



FMC Idaho LLC, Pocatello, Idaho

**Identification and Evaluation of
P4 Treatment Technologies**

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Section 1.0 Introduction

1.1 OBJECTIVE AND SCOPE OF THIS REPORT

The Supplemental Feasibility Study (SFS) for the FMC Plant OU will present the identification, screening and evaluation of remedial technologies and alternatives for all of the COCs and media identified in the *Supplemental Remedial Investigation Report for the FMC Plant OU (SRI Report)*; MWH, 2008). The SFS will include significant focus on options and technologies potentially effective to remediate elemental phosphorus (P4) in the subsurface due to the unique risks associated with management of P4. This report provides a summary of the process undertaken for the identification and preliminary screening of treatment technologies specific to P4 in the subsurface in advance of the SFS, to initiate discussion with EPA on appropriate options and technologies to carry forward into the detailed evaluation of alternatives.

This summary focuses on treatment technologies, both in-situ and ex-situ, for remediation of P4-impacted soils and groundwater at the FMC Plant Site. Non-intrusive remediation technologies, although they are potentially viable options, are not discussed in this report, but will be examined in the SFS screening and evaluation process. These non-intrusive technologies include the following:

- Institutional Controls – Fencing, Access Restrictions/Controls and Monitoring
- Containment – Capping and Surface Controls

In the SFS Report prepared for the FMC Plant OU, one or more of these non-intrusive remedial options may be combined to create non-intrusive alternatives for site remediation. They also may be considered as adjuncts to remedial alternatives that include active intrusion and treatment. Non-intrusive alternatives are particularly relevant when addressing P4 soil contamination due to the significant worker health and safety and environmental risks associated with active treatment of such contamination.

Ancillary process options that would be necessary to complete the overall P4 treatment train are identified and described in Section 2.0 as these are integral to the overall remedial alternatives that are evaluated here (e.g., excavation of P4-impacted soil is necessary to feed the material to an ex-situ treatment process). The processes also were evaluated with respect to their treatment of metals and radionuclides that also are found with P4-contaminated soils at the site. Note that for this document, “P4-impacted soils” is intended to include all soils and/or fill materials that are contaminated with elemental phosphorus at levels above the remedial action objective (RAO) for P4 in soils and ranging up to 50% P4 or greater.

In 2003, EPA prepared a similar report that evaluated possible treatment technologies for historic ponds at the FMC site containing P4 (in addition to metals and radionuclides). The EPA report entitled *Treatment Technologies for Historic Ponds Containing Elemental Phosphorus – Summary and Evaluation (2003 Treatment Technologies Report, EPA, 2003)* was used by FMC in preparation of this document. In addition, FMC reviewed pertinent information from other

elemental phosphorus sites, including manufacturing facilities, where the investigation and remediation included action for P4 in the subsurface. Table 1-1 presents a list of the commercial and military P4 sites and a summary of the remedy selected (or proposed) for the P4 soils and/or wastes, including waste ponds, at these sites. The table also indicates the lead Agency for the listed sites.

Other sources of information that were used for the identification and screening of technologies include the following:

- Review of internal FMC technical documents related to P4 experimentation, handling, neutralization, and safety practices
- Discussion with personnel at other P4 manufacturing facilities and review of technical information from these sources related to P4 treatment
- Search of Internet for technical documents related to P4 treatment

Section 5.0 of this report reviews the findings reached in the *2003 Treatment Technologies Report* and, considering the more recent information included in this summary report, reviews and updates those findings.

This summary, although not specifically required under the SRI/SFS AOC and SOW, is intended to assist in development of the SFS Report and constitutes the first step in the SFS Technology Screening Process.

1.2 REGULATORY BACKGROUND

The FMC Plant Operable Unit (OU) is a part of the larger Eastern Michaud Flats (EMF) Superfund Site, and is located in southeastern Idaho, approximately 2.5 miles northwest of Pocatello, Idaho. The EMF Site was listed on the National Priorities List (NPL) on August 30, 1990. The EMF Site includes two adjacent production facilities, a former FMC Corporation elemental phosphorus processing plant that ceased operation in 2001 and a phosphate fertilizer processing facility operated by the J.R. Simplot Company. The EMF Site is shown on Figure 1-1 and encompasses both the FMC and Simplot plants and surrounding areas affected by releases from these facilities. FMC, Simplot and EPA entered into a Comprehensive Environmental Response, Compensation and Liability Act (CERCLA) Administrative Order on Consent (AOC) in May 1991 under which the companies agreed to conduct a Remedial Investigation/Feasibility Study (RI/FS) for the site. During the RI/FS the site was divided into three "Subareas:" 1) the FMC Subarea, consisting of the FMC Plant Site (where elemental phosphorus production took place) and other FMC-owned properties at the site; 2) the Simplot Subarea, consisting of the Simplot plant and other Simplot-owned properties at the site; and 3) the Off-Plant Subarea, consisting of the remainder of the site. EPA changed these designations to the FMC Plant OU, the Simplot Plant OU, and the Off-Plant OU after its June 1998 *Record of Decision for the EMF Site (1998 ROD, EPA, 1998)*.

FMC ceased production of elemental phosphorus from phosphate ore at its Pocatello facility in December 2001. This led EPA and FMC to enter into an AOC in October 2003 (SRI/SFS AOC) for a Supplemental Remedial Investigation and Feasibility Study (SRI/SFS) at the FMC Plant OU. This was driven primarily by EPA's finding that additional investigations and evaluations were needed at the plant areas that had been actively operated at the time of the RI/FS but where operations had terminated with the plant shutdown. After the SRI/SFS is completed, it is anticipated that EPA will issue an Amended ROD specifying the FMC Plant OU remedial action requirements.

