.5 Clarifiers

Clarifiers are widely used in the treatment of “phosphy water” or aqueous streams containing phosphorus. The incoming stream is frequently treated with polymers to increase the rate of sedimentation. The phosphorus is concentrated in the sludge, which must then be treated with the hydrolysis process described in section 2.3.3. Wastewater plants using clarifiers frequently employ sand filters downstream of the clarifier as a final polishing step before discharge. The solids removed by the sand filter are still rich in phosphorus, and must be treated like the clarifier sludge.

3.2.7.6 Hydrocyclones

Much like centrifuges, hydrocyclones utilize centrifugal force to separate the components of aqueous slurry by density. They utilize the energy in the flow of the stream, rather than a separate motor. They are highly effective on coarse separations, like sand or coal slurries, but have the same drawback as horizontal decanter centrifuges when used on phosphorus-rich slurry: the density of the phosphorus lies between that of water and the inert solids so there is no clean separation.

3.2.7.7 Closed-Chamber Evaporation

This category describes devices that have heating elements inside pressure vessels. They include the Thin Film or Scraped-Surface Evaporators and while there is no record of use on phosphorus sludge, one paper suggests their applicability. These devices use heat to melt or vaporize the various components of the slurry. Vapors are removed through a pressure reducing valve and re-condensed for recovery. They are used in separating colloidal slurries and at least one writer speculated that they have application in separation of phosphorus slurry. How they would be applied is unclear since the water in the slurry would evaporate at a lower temperature than the phosphorus, and one would be left with a pressure vessel full of dense solids glued together with residual phosphorus that did not vaporize. One variant of the closed-chamber phase separation process placed the chamber under vacuum to enhance the vaporization process.

3.2.7.8 Organic Extraction

Organic solvents, primarily xylene, are used in laboratories to extract phosphorus from sludge for the purpose of measuring the quantity of phosphorus in the sludge. One writer proposed this method for removing the phosphorus from the clarifier sludge, and carbon disulfide was identified as a potential candidate. As with the laboratory analysis, the solvent would be distilled to recover the phosphorus. Recycling could be used to reduce the required amount of solvent. To the best of our knowledge, this process has never been used or tested outside of the laboratory environment.

3.2.7.9 Freeze/Thaw Separation

This process involves heating of the sludge until the phosphorus melts, and then dispersing it into a cool bath where the phosphorus solidifies as it falls through the water column. The theory had the phosphorus congealing into large articles without entraining the inert solids to which it was bound in the solid clarifier sludge. As with large-scale xylene extraction, the theory was never tested beyond laboratory scale demonstration under very controlled conditions.

3.3 Off-Site Treatment

3.3.1 Commercial Incineration

Process Description:

Clarifier sludge is transported to a commercial hazardous waste incineration facility, by truck or rail, for disposal by high temperature incineration. The most likely method of packaging is (open) headed steel drums, but bulk containerization remains an option to reduce packaging and transportation costs. Rate of disposal at each commercial facility may be limited by permit conditions, so more than one source of disposal may be required. Some facilities may shred the drums, others may process them intact.

Byproduct/Residuals

Solids: Kiln residuals include drum residuals and bottom ash from inert material in clarifier sludge. Fine ash and P_2O_5 carried in the gas stream is removed with the facility air pollution control system.

Liquids: Scrubber liquids from the air pollution control system will be treated with a pretreatment system in accordance with the facility's permit conditions.

Gases: Acid vapors in the incinerator off-gas stream will be neutralized in the scrubber system.

State of Development:

Fully mature commercial technology with competitive pricing is available. Franklin has made no contact with companies that could process the clarifier material or who may have equipment available to process this material.

Flow Diagram:

Dependent on specific facility.

3.3.2 Recycle at Other P_4 Sites

Process Description:

Clarifier sludge is transported to another phosphorus facility, by truck or rail, and the phosphorus is recovered using the facility's existing processes. The most likely method of packaging is (open) headed steel drums, but bulk containerization remains an option to reduce packaging and transportation costs. A purpose-built container unloading system may be required.

Byproduct/Residuals

Solids: Inert solids in the clarifier sludge would be processed and disposed using the facility's standard practices.

Liquids: Similar to that of solids.

Gases: Similar to that of solids.

State of Development:

Recycling of phosphorus may be sufficient to obtain a RCRA exemption. Franklin has made no contact with companies that could process the clarifier material or who may have equipment available for processing this material.

Flow Diagram:

Dependent on specific facility.