1.3 FMC SITE DESCRIPTION AND OPERATIONAL HISTORY

1.3.1 FMC Site Description

The FMC Plant Site is located approximately 2.5 miles northwest of Pocatello, Idaho, and 1 mile southwest of the Portneuf River, a tributary of the Snake River. The FMC Plant Site is south of Highway 30, covers approximately 1,150 acres, and historically contained all of the process operations used for the production of elemental phosphorus. The Plant Site adjoins the western boundary of the Simplot Don Plant, as shown on Figure 1-1. There are an additional 212 acres owned by FMC located north of Highway 30 (excluding the 9-acre Tesco property) that are also part of the FMC OU, but which have not been identified as areas with P4 contamination. Figure 1-1 also shows where the FMC OU is located in the State of Idaho and in relationship to the municipalities of Pocatello and Chubbuck. The FMC Plant OU is on privately-owned fee land, most of which is located within the exterior boundaries of the Fort Hall Indian Reservation.

A more detailed description of the site's physical characteristics can be found in Section 2.0 of the *SRI Report*. Additional detailed information on the geology and hydrogeology of the EMF Site study area and the FMC Plant OU is presented in Sections 3.1 and 3.3, respectively, of the *EMF RI Report*, as well as Section 2.0 of the *Groundwater Current Conditions Report for the FMC Plant Operable Unit* (MWH, October 2008).

1.3.2 Historic FMC Plant Process Description

The FMC Plant Site produced elemental phosphorus (P4) from phosphate-bearing shale ore mined regionally. Figure 1-2 shows the location of process areas of the site and the remediation units (RUs) identified for performing the SRI. Ore was shipped to FMC via the Union Pacific Railroad during the summer months and stockpiled (in RU 7). The ore was crushed, screened, and formed into briquettes prior to heat treatment (known as calcining). The calcining process (located within RU 8) involved heating the ore briquettes to a sintering temperature of approximately 1,200°F to form nodules. Carbon monoxide (CO), a by-product of the phosphorus furnace reaction, was used as fuel to fire the calciners. The nodules were blended with coke and quartzite (known as silica) to make the phosphorus furnace feed. This mix of nodules, coke and silica was fed into four electric arc furnaces (located within RU 1). The furnace reaction primarily yielded gaseous P4, CO gas, slag, and ferrophos (FeP). The P4 gas was subsequently condensed to a liquid state and stored in sumps and tanks in the furnace building and phos dock prior to shipment off-site as product.

P4 will burn upon contact with air. Therefore, to prevent oxidation, the condensed phosphorus product was kept covered with water from the time it was produced through loading and transport off-site. All of the elemental phosphorus product manufacturing and handling processes were located within RU 1, with the exception of long-term phosphorus storage tanks located in RU 6.

Process water (known as phossey water) was used to isolate elemental phosphorus from contact with air and to slurry precipitator dust (a furnace by-product). Phossey water and precipitator slurry were typically managed separately in a series of surface impoundments located to the west of the elemental phosphorus furnaces. A number of these surface impoundments (Ponds 8S, 11S, 12S, 13S, 14S, 15S, 16S, 17S, 18A, 8E, and 9E) were closed and capped under EPA-approved RCRA closure plans and are not subject to the SRI/SFS (designated as RU 22a). Numerous other surface impoundments were historically dewatered and/or covered. These ponds, which had ceased receiving wastes prior to termination of their Bevill exemption and thus were not subject to RCRA, are located within RU 22b. The railroad swale (designated as RU 22c) was designed as a stormwater retention area but also received phossey water (and therefore P4) from process spills in the furnace building and phos loading dock.

More detailed information regarding the ore processing, by-product handling, and waste management operations at the FMC Plant Site is provided in Sections 1.1.2 through 1.1.3 of the *EMF RI Report*.

1.3.3 Description of FMC Plant Site P4 Product and P4-Containing By-Products

The following subsections provide a brief description of P4 and other materials (precipitator solids, phossey solids, and native soil) that could be expected to be encountered along with P4 at the FMC Plant Site and thus are important in evaluating P4 treatment technologies during the SFS. It should be noted that slag and ore from the P4 manufacturing process would also be expected to be encountered along with P4. A description of these materials can be found in Sections 1.3.3.1 and 1.3.3.2 of the *SRI Report*, respectively.

1.3.3.1 Description of P4

The primary product from the FMC facility was white (or yellow) phosphorus. Elemental phosphorus (P4) exists in three distinct configurations called allotropes, all with the same molecular weight, but each differing significantly from the other allotropes in physical and chemical characteristics. The chemical formula for all allotropes of elemental phosphorus is P4; however, they have different names according to their respective colors, including black, red, violet, and white (sometimes called yellow due to impurities). While some transformation of white (or yellow) P4 may have occurred at the FMC Plant Site at very insignificant rates, by far the predominant allotrope expected to be encountered on site is white (or yellow). Therefore, the SFS technology screening will be limited to white P4.

Physical & Chemical Characteristics: White P4 is a waxy solid that may be colorless, white, or yellow, and has a garlic-like odor. Table 1-2 provides a summary of some of the physical properties of P4, which shows that it is relatively insoluble in water, with a solubility of 3 mg/L at 15°C.