ATTACHMENT 1

INDEX OF PHOSPHORUS FILES

Index of Franklin's Phosphorus Files

Revision Date: 4/6/2007

Category	Entry	Document Name	Date	No. Pages	Author(s)	Notes	weblink	Related Technology Type(s)	Facility	Hard Copy (HC) or Electronic Copy (EC)
A. Technology Screening	1	In Situ Treatment Technologies for Contaminated Soil	~2006	35	EPA	ENGINEERING FORUM ISSUE PAPER	http://www.epa.gov/tio/isp/download/54206013.pdf	Solidification/ Stabilization, Chemical Oxid., Thermal Treatment, In-situ Vitrification		HC
	2	Ex-Situ Remediation Technologies For Contaminated Sites		5	Environment Canada Ontario Region - Environmental Protection Branch Environmental Contaminants & Nuclear Programs Division	Tab #23	http://www.on.ec.gc.ca/pollution/ecnpd/tabs/tab23-e.html	Chemical Oxidation, Thermal Desorption, Incineration, Excavation, Vitrification		HC
	3	Summary and Evaluation for White Phosphorus Remediation: A Literature Review	Oct-96	71	USACE; Yilda B. Rivera, Trudy Olin, R. Mark Bricks	Technical Report IRRP-96-017	http://el.ercd.usace.army.mil/elpubs/pdf/trirp96-7.pdf	In-situ WAO, Chem Oxid. Lime Addition, Infrared Desorption, Air-drying, Pond-draining		HC
	4	Phosphates		16	Energy and Environmental Profile of the U.S. Mining Industry		http://www.eere.energy.gov/industry/mining/pdfs/phosphate.pdf	H3PO4 Production		HC
	5	Identification and Description of Mineral Processing Sectors and Waste Streams (Executive Summary)	Apr-98	29	US EPA	FINAL Technical Background Document	http://www.epa.gov/epaoswer/other/mineral/part1.pdf			HC
	6	Identification and Description of Mineral Processing Sectors and Waste Streams - Phosphorus Production	Apr-98	90	US EPA	FINAL Technical Background Document	http://www.epa.gov/epaoswer/other/mineral/part5.pdf			EC
	7	Identification and Description of Mineral Processing Sectors and Waste Streams - H3PO4 Production	Apr-98	89	US EPA	FINAL Technical Background Document	http://www.epa.gov/epaoswer/other/mineral/part7.pdf			EC
	8	TOXICOLOGICAL PROFILE FOR WHITE PHOSPHORUS (STAND ALONE DOCUMENT)	Sep-97	209	Prepared by: Sciences International, Inc. Under Subcontract to: Research Triangle Institute Under Contract No. 205-93-0606	Prepared for: U.S. DEPARTMENT OF HEALTH AND HUMAN SERVICES Public Health Service Agency for Toxic Substances and Disease Registry	http://www.atsdr.cdc.gov/toxprofiles/t103-p.pdf	Incineration, Open burning		HC - Separate Binder
	9	Solidification/Stabilization Resource Guide	Apr-99	91	EPA	EPA/542-B-99-002	http://www.epa.gov/tio/download/remed/solidstab.pdf			EC
	10	EVALUATION CRITERIA GUIDE FOR WATER POLLUTION PREVENTION, CONTROL, AND ABATEMENT PROGRAMS	Apr-87	150	Headquarters, Department of the Army	TM 5-814-8	http://www.usace.army.mil/publications/armymtm/tm5-814-8/entire.pdf			EC
	11	Background Report on Fertilizer Use, Contaminants and Regulations	Jan-99	395	EPA	EPA 747-R-98-003	http://www.epa.gov/oppt/pubs/fertilizer.pdf			EC
	12	Proceedings of the Third International Symposium on Phosphogypsum	Dec-90	72	Univ. of Miami (Florida Institute of Phosphate Research)	Pub. No. 01-060-083	http://fipr1.state.fl.us/fipr/fipr1.nsf/a1380a2dc3df745f85256b4b006398eb717191dd26b9af5a185256b2e00642536/\$FILE/01-060-083suppFinal.pdf			EC
	13	Lecture 14 Miscellaneous topics in remediation: New remediation technologies; technical impracticability; and gasoline additives		52			http://ocw.mit.edu/NR/rdonlyres/Civil-and-Environmental-Engineering/1-34Spring2004/E5C60D08-0001-4A12-BFFE-470CCC89BD91/0/lecture14.pdf			EC
	14	Technology Screening Guide for Radioactively Contaminated Sites	Nov-96	203	EPA	EPA 402-R-96-017	http://www.epa.gov/superfund/resources/radiation/pdf/techguide.pdf			EC
B. Treatment Technologies	1	Treatment Technologies for Historical Ponds Containing Elemental Phosphorus - Summary and Evaluation	Aug-03	98	U.S. Environmental Protection Agency Office of Solid Waste and Emergency Response Washington, DC 20460	EPA 542-R-03-013	http://www.epa.gov/tio/download/remed/epa542r03013.pdf	Solidification/ Stabilization, Caustic Hydrolysis, Chemical Oxid., Mechanical Aeration, Incineration, Thermal Desorption		HC
	2	On-Site Incineration: Overview of Superfund Operating Experience	Mar-98	37	US EPA	EPA-542-R-97-012	http://clu-in.org/download/remed/incpdf/incin.pdf	General Incineration		HC
	3	Solidification/Stabilization Use at Superfund Sites	Apr-99	23	EPA	EPA/542-R-00-010	http://www.clu-in.org/download/remed/ss_sfund.pdf	General Solidification/ Stabilization		HC
	4	Removal of elemental phosphorus from electric furnace sludges of various origins		2	Irvin A. Jefcoat, Sundeep Potluri The University of Alabama, P.O. Box 870203, Tuscaloosa, Alabama 35487-0203	ABSTRACT for Article	http://www3.interscience.wiley.com/cgi-bin/abstract/112734928/ABSTRACT?CRETRY=1&SRETRY=0			HC
	5	Remediation Technology Cost Compendium – Year 2000	Sep-01	77	US EPA	EPA-542-R-01-009	http://www.clu-in.org/download/remed/542r01009.pdf			HC
	6	Onsite Wastewater Treatment Systems Technology Fact Sheet 8 Enhanced Nutrient Removal-Phosphorus		5	US EPA	EPA 625/R-00/008	http://www.epa.gov/nrmrl/pubs/625r00008/html/html/tfts8.htm			HC
	7	Remediation Technology Vendors		16	US EPA TIP		http://clu-in.org/download/vendorinfo/Remediation_Technologies.pdf			HC