The primary processes for chemical transformation of P4 are oxidation and hydrolysis. In a solid phase such as in soil, P4 oxidizes spontaneously with oxygen in air to form phosphorus pentoxide (P₄O₁₀, commonly expressed as P₂O₅), which exists as a particulate at ambient conditions. Phosphorus pentoxide has a strong affinity for water and will react with water (hydrolyze), including moisture from the atmosphere, to form various phosphorus acids, primarily orthophosphoric acid (H₃PO₄). In water, dissolved P4 is oxidized by dissolved oxygen (DO) to form various forms of soluble phosphorus acids, including H₂PO₄⁻, HPO₄⁻², and PO₄⁻³. In water with other dissolved ions, and depending on environmental conditions such as pH and Eh, these acids may be further converted to a solid metal phosphate compound such as calcium phosphate. The rate of phosphorus oxidation in water is governed by the form of the phosphorus (dissolved or suspended), DO concentration, salt concentration, metal ion concentration, pH, and temperature.

Table 1-2. Physical Properties of White P4

Physical Property	Characteristic
Chemical Formula	P4
Appearance	White (or yellow) waxy solid at ambient temperatures
Boiling Point	280.5°C
Flash Point	Spontaneously combusts in air
Melting Point	44.1°C
Molecular Weight	123.89
Solubility	In water: 3 mg/L at 20°C
Vapor Pressure	0.026 mm Hg at 20°C

P4 also is hydrolyzed in water to form phosphine (PH₃) and lesser amounts of phosphorus acids. PH₃ is a toxic gas that has a low solubility, and thus is expected to migrate from the water to the air; the portion of phosphine that dissolves is generally oxidized to form the above-referenced forms of phosphorus acids. The rate of hydrolysis of P4 is enhanced by an increase in the pH of the water reacting with the white phosphorus (WP). (USACE, 1996)

P4-impacted soils are known (or suspected) to be present in the following areas of the FMC Plant Site:

- RU 1 – Furnace building, secondary condenser, and phos loading dock due to leaks and spills from production processes and waste management;
- RU 2 – Slag pit due to leaks and spills from production processes and waste management;

- RU 13 – Pond 8S recovery process area and metal scrap preparation area due to management of waste materials in the adjacent old pond area;
- RU 22b – Old pond area due to management and disposal of P4 containing wastes;
- RU 22c – Railroad swale, due to phosphy water spills entering stormwater sewers and discharging to the stormwater retention pond; and
- Areas containing underground piping or sewer lines that carried phosphy water, precipitator slurry, or CO gas, and therefore could contain P4 (RUs 1, 2, 3, 8, 12, 13, 22b, and 24) which may have P4 remaining in pipes or which may have leaked from pipes.

P4-impacted groundwater has been identified immediately downgradient (flowing to the northeast) of RUs 1 and 2. P4 in the capillary fringe soils immediately above groundwater have been identified in RUs 3 and 7, associated with this P4-impacted groundwater.

Section 1.3.4 provides a description of each of these areas, including the types of materials to be encountered along with the P4, particle sizing, P4 concentrations, and depth of P4 contamination. The physical setting in which the P4 is found and the nature of the P4 are important factors in screening and evaluating potential remedial options.

1.3.3.2 Description of Precipitator Solids

Precipitator solids (otherwise referred to as precipitator slurry, precipitator dust, and/or fluid bed dryer slurry/prills) were produced in the electrostatic precipitators immediately downstream of the phosphorus furnaces. The precipitator solids consisted of furnace feed dust and condensed constituents that had boiled off in the high temperatures of the furnace (including metals, radionuclides, and P4). Prior to 1955 precipitator solids were handled dry. After 1955, a slurry system was installed for all the precipitators with the resulting slurry being pumped to a series of ponds located in RU 22b. When possible (e.g., phosphorus content was not too high), precipitator slurry was allowed to air dry in these ponds. Dried precipitator slurry (precipitator solids) was reclaimed from these ponds and sold as a fertilizer additive due to its high zinc content.

Precipitator dust contained in any of the historical ponds is assumed to have some level of P4 remaining in the sediment matrix at concentrations ranging from 0 ppm to 10,000 ppm. However, it is important to note for the SFS technology screening that addition of precipitator slurry to historical ponds may have locally concentrated P4 to much higher levels (e.g., liquid P4 was known to have accumulated at the discharge area of piping into the ponds, resulting in a large frozen mass of highly concentrated [50% or higher] P4).

Physical, Radiological and Chemical Characteristics: Precipitator solids are typically described as “fine-grained, dark-gray-to-black material.” While the particle size of precipitator dust is relatively uniform, cover materials such as slag and ore placed on historical ponds certainly would impact particle size distribution of materials in these ponds.

A summary of radiological sampling results for precipitator solids is presented in Table 1-3 of the *SRI Report* and these activities are also presented in Table F-1 of the *RI Update Memo*. Elevated levels of lead-210 and polonium-210 are associated with precipitator solids (labeled “Precipitator Slurry/Phossey Wastes” in Table 1-3 of the *SRI Report*). In addition, precipitator solids were sampled as part of the SRI fill characterization study and analyzed for gross alpha, gross beta, radium-226, uranium-238, potassium-40, lead-210, and polonium-210. The radionuclide sample results from the SRI are discussed in Section 4.27 of the *SRI Report*.

Table 1-4 of the *SRI Report* presents total metals and fluoride concentrations in historical precipitator solids samples. In addition, precipitator solids were sampled as part of the SRI fill characterization study and analyzed for fluoride and metals. The fluoride and metal sample results from the SRI are presented in Section 4.27 of the *SRI Report*.

In addition to ponds in RU 22b, precipitator solids were known to be present (or have been identified through sampling) in the following areas:

- RU 1 – Precipitator dust and slurry was generated within the furnace building.
- RU 2 – Releases of precipitator slurry were at times washed from the furnace building into the slag pit.
- RU 10 – During the SRI, solids containing precipitator slurry were identified in the sediment in the non-contact water cooling pond. These solids were likely from spills of precipitator slurry within the furnace building that became co-mingled with non-contact cooling water.
- RU 12 – During the RI, solids identified as precipitator solids were identified within the western edge of RU 12. Although there are no historical records to indicate that a surface impoundment ever existed in this area, pond solids may have been stockpiled or spilled in this area during precipitator dust recovery.
- RU 13 – During the SRI, solids containing precipitator solids (identified as a red fill) were identified within RU 13. Although there are no historical records to indicate that a surface impoundment ever existed in this area, pond solids (or soils impacted by pond leaching) may have been stockpiled (or used as fill in this area).
- Areas containing underground piping or sewer lines that carried precipitator slurry (and therefore could contain P4) are located in RUs 1, 2, 12, 13, 22b, and 24.

1.3.3.3 Description of Phossey Solids

Phossey solids, otherwise referred to as phossey water solids, oxidized phossey solids, and/or phossey slurry, were produced throughout the phosphorus manufacturing process and were typically solids (consisting of ore dust, coke, dust, silica dust, slag dust and/or precipitator dust) containing phosphorus within a phossey water stream. The phossey solids accumulated within the water stream as a result of contact with phosphorus-containing process streams (e.g., phosphorus product and phosphorus sludge). These various phossey water streams were accumulated within

sumps/drains/tanks and pumped to slurry ponds located to the west of the furnace building (in RU 22b), where the phosby solids were allowed to settle and accumulate. These ponds were maintained with a water cover to prevent oxidation of phosphorus with air. Early phosby water ponds, i.e., those that ceased operation before RCRA management requirements became applicable, were eventually “closed” by dewatering and being covered with other fill materials such as precipitator dust slag, and/or native soils. These pre-RCRA historic ponds are located in RU 22b.

Phosby solids contained in any of the historical ponds or railroad swale are assumed to have some level of P4 remaining in the sediment matrix, at concentrations ranging from 0 ppm to 10,000 ppm. However, it is important to note for the SFS technology screening that addition of phosby solids to historical ponds may have concentrated P4 to much higher levels. For example, liquid P4 was known to have accumulated at the discharge area of piping into the ponds, resulting in a large frozen mass of highly concentrated (50% or higher) P4.

Physical, Radiological and Chemical Characteristics: Phosby solids that were allowed to dry typically resulted in oxidation of the phosphorus, leaving gray to dark-gray or black sediments. However, the appearance of phosby solids can vary depending on the other types of solids with which they are found (i.e., ore, coke, slag, silica or precipitator dust). While the particle size of phosby solids is relatively uniform, cover materials such as slag and ore certainly would impact the particle size distribution of materials in historical ponds.

A summary of radiological sampling results for phosby solids is presented in Table 1-3 of the *SRI Report*. These activities are also presented in Table F-1 of the *RI Update Memo*. An additional phosby solids sample was collected as part of the SRI fill characterization study and analyzed for gross alpha, gross beta, radium-226, uranium-238, potassium-40, lead-210, and polonium-210. All the SRI radionuclide sample results are discussed by RU in Section 4.27 of the *SRI Report*.

Table 1-4 of the *SRI Report* presents total metals and fluoride concentrations in historical phosby solid samples. In addition, a phosby solids sample was collected as part of the SRI fill characterization study and analyzed for fluoride and metals. The fluoride and metal sample results from the SRI are presented in Section 4.27 of the *SRI Report*.

In addition to ponds in RU 22b, phosby water and phosby solids were known to be present, or have been identified through sampling, in the following areas:

- RU 1 - Most phosby water was generated within the furnace building, phos dock and secondary condenser where P4 was produced, stored, and recovered.
- RU 2 – Releases of phosby water were at times washed from the furnace building into the slag pit.
- RU 12 – During the RI, solids identified as precipitator solids were identified within the western edge of RU 12. Although there are no historical records to indicate that a surface impoundment ever existed in this area, pond solids may have been stockpiled or spilled in this area during precipitator dust recovery.

- RU 13 – During the SRI, solids containing precipitator solids (identified as a red fill) were identified within RU 13. Although there are no historical records to indicate that a surface impoundment ever existed in this area, pond solids (or soils impacted by pond leaching) may have been stockpiled or used as fill in this area.
- RU 22c - Phosphy water spills to the surface in the furnace building or phos dock were often captured in the storm sewer system, which discharged to the railroad swale (stormwater retention pond).
- Areas containing underground piping or sewer lines that carried phosphy water (and therefore could contain P4) are located in RUs 1, 2, 3, 12, 13, 22b, and 24.

1.3.3.4 Description of Native Soils

Surface soils at the FMC Plant OU originated from deposition by fluvial erosion and deposition (alluvium), collection at the base of slopes (colluvium), weathering in place (residuum), and deposition by wind (loess). As described in Section 1.2 of the *EMF RI Report* and in Section 2.2.2 from the *FS Report*, the area where the FMC Plant OU is located is underlain to some depth by soils consisting of calcareous silts and clays (loess). These silts and clays have an average pH greater than 8 and, because of their calcareous nature, a high buffering capacity. The high pH will act to neutralize acidic materials, precipitate cations that form carbonate solutions, and provide for numerous cation exchange opportunities for trace elements. The silts are of greatest thickness in the western and central portions of the FMC Plant Site and extend to the south beyond the FMC Plant OU boundary (BEI, 1997).