Category	Entry	Document Name	Date	No. Pages	Author(s)	Notes	weblink	Related Technology Type(s)	Facility	Hard Copy (HC) or Electronic Copy (EC)
C. Patents	1	Removal of elemental phosphorus from mixtures with other solids	Nov-99	7	Charles N. Sturdivant, George Walter Luxbacher, Mohan Singh Saran, Kenneth Raburn Price	US Patent Issued on September 10, 2002	http://www.patentstorm.us/patents/6446812.html	CNS- GSHI Mechanical Separation of P4 from other solids		HC
	2	Recovery of elemental phosphorus from phosphorus sludge	Aug-99	6	Saran, Mohan S.; Brooks, James R.; Potts, David C.	US Patent Issued on September 17, 2002	http://www.patentstorm.us/patents/6451276.html	GSHI Chromic Acid Oxidation, (also mentions H2O2, HNO3, O2)		HC
	3	Waste water treatment system for elemental phosphorous removal	Feb-81	4	Bennett, W. Clark; Garrett, Theodore T.;	Publication Date: 9/6/1983	http://www.freepatentsonline.com/4402833.html	Lime addition, aeration, filtration, carbon bed		HC
	4	Preparation of phosphatic feedstock from phosphorus-containing waste	Jun-98	12	Barber, James C.;	Publication Date: 4/18/2000	http://www.freepatentsonline.com/6051201.html	Preparation of Feedstock		HC
	5	A PROCESS FOR TOTAL ENVIRONMENTAL REMEDIATION OF A PHOSPHORUS CONTAMINATED SITE	May-03	5	Saran, Mohan Singh; Luxbacher, George Walter;	Publication Date: 12/2/2004	http://www.freepatentsonline.com/20040241073.html			HC
	6	Processes for the disposal and recovery of phossy water	May-95	15	Barber, James C	Publication Date: 8/27/1996	http://www.freepatentsonline.com/5549878.html			HC
	7	Apparatus for high speed air oxidation of elemental phosphorous wastes in aqueous medium	Jul-94	13	Hanna, John; Jung, Joon-Oh;	Publication Date: 5/7/1996	http://www.freepatentsonline.com/5514352.html	HSAD		HC
	8	Conversion of precipitator dust into phosphorus furnace feedstock	Oct-89	14	Barber, James C.;	Publication Date:11/6/1990	http://www.freepatentsonline.com/4968499.html			HC
D. Conversations	1	Jim Sieverson (FMC Pocatello, ID)	Feb-07	1	G. Prater, FEG	(208) 236-8212; jim_sieverson@fmc.com				HC
	2	Kelly Madalinski (EPA TIO)	Mar-07	1	G. Prater, FEG	(703) 603-9901 madalinski.kelly@epa.gov				HC
E. Eagle River Flats	1	In-Situ Remediation of White Phosphorus in Wetlands	1998	1	Michael R. Walsh, Marianne E. Walsh, and Charles M. Collins	(Abstract) Conference Proceeding Paper	http://www.pubs.asce.org/WWWdisplay.cgi?9804750		Eagle River Flats	EC
	2	Method for attenuation of white phosphorus contamination in wetlands	2000	1	WALSH Michael R. (1) ; WALSH Marianne E. (1) ; COLLINS Charles M. (2)	(Abstract) Journal of environmental engineering (J. environ. eng.) ISSN 0733-9372 CODEN JOEEDU, 2000, vol. 126, no11, pp. 1013-1018 (26 ref.)	http://cat.inist.fr/?aModele=afficheN&csid=1536426		Eagle River Flats	EC
	3	Alaska Department of Environmental Conservation Contaminated Sites Database Site Report for Fort Rich OUC Eagle River Flats	11/11/80 - 2/6/07	49	Louis Howard - 9072697552	Report - a table with dated entries	http://www.dec.state.ak.us/spar/csp/search/csites_report.asp?Reckey=198821X825601		Eagle River Flats	EC
	4	Enhanced Natural Remediation of White-Phosphorus-Contaminated Wetlands through Controlled Pond Draining	Nov-99	31	Michael R. Walsh, Marianne E. Walsh, and Charles M. Collins	CRREL Report 99-10 (US Army Corps of Engineers@ Cold Regions Research & Engineering Laboratory)	http://www.crrel.usace.army.mil/library/crrelreports/CR99_10.pdf		Eagle River Flats	EC
	5	CRREL, Army clean up contaminated Alaskan marsh	May-01	3	Article by Marie Darling Photo by Mike Walsh Cold Regions Research and Engineering Laboratory	Engineer Update	http://www.hq.usace.army.mil/cepa/pubs/may01/story14.htm		Eagle River Flats	EC
	6	Dredging as Remediation for White Phosphorus Contamination at Eagle River Flats, Alaska	Aug-98	39	Michael R. Walsh and Charles M. Collins	CRREL Report 98-5	http://www.crrel.usace.army.mil/library/crrelreports/CR98_05.pdf		Eagle River Flats	EC
	7	Dredging in an Active Artillery Impact Area Eagle River Flats, Alaska	Sep-96	51	Michael R. Walsh, Edwin J. Chamberlain, Karen S. Henry, Donald E. Garfield and Ed Sorenson	Special Report 96-22	http://www.crrel.usace.army.mil/library/specialreports/SR96_22.pdf		Eagle River Flats	EC
	8	Eagle River Flats Remediation Project Comprehensive Bibliography—1950 to 1998	Aug-99	106	Sae-Im Nam, Michael R. Walsh, Charles M. Collins, and Lisa Thomas	Special Report 99-13	http://www.crrel.usace.army.mil/library/specialreports/SR99_13.pdf		Eagle River Flats	EC
	9	Eagle River Flats Remediation Project Comprehensive Bibliography—1998 to 2003	Aug-03	54	Michael R. Walsh	ERDC/CRREL TR-03-15	http://www.crrel.usace.army.mil/library/technicalreports/TR03-15.pdf		Eagle River Flats	EC
	10	Persistence of White Phosphorus Particles in Sediment	Nov-95	51	Marianne E. Walsh, Charles M. Collins and Charles Racine	CRREL Report 95-23	http://www.crrel.usace.army.mil/library/crrelreports/CR95_23.pdf		Eagle River Flats	EC
	11	Operable Unit C: Remedial Action Work Plan and Final Design for Eagle River Flats (1999)	Apr-99	5	CH2M Hill	CERCLA Document. CH2M Hill Contract Report to U.S. Army Alaska, Directorate of Public Works, Fort Richardson, Alaska. April 1999	http://www.crrel.usace.army.mil/erl/bibliography/cercladocs/cercladoc10.html		Eagle River Flats	EC
	12	White Phosphorus Contamination of Salt Marsh Sediments at Eagle River Flats, Alaska Part II. Remedial Investigation Report (1993)	1993	4	C.H. Racine, M.E. Walsh, C.M. Collins, D. Lawson, K. Henry, L. Reitsma, B. Steele, R. Harris, and S.T. Bird	CRREL Contract Report to the U.S. Army Environmental Center, Aberdeen Proving Ground, MD AEC Report No. ENAEC-IR-CR-93063	http://www.crrel.usace.army.mil/erl/bibliography/contracts/contract46.html		Eagle River Flats	EC
F. FMC-Astaris	1	Memo from Jim Sieverson to Dan Bersanti	Mar-07	2	Jim Sieverson	FMC Technology Evaluation Information			FMC	HC
	2	Supplemental Information requested by EPA regarding Treatment of Phosphorus-Containing Pond Solids at FMC	Dec-97	51	Summit Law Group (David Heineck or Rob Hartman)	A&W Lead Pot Still, Stauffer Rotary Sludge Still, Russian Acid Furnace, Wet Oxidation, Plant Recycle, Rotary Dryer/Calciner, Steam Stripping, Pond Drying & Oxidation, Hydrolysis		Lead Pot Still, Rotary Still, Russian Acid Burner, Wet Oxid, Recycle as Feed, Rotary Dryer/Calciner, Steam Distillation, Pond Drying, Hydrolysis	FMC	HC