The stratigraphy of the FMC Plant OU generally can be described as discontinuous layers of unconsolidated sediments deposited on an erosional surface that was incised in volcanic bedrock. The sedimentary units immediately above the bedrock are gravels derived from volcanic rocks. The stratigraphy at the FMC Plant OU includes, in ascending order, volcanic bedrock units (rhyolite, tuff, and some basalt), coarse volcanic and quartzitic gravels, fine-grained sediments of the American Falls Lake Bed, Michaud gravels, Aberdeen alluvial terrace deposits (locally) and loess deposits of calcareous silts and clays. Loess is present at both higher elevations and lower elevations of the site in varying thicknesses. Loess deposits are much thicker in portions of drainages where they have been reworked and redeposited.

1.3.4 Description of Areas (RUs) Where P4-Impacted Soils Are Expected

Because of the differing process operations within the FMC Plant Site that managed P4 product and P4-containing waste, different areas of the site that are known or suspected of having P4-impacted soils have varying physical settings in which P4 is or may be encountered in the subsurface. Deposited P4 is typically associated with varying amounts of slag, ore, precipitator solids, phosphy solids, and native soils. In order to effectively screen and evaluate P4 treatment technologies and, as discussed in Section 2.0, the ancillary processes necessary to implement a treatment technology, it is critical to understand the following physical properties in each differing area of the site:

- Relative P4 concentrations and the variability of P4 concentrations across the area;
- Depth of P4 deposition;
- Total volume of P4 and impacted fill that must be handled and processed;
- Particle size distribution, not only of the frozen P4 particles, but also of other fill materials and soils associated with the P4-impacted matrix; and
- Other fill materials (and associated COCs) included in the P4-impacted matrix that must also be treated or handled.

Table 1-3 provides a summary of these physical characteristics for the areas of P4-impacted soils. These physical characteristics for each of the areas of P4-impacted soils are further described in the following subsections.

1.3.4.1 Furnace Building, Phos Dock & Secondary Condenser (RU 1) and Slag Pit (RU 2)

RU Description: RU 1 is 4.1 acres in size and encompasses the locations of the former furnace building, secondary condenser, and phos dock. These were the primary P4 product production, storage, and handling areas within the FMC Plant Site. The furnace building contained electric arc furnaces, primary condensers, P4 sumps, and various tanks. The secondary condenser was downstream of the furnaces and provided final recovery of P4 product, collecting that in a single sump. P4 from the furnace sumps and the secondary condenser sump was pumped to the phos dock for storage and loading onto rail cars for shipment. Because of the pyrophoric nature of the P4, the P4 product was contained within a closed system, consisting of piping, pumps and tanks, and was always covered with water to prevent the P4 from contacting air. Water that came into contact with P4 was known as phosy water and typically contained small particles of P4, ore dust, coke dust, silica dust, and P4 reaction products. This phosy water was pumped via underground and aboveground piping to ponds in RU 22b.

Furnace offgas, containing primarily CO and P4 gases, passed through an electrostatic precipitator in which particulate was removed to clean the offgas stream. The dust collected in the electrostatic precipitator, known as precipitator dust, was then slurried with recycled water and pumped via underground and aboveground piping to ponds in RU 22b and RU22a (RCRA Ponds).

RU 2 is 3.7 acres in size and encompasses the former slag pit located immediately south of the furnace building (RU 1). It is an area where molten slag from the furnaces was poured, cooled, broken, and loaded onto slag haul trucks to be placed on the slag pile (RU 19). In 1999-2000, FMC converted to slag ladling, where the molten slag was poured from the furnaces into ladles. The ladles were truck mounted, allowing for the molten slag to be transported to the slag pile where it was poured down the face of the slag pile and allowed to cool and solidify. Prior to implementing slag ladling, the soils beneath RUs 1 and 2 (down to groundwater) were heated by the molten and cooling slag to above the 44°C melting point of P4.

The heated column of soil located beneath the furnace building and slag pit respectively at RUs 1 and 2 would allow the P4 from surface and subsurface spills, such as spills or releases from product sumps, underground piping, and slag pit catch basins, to remain as a liquid and thus move downward to groundwater (to a depth of approximately 85 feet). The phos dock and secondary condenser are positioned well outside the 44°C isotherm; thus, there is limited potential for migration of P4 downward to the groundwater in these areas.

P4 therefore likely exists in soils and fill materials to a depth of 10 feet throughout RUs 1 and 2 at concentrations varying from 0 to 50%, with the highest concentrations being immediately under P4 product sumps. Within the 44°C isotherm, P4 likely exists throughout the soil column to groundwater. As liquid P4 likely filled the void spaces between soil particles in the vadose zone, concentrations up to 30% may be possible.

Fill Materials: As summarized on Table 4-2 of the *SRI Report*, the surface of RU 1 and RU 2 is made of up of slag, concrete foundations, asphalt with slag aggregate, and silica. The subsurface fill materials around the perimeters of RUs 1 and 2 consist primarily of slag, concrete foundations, and reworked native soils and slag. Although not visually identified, process knowledge has identified precipitator solids as an incidental fill material in RUs 1 and 2. The native soil interface around the perimeters of the RUs ranges between 1.5 and 20 feet bgs. With a predominance of slag on the surface, particle size distribution down to 20 feet bgs would range from very fine to plus 6-inch. The concrete slabs within RU 1 range from 2 feet to 10 feet in thickness and are highly steel reinforced.