Category	Entry	Document Name	Date	No. Pages	Author(s)	Notes	weblink	Related Technology Type(s)	Facility	Hard Copy (HC) or Electronic Copy (EC)
	3	Summary Characterization and Cap Infiltration Eval of the Old Phossy Ponds Area and Old Calciner Solids Storage Area, FMC Subarea, Eastern Michaud Flats Site	Mar-97	18	FMC (Rob Hartman)				EMF	HC
	4	Information Responding to EPA and Tribal Comments on Pond 8S Closure Plan	Aug-97	11	Rob Hartman			Excavation and On-site Disposal, Stabilization/fixation, Separation, Dewatering, Aeration, Incineration, Desorption, WAO, Oxidation/reduction, hydrolysis, extraction, enhanced biodegradation	FMC	HC
	5	Low Cost Alternatives	Nov-94	7	FMC	FMC Option Summary with Brief Process Description, Cost, Risks		Caustic Hydrolysis, Steam Distillation, Concentration and Recycle, P4 Evap, Pot Stills	FMC	HC
	6	Phossy Waste Mgt Project: Caustic Hydrolysis Process Development Report Technology Development Process Section II	Mar-93	74	J.R. Brummer			Report discussing FMC Phase 1 and 2. Brief discussion on almost all P4 companies in world.	FMC	HC
	7	Bibliography on Arsenic, Phosphorus, and Fate&Transport	Jan-92	35	Bechtel Environmental, Inc.				FMC	HC
	8	Drinking Water Health Advisory: Munitions	Dec-92	48	US EPA (Rob Hartman file) (RA 1235 D57 1992)	Toxological Information			FMC	HC
	9	Summary Review of Phossy Pond Characterization and Treatment Options Eval (provided to EPA)	Nov-97	7	FMC	Brief Report on Feasibility Issues		Caustic Hydrolysis, cement/CKD fixation, oxidation, distillation, recovery, fluid bed dryer, acid extraction, solvent extraction, chlorine treatment, H2O2 treatment, Wet Oxidation, Dry Oxidation/Rotary Flash Dryer, Chemical Stabilization, Aeration, thermal (IR, microwave, combustion desorption) Reprocess-furnace feed	FMC	HC
	10	Complaint - USA vs. FMC		15	US EPA Region 10		http://yosemite.epa.gov/r10/owcm.nsf/28100b370f1499368825650005dcd2/202cb380694b3166882566ab00779fc5!OpenDocument		FMC	EC
	11	Legal Memo Decision and Order shoban-fmc 030706	~2006	18			http://www.indianz.com/docs/court/shobanfm030706.pdf		FMC	EC
	12	Public Health Assessment EASTERN MICHAUD FLATS CONTAMINATION Bannock County, Idaho; Power County, Idaho; Fort Hall Indian Reservation	Jul-04	92	Bureau of Community and Environmental Health Division of Health Idaho Department of Health and Welfare And U.S. Agency for Toxic Substances and Disease Registry	DRAFT for Public Comment	http://www.healthandwelfare.idaho.gov/_Rainbow/Documents%5CHealth/Eastern%20Michaud%20PHA%20public.pdf		FMC	EC
	13	FMC Fact Sheet 10-98	Oct-98	7	US EPA Region 10	EPA/DOJ Resource Conservation and Recovery Act Enforcement Case Against the FMC Corporation	http://yosemite.epa.gov/r10/owcm.nsf/28100b370f1499368825650005dcd2/9b6f042db446595e882566ab00741e20!OpenDocument		FMC	EC
	14	FMC Press Release 10-98	Oct-98	3		FMC To Pay Largest RCRA Settlement in Environmental Enforcement History	http://yosemite.epa.gov/r10/owcm.nsf/28100b370f1499368825650005dcd2/490171c63ebcfa8c882566ad007d9af5!OpenDocument		FMC	EC
	15	FMC RCRA Settlement 10-98	Oct-98	3	US EPA Region 10	FMC To Pay Largest RCRA Settlement in Environmental Enforcement History	http://yosemite.epa.gov/r10/owcm.nsf/28100b370f1499368825650005dcd2/86349936177ae73388256768006fab90!OpenDocument		FMC	EC
	16	FMC Settlement Article		3		Manifest Destiny's New Face: "Soft-Selling" Tribal Heritage Lands for Toxic Waste	http://www.findarticles.com/p/article/s/mi_qa3805/is_200401/ai_n9379579/pg_5		FMC	EC
	17	Environmental Fact Sheet	Dec-06	2	Sue Skinner, EPA Community Involvement Coordinator, 208-478-1680 or skinner.susan@epa.gov	Eastern Michaud Flats EPA Orders FMC Action December 2006	http://yosemite.epa.gov/R10/CLEANUP.NSF/sites/emichaud/\$FILE/SEID%20fact%20sheet.pdf		FMC	EC
	18	US EPA Southeast Idaho Update	Jul-99	5	Idaho Division of Environmental Quality Pocatello Regional Office 224 South Arthur Pocatello, Idaho 83204 (208) 236-6160		http://yosemite.epa.gov/R10/IOO.NSF/1887fc8b0c8f2aee8825648f00528583/5ec8dda6ec667ad8882567a70072836a!OpenDocument		FMC	EC
	19	US EPA Southeast Idaho Update	Oct-01	5	John Iani, Regional Administrator; Charles Bert, Public Involvement Coordinator	Open Letter from the Environmental Protection Agency; Highlighting EPA Activities in Pocatello, Fort Hall, and Surrounding Areas	http://yosemite.epa.gov/R10/IOO.NSF/234f65bb5150b0b8825650f00716eb0/1daea8fbbc270ee988256a2500610213/\$FILE/SEIdahoUpdateOctober2001.pdf		FMC	EC
	20	Stimulating Smarter Regulation: 2002 Report to Congress on the Costs and Benefits of regulations and Unfunded Mandates on State, Local, and Tribal Entities	2002	163	Office of Management and Budget Office of Information and Regulatory Affairs	see page 158	http://www.whitehouse.gov/omb/inf/oreg/2002_report_to_congress.pdf		FMC	EC

Category	Entry	Document Name	Date	No. Pages	Author(s)	Notes	weblink	Related Technology Type(s)	Facility	Hard Copy (HC) or Electronic Copy (EC)
	21	EPA Superfund Record of Decision: EASTERN MICHAUD FLATS CONTAMINATION	1998	172	US EPA Region 10	EPA/ROD/R10-98/034; EPA 541-R98-034	http://www.epa.gov/superfund/sites/rods/fulltext/r1098034.pdf		FMC	EC
	22	Remedial Investigation Report for the Eastern Michaud Flats Site, Part 1 Executive Summary	Aug-96	125	Bechtel Environmental, Inc.		http://yosemite.epa.gov/r10/CLEA_NUP.NSF/22f04d62fa63974288256da6005f9868/f8290605e3fe096f88256e010063a5bc/\$FILE/R1%20Repo rt.pdf		FMC	EC
	23	ATTACHMENT A STATEMENT OF WORK EASTERN MICHAUD FLATS SUPERFUND SITE - FMC PLANT OU - SUPPLEMENTAL REMEDIAL INVESTIGATION AND FEASIBILITY STUDY	Oct-03	20			http://yosemite.epa.gov/r10/CLEA_NUP.NSF/9f3c21896330b4898825687b007a0f33/41199131114ae8ec88256517006c051c/\$FILE/EMF%20SRI-SFS%20SOW%2010-9-03%20final.pdf		FMC	EC
	24	Notice of Data Availability for Additional Information Submitted by FMC/Astaris LLC Regarding the Case-By-Case Extension of the Land Disposal Restrictions (LDR) Effective Date for Hazardous Wastes Generated at Their Pocatello, Idaho Facility	2001	6	US EPA	Federal Register: April 24, 2001 (Volume 66, Number 79)	http://www.epa.gov/fedrgstr/EPA-WASTE/2001/April/Day-24/f10247.htm		FMC	EC
	25	Renewal of Case-by-Case Extension of the Land Disposal Restrictions (LDR) Effective Date for Hazardous Wastes Generated by FMC/Astaris Idaho LLC	2001	12	US EPA	Federal Register: May 21, 2001 (Volume 66, Number 98)	http://www.epa.gov/fedrgstr/EPA-WASTE/2001/May/Day-21/f12880.htm		FMC	EC
	26	Haz Waste Mgt at FMC		2	US EPA		http://yosemite.epa.gov/r10/owcm.nsf/28100b370f14993688256500005dcd2/d1be33c1c2024e12882566ab006ee58e1OpenDocument		FMC	EC
G. FMC Consent Decree	27	FMC Consent Decree	May-06	23	US EPA Region 10		http://yosemite.epa.gov/r10/owcm.nsf/28100b370f14993688256500005dcd2/093c6146ad29edb3882566ab00752decd1OpenDocument		FMC	EC
	28	FMC Consent Decree Attachments; ATTACHMENT A COMPLIANCE SCHEDULE	May-06	5	US EPA Region 10		http://yosemite.epa.gov/r10/owcm.nsf/28100b370f14993688256500005dcd2/83a0c06d807be1e4882566ad00011d241OpenDocument		FMC	EC
	29	FMC Consent Decree Attachments; ATTACHMENT B COMPLIANCE SCHEDULE	May-06	17	US EPA Region 10		http://yosemite.epa.gov/r10/owcm.nsf/28100b370f14993688256500005dcd2/589d1699ed94fbb0882566ad0070866a1OpenDocument		FMC	EC
	30	FMC Consent Decree Attachments; ATTACHMENT C COMPLIANCE SCHEDULE	May-06	6	US EPA Region 10		http://yosemite.epa.gov/r10/owcm.nsf/28100b370f14993688256500005dcd2/85ba60af46b0cf85882566ac006861711OpenDocument		FMC	EC
	31	FMC Consent Decree Appendices; Appendix 1 INFORMATION TO BE SUBMITTED ON THE LDR TREATMENT AND OFF-GAS SYSTEM	May-06	2	US EPA Region 10	Unit and Overall System Basis	http://yosemite.epa.gov/r10/owcm.nsf/28100b370f14993688256500005dcd2/fb99f09dfefeb28cc2882566ad001fcbf1OpenDocument		FMC	EC
	32	FMC Consent Decree Appendices; Appendix 2 Furnace Building and Phos Dock Upgrades	May-06	4	US EPA Region 10		http://yosemite.epa.gov/r10/owcm.nsf/28100b370f14993688256500005dcd2/9f017a2b3c6a7c73882566ad0002f7371OpenDocument		FMC	EC
	33	FMC Consent Decree Appendices; Appendix 3 Furnace Building Flow Diagram Phos Dock Flow Diagram Map of Ponds and Property at the FMC Pocatello Facility	May-06	1	US EPA Region 10	Please request a copy from the U.S. EPA Region 10 contact Andy Boyd at: (206) 553-1222 or (800) 424-4372 Ext. 1222	http://yosemite.epa.gov/r10/owcm.nsf/28100b370f14993688256500005dcd2/953ebe1e22611c34882566ad00048e391OpenDocument		FMC	EC
H. FMC Health Consultation	34	ATSDR - HEALTH CONSULTATION (Table of Contents) EASTERN MICHAUD FLATS CONTAMINATIONPOCATELLO, BANNOCK AND POWER COUNTIES, IDAHO	1999	4	Gregory V. Ulirsch, Technical Project Officer/Environmental Health ScientistSuperfund Site Assessment BranchDivision of Health Assessment and Consultation, ATSDR; Debra Gable, Technical Project Officer Superfund Site Assessment Branch Division of Health Assessment and Consultation, ATSDR	Table of Contents	http://www.atsdr.cdc.gov/hac/PHA/easternmichaud/emf_toc.html		FMC	EC
	35	ATSDR - HEALTH CONSULTATION (Summary, Purpose, Background) EASTERN MICHAUD FLATS CONTAMINATION POCATELLO, BANNOCK AND POWER COUNTIES, IDAHO	1999	7			http://www.atsdr.cdc.gov/hac/PHA/easternmichaud/emf_p1.html		FMC	EC
	36	ATSDR - HEALTH CONSULTATION (Discussion) EASTERN MICHAUD FLATS CONTAMINATION POCATELLO, BANNOCK AND POWER COUNTIES, IDAHO	1999	26			http://www.atsdr.cdc.gov/hac/PHA/easternmichaud/emf_p2.html		FMC	EC
	37	ATSDR - HEALTH CONSULTATION (Conclusions, Recommendations, Public Health Action Plan, Site Team Authors, References, Figures, and Tables) EASTERN MICHAUD FLATS CONTAMINATION POCATELLO, BANNOCK AND POWER COUNTIES, IDAHO	1999	14			http://www.atsdr.cdc.gov/hac/PHA/easternmichaud/emf_p3.html		FMC	EC