Below 20 feet bgs and within the 44°C isotherm, the P4 is likely to be within native soils, consisting of gravelly silts and sands in the upper three to nine feet, followed by 20 to 30 feet of silt to sandy silt, 40 to 50 feet of coarse sands, gravels, and cobbles, and finally 10 feet of silts and sandy silts at the capillary fringe.

As discussed in Section 4.2 of the *SRI Report*, groundwater is encountered at a typical depth of 85 feet bgs. P4 was encountered (as evidenced by slight smoking) at the capillary fringe in 2 borings in RU 3 and at 1 boring in RU 7, both immediately downgradient to the northeast of RU 1. Based upon the 2-foot split spoon interval that was sampled and observed, the P4 was limited to a 2-foot interval immediately above the groundwater. Based upon the amount of smoking observed in the capillary fringe sample, it is estimated that the P4 concentration was at least 1,000 ppm but well below 10,000 ppm.

As discussed in Section 4.2.4 of the *SRI Report*, the P4 estimated to be present combined within RUs 1 and 2 is 580 to 5,470 tons. RUs 1 and 2 contain total estimated fill volumes of 56,580 yd³ and 20,485 yd³ respectively.

Summary of Pertinent SFS Information for RUs 1 and 2:

- P4 concentrations vary from 0 to 50% across the RUs at depths down to 10 feet, 0 to 30% in soils down to the capillary fringe at 80 feet bgs (within the 44°C isotherm), and 1,000 to less than 10,000 ppm within the 2-foot capillary fringe encountered at about 83 feet bgs;

- Total estimated mass of P4 is 580 to 5,470 tons and total estimated volume of fill is 77,065 yd³;
- Particle size distribution for fill materials would range from minus ¼-inch to plus 6-inch, (with crushed slag amassing to form monolithic particles several feet in diameter in some areas) with a similar range for native soils; and
- Other fill materials include slag, concrete, asphalt, silica, phossey solids, precipitator solids, and underground piping (see Section 1.3.4.4).

1.3.4.2 Historical Surface Impoundment Area (RUs 13 and 22b)

RU Description: RU 13 is 3.6 acres in size and is located in the south-central portion of the FMC Plant Site, as shown on Figure 1-2. It is immediately southwest of RU 12 and is adjacent to several old ponds. RU 13 is north of a portion of RU 22b (old phossey water ponds). Because RUs 13 and 22b share a common boundary and have similar fill materials, this report evaluates them together. Although RU 13 was never documented to have been used directly in the P4 production process operation, in the mid-1980s a process was developed, built, and tested on the northern side of Pond 8S to recover P4 from Pond 8S. This process (the Pond 8S recovery process) was located within the RU 13 boundaries. The Pond 8S recovery process was shut down, closed and removed in 1993. Pond solids may have been stockpiled or used in RU 13 as fill material prior to construction of the Pond 8S recovery process.

RU 22b is 37.7 acres in size and consists of four separate parcels in the western portion of the FMC Plant Site as shown on Figure 1-2. As described above, waste streams that contained P4 (i.e., phossey water and precipitator slurry) were slurried and pumped to a series of ponds at RU 22b. The hydraulic head at the old ponds was removed through solar evaporation.

In 1954, the initial ponds in RU 22b were created and began receiving phossey water. In 1955, a slurry system was installed for all the precipitators with the resulting slurry similarly being pumped to ponds within RU 22b. When possible (e.g., phosphorus content was not too high), precipitator slurry was allowed to air dry in these ponds. Dried precipitator slurry (precipitator solids) was reclaimed from these ponds and sold as a fertilizer additive due to its high zinc content. All of the ponds located in RU 22b (with the exception of Pond 10S) were closed during a period from 1972 through 1976 by being covered with various materials, including native soil, dried precipitator dust and prills, ore, and slag.

Precipitator solids and phossey solids contained in any of the historical ponds is assumed to have P4 remaining in the sediment matrix at concentrations ranging from 0 ppm to 10,000 ppm. However, it is important to note for the SFS technology screening that addition of precipitator slurry to historical ponds may have concentrated P4 to much higher levels, for example through the accumulation of liquid P4 at the piping discharge area as the heated phossey water/precipitator slurry stream discharged into the surface impoundment. P4 in the liquid phase tended to immediately freeze upon entering the surface impoundment and create a large frozen mass of highly concentrated P4 (50% or higher). During operation of the ponds, the piping discharge point was periodically moved to prevent “islands” of sediments from extending above the water

line. Therefore, areas of highly concentrated P4 associated with the pipe discharge are variably distributed throughout the pond sediments.

Fill Materials: As summarized on Table 4-2 of the *SRI Report*, the fill materials within RUs 13 and 22b consist of slag, concrete foundations, asphalt with slag aggregate, precipitator solids, phosphy solids, ferrophos, underground piping and reworked native soils (i.e., native soils that have been mechanically mixed with other fill materials). Fill depth within RU 13 ranges from 1 to 25 feet. Fill depth within RU 22b ranges from 0 to 44 feet.

As discussed in Section 4.13.4 of the *SRI Report*, the mass range of P4 estimated for RU 13 is 25 to 60 tons. The total volume of all fill materials at RU 13 is 66,630 yd³. As discussed in Section 4.18.4 of the *SRI Report*, the mass range of P4 estimated for RU 22b is 4,440 to 10,800 tons. The total volume of all fill materials for RU 22b is 595,820 yd³.

Summary of Pertinent SFS Information for RUs 13 and 22b:

- P4 concentrations vary from 0 to 50% across the RUs;
- Depth of P4 contamination extends to 44 feet bgs (maximum depth of former ponds / fill material);
- Total estimated mass of P4 is 4,465 to 10,860 tons and total estimated volume of fill is 662,450 yd³;
- Particle size distribution for fill materials would range from minus ¼-inch to plus 6-inch , (with crushed slag often becoming compacted in-place to form monolithic layers up to several feet in thickness in some areas as observed during the SRI trenching conducted at RU22c); and
- Other fill materials include slag, concrete, asphalt, ore materials, phosphy solids, precipitator solids, ferrophos, and underground piping (see Section 1.3.4.4).

1.3.4.3 Railroad Swale (RU 22c)

RU Description: RU 22c is 2.4 acres in size and is located to the north of the P4 production areas along the northeastern boundary of the FMC Plant Site, as shown on Figure 1-2. The railroad swale was designed as a stormwater retention area. It received stormwater from the underground storm sewer piping within the plant production area. However, phosphy water spills and releases from the furnace building and phos dock also discharged to the railroad swale, either through the underground storm sewer piping or by over-surface flows. As a result, the railroad swale received not only stormwater but also P4 and phosphy solids. Because the railroad swale ran parallel to the ore stockpile, ore dust was also likely to have blown into the swale. In the mid-1980s the railroad swale was dug out to a depth of 10 to 20 feet and backfilled with slag. It was partially lined in 1993 to reduce infiltration of water into the subsurface.

Although the railroad swale received phosphy water (and associated P4), this discharge was at ambient temperatures. Therefore, the P4 deposition was different than in the ponds within RU

22b, i.e., there is no evidence of concentrated areas of P4 in the railroad swale. During the SRI, one trench across the railroad swale was found to contain P4, as evidenced by slight smoking. It is presumed, based upon the SRI sampling and process knowledge that P4 concentrations in the sediment matrix within the railroad swale are fairly consistent and range from 0 ppm to less than 10,000 ppm.

Fill Materials: As summarized on Table 4-2 of the *SRI Report*, the fill materials within RU 22c contain slag (presumed to minus 2-inch be crushed slag), phoshy solids, and ore. Fill depth within RU 22c ranges from 5 to 20 feet (based upon historical knowledge and SRI findings).

As discussed in Section 4.19.4 of the *SRI Report*, the mass range of P4 estimated for RU 22c is 4 to 10 tons. The estimated total volume of all fill materials for RU 22c is 40,607 yd³.

Summary of Pertinent SFS Information for RU 22c:

- P4 concentrations vary from 0 to less than 10,000;
- Depth of P4 contamination extends to 20 feet bgs;
- Total mass of P4 is 4 to 10 tons and total volume of fill is 40,607 yd³;
- Particle size distribution for fill materials would range from minus ¼-inch to 2-inch (with crushed slag amassing to form monolithic particles several feet in diameter in some areas); and
- Other fill materials include slag, phoshy solids, and ore.

1.3.4.4 Areas with Underground Piping Suspected of Containing P4

There are a number of RUs that contain underground piping that were used to carry phoshy water, precipitator slurry or CO gas from the furnace building, slag pit and phos dock to other areas of the plant. Underground storm water piping that at times likely conveyed phoshy water also is present in RUs 1, 3, and 24. All this underground piping was left in place during decommissioning of the plant and, while it was allowed to gravity drain, it was not cleaned in place. As such, the underground piping may contain P4. RUs where these underground piping or stormwater lines that exist are RUs 1, 2, 3, 8, 12, 13, 22b, and 24. Underground piping was constructed of mild steel, although the storm water piping in RUs 1 and 3 was constructed of concrete. While the underground piping was likely placed at least 3 to 5 feet below grade at the time of installation to protect against freezing, additional fill may have been placed on top of older piping such that some piping may be up to 10 to 15 feet below the current surface.

In contrast to the P4 processes in RU 1, the old underground pipelines that transported precipitator slurry or phoshy water to the phoshy ponds in RU 22b were not heated. The old pipelines were placed underground to prevent the wastewater in the pipelines from freezing during winter conditions. The P4 wastewater from RU 1 was at typical operating temperatures (60 to 66 C) when pumped into the pipelines. The temperature of the wastewater in the old

underground pipelines would not have added a significant heat load, in terms of increased temperature, to the surrounding soil beyond a few feet from these lines.

Soil temperatures are not elevated above a natural range of subsoil temperatures (approximately 12 to 17 C) in the subsurface beneath the precipitator slurry and phosphy water pipelines, excluding those segments of pipelines in RUs 1 and 2 that were within the 44° C isotherm associated with the slag pit. In the areas outside the 44° C isotherm in RUs 1 and 2, a release of P4 to the subsurface (e.g., pipeline leak) would freeze fairly rapidly and be immobilized in an area near the point of release. Migration of P4 beyond a few feet from the lines would have been limited to dissolved P4 at a concentration below the solubility limit of P4.

One underground CO line remains within RU 8, consisting of the former CO feed line to the calciners. While this CO line may contain a small quantity of fairly pure P4, the CO line most likely did not leak because a leaking CO line would have been detected immediately.

Underground storm water lines in RUs 1, 3, and 24 did carry phosphy water to the railroad swale. There is potentially some P4 remaining in the bottom of these storm sewer lines, although since these streams were managed at ambient temperatures, P4 would likely not have accumulated. Leaks may have occurred at the cement piping joints, although migration of P4 beyond a few feet would not be expected.