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	38	ATSDR - HEALTH CONSULTATION (Appendices) EASTERN MICHAUD FLATS CONTAMINATION POCATELLO, BANNOCK AND POWER COUNTIES, IDAHO	1999	1		Appendices	http://www.atsdr.cdc.gov/hac/PHA/easternmichaud/emf_p4.html		FMC	EC
I. Crane Army Ammunition Activity	1	White Phosphorus to Phosphoric Acid conversion Facility (Crane Army Ammunition Activity)	Oct-97	58	Randall Burcham	Fax from Randall Burcham to Michelle Whisman at Tetra Tech. Describes Crane process		H3PO4 Recovery	Crane	HC
J. Occidental	1	DOCUMENTATION OF ENVIRONMENTAL INDICATOR DETERMINATION RCRA Corrective Action Environmental Indicator (EI) RCRIS code (CA725)		31	Paul J. Merges , Ph.D.; Director, Bureau of Radiation & Hazardous Site Management; NYSDEC	OCCIDENTAL CHEMICAL CORPORATION; Buffalo Avenue Niagara Falls, New York	http://www.epa.gov/region02/waste/occ_b725.pdf		Stauffer	EC
K. Stauffer	1	STAUFFER CHEMICAL - TARPON SPRINGS Placed on National Priorities List: May 31, 1994 HWC#95	Jul-06	6		Between Anclote Blvd. and the Anclote River Tarpon Springs, Florida District: Southwest Site Lead: EPA	http://www.dep.state.fl.us/waste/quick_topics/publications/wc/sites/summary/095.pdf		Stauffer	EC
	2	Administrative Record Index for the Stauffer Chemical Co. (Tarpon Springs) NPL Site	Jul-98	15		NPL Site			Stauffer	EC
	3	Administrative Record Index for the Stauffer Chemical Co. (Tarpon Springs) NPL Site	Jun-99	1		Explanation of Significant Differences			Stauffer	EC
	4	Administrative Record Index for the Stauffer Chemical Co. (Tarpon Springs) NPL Site	Aug-99	1		Explanation of Significant Differences #2			Stauffer	EC
	5	Administrative Record Index for the Stauffer Chemical Co. (Tarpon Springs) Removal Site	Nov-97	3		Removal Site			Stauffer	EC
L. Stauffer Consent Decree	6	Stauffer Consent Decree	Oct-05	93	US EPA Region 4	Case 8:05-cv-01024-SDM-TGW Document 9	http://www.epa.gov/region4/waste/npl/nplfn/stauffer/staufferconsentdecree2005.pdf		Stauffer	EC
	7	Record of Decision The Decision Summary Operable Unit 1	1998	77	US EPA Region 4		http://www.epa.gov/region4/waste/npl/nplfn/stauffer/staufferrod.pdf		Stauffer	EC
	8	Stauffer Tarpon Springs NPL Site Explan of Sig Diff No.1	Jun-99	7	US EPA Region 4		http://www.epa.gov/region4/waste/npl/nplfn/stauffer/esd1.pdf		Stauffer	EC
	9	Stauffer Tarpon Springs NPL Site Explan of Sig Diff No.2	Aug-99	8	US EPA Region 4		http://www.epa.gov/region4/waste/npl/nplfn/stauffer/esd2.pdf		Stauffer	EC
	10	Stauffer Tarpon Springs NPL Site Explan of Sig Diff No.3	Mar-00	6	US EPA Region 4		http://www.epa.gov/region4/waste/npl/nplfn/stauffer/esd3.pdf		Stauffer	EC
	11	Agreement to Conduct Studies	Aug-00	22	US EPA Region 4		http://www.epa.gov/region4/waste/npl/nplfn/stauffer/agree800.pdf		Stauffer	EC
	12	SCOPE OF WORK AGREEMENT TO CONDUCT STUDIES TO INCLUDE: GEOPHYSICAL STUDIES, TREATABILITY STUDIES, AND GROUNDWATER CHARACTERIZATION STUDIES AT THE STAUFFER CHEMICAL COMPANY SUPERFUND SITE TARPON SPRINGS, PINELLAS COUNTY, FLORIDA		16	US EPA Region 4		http://www.epa.gov/region4/waste/npl/nplfn/stauffer/drassow.pdf		Stauffer	EC
	13	SCOPE OF WORK FOR THE REMEDIAL DESIGN / REMEDIAL ACTION (RD/RA) STAUFFER CHEMICAL SUPERFUND SITE Tarpon Springs, Pinellas County, Florida 10141576	2005	27	US EPA Region 4		http://www.epa.gov/region4/waste/npl/nplfn/stauffer/SOWforRDRAppd.pdf		Stauffer	EC
	14	Superfund Memorandum of Understanding between the Florida Department of Environmental Protections and the US EPA Region 4	Jul-04	4			http://www.epa.gov/region4/waste/npl/nplfn/stauffer/mou.pdf		Stauffer	EC
	15	Site Briefing for Stauffer Chemical Company Superfund Site Tarpon Springs, Florida United States Environmental Protection Agency Region 4	Nov-99	12			http://www.epa.gov/region4/waste/npl/nplfn/stauffer/brief.pdf		Stauffer	EC
	16	SUPERFUND FACT SHEET RESULTS OF EPA GAMMA RADIATION SURVEYS A SAMPLING OF SLAG MATERIALS TAKEN IN THE T SPRINGS AREA IN JUNE - AUGUST 1998	Aug-98	9	US EPA Region 4		http://www.epa.gov/region4/waste/npl/nplfn/stauffer/fact.pdf		Stauffer	EC
	17	SUPERFUND FACT SHEET Community Advisory Group	May-00	4	US EPA Region 4		http://www.epa.gov/region4/waste/npl/nplfn/stauffer/cagfact.pdf		Stauffer	EC
M. Long Harbor, NF	1	Independent Review Long Harbor EIS Part II	Aug-94	8	Smith Environmental Tech. Corp. (BA 12767)	Related excerpts provided by Rhodia		Solvent Extraction, Sludge to Fertilizer, Encapsulation, In-situ Chemical Oxidation, In-situ Vitrification	Long Harbour, NF	HC
	2	Preliminary Evaluation of Decommissioning Options for No. 1 Pond and Mud Hole Areas Elemental P4 Plant Site Long Harbour, NF	Oct-93	4		Related excerpts provided by Rhodia		Mud-still, In-situ Natural Oxidation	Long Harbour, NF	HC
N. Rhodia, Silver Bow	1	Montana DEQ Letter and Info	Jun-06	Many	Mark Hall (MDEQ)	Multiple documents including MES process and patents		In-situ Forced Air Oxid, P4 Evap, P4 Recovery similar to GSHI front-end, GSHI Chromic Acid Patent, FEG Ref Info.	Rhodia, Silver Bow	HC
	2	Waste Plan - Volume I (STAND ALONE DOCUMENT)	Nov-01	Many	Rhodia			Capping, P4 Vaporization Roaster, Mobile Incin, Zimpro Anoxic H3PO4 Production, GSHI P4 Recovery, Thermal Oxid H3PO4 Recovery, Chemical Oxid	Rhodia, Silver Bow	HC - Separate Binder