P4 concentrations within the underground piping may range from 1% to 100%. As discussed in Section 4.26.4 of the *SRI Report*, the mass range of P4 estimated collectively within the remaining phosphy water and precipitator slurry underground pipelines is between 2.8 and 28 tons. The P4 estimated within the single remaining underground CO line is between 0.2 and 1.8 tons. The underground storm water piping is estimated to contain between 0.13 and 0.6 tons of P4. These P4 mass estimates do not include potential leakage or loss at pipeline cleanouts (from maintenance) that may have occurred but is not quantifiable.

Summary of Pertinent SFS Information for Underground Piping:

- P4 concentrations vary from 1% to 100% throughout the underground piping;
- Depth of P4 contamination is estimated to be no deeper than 15 feet below the current surface;
- Total volume of P4 is estimated to be between 3.13 to 30.4 tons collectively for all the underground piping;
- Other fill material in and around the underground piping includes slag, phosphy solids, precipitator solids, ore, and native soils.

1.4 REPORT ORGANIZATION

The remainder of this document is organized as follows:

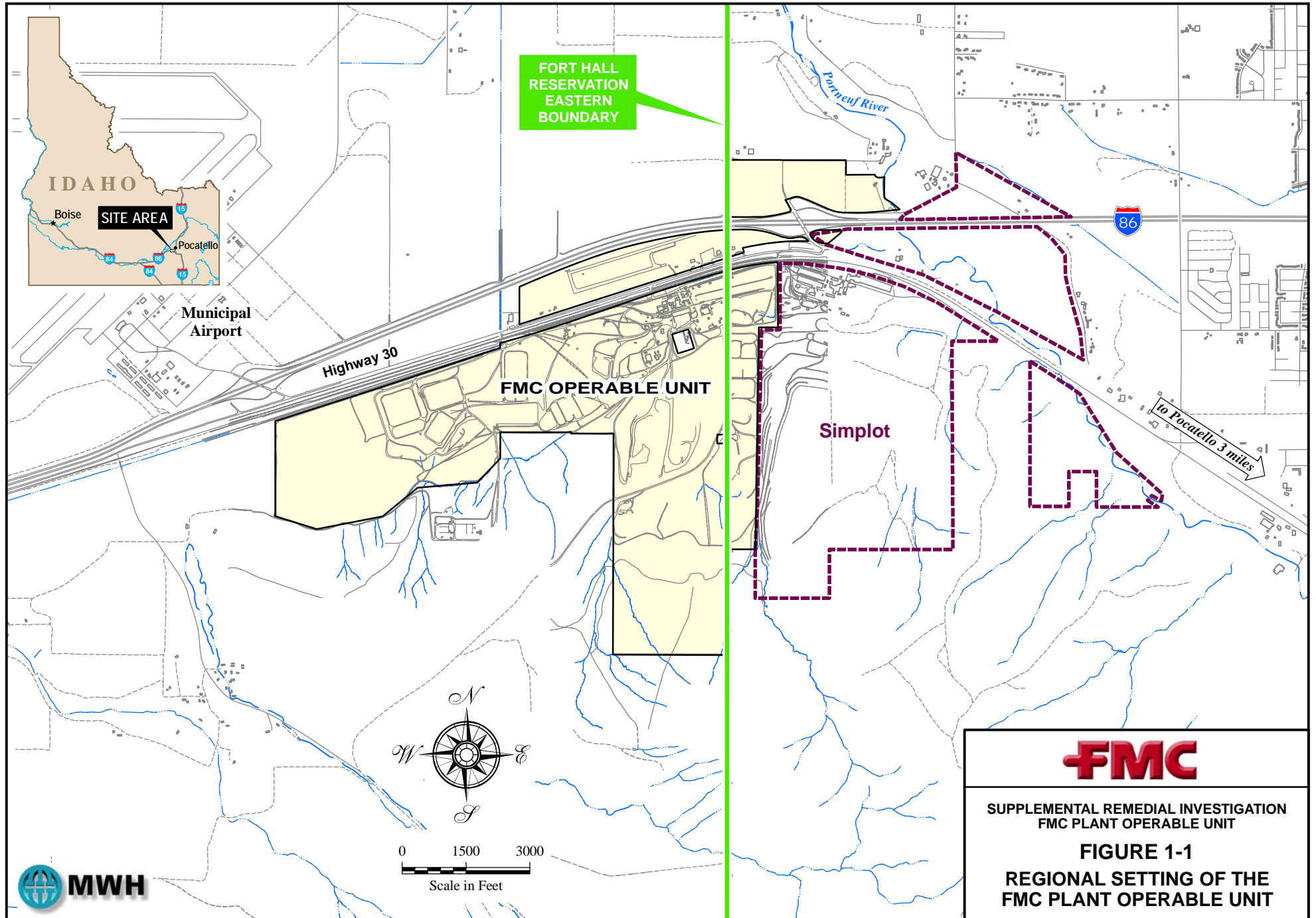
Section 2.0 – Ancillary P4 Technology Processes - primarily discusses the processes that are required on the upstream and downstream sides of the treatment train that have to be considered when implementing these active technologies at full scale.

Section 3.0 –Elemental Phosphorus Treatment Technologies for Soil – discusses each technology identified for potential applicability to P4-impacted soils.

Section 4.0 – Elemental Phosphorus Treatment Technologies for Groundwater – discusses each technology identified for potential applicability to P4-impacted groundwater.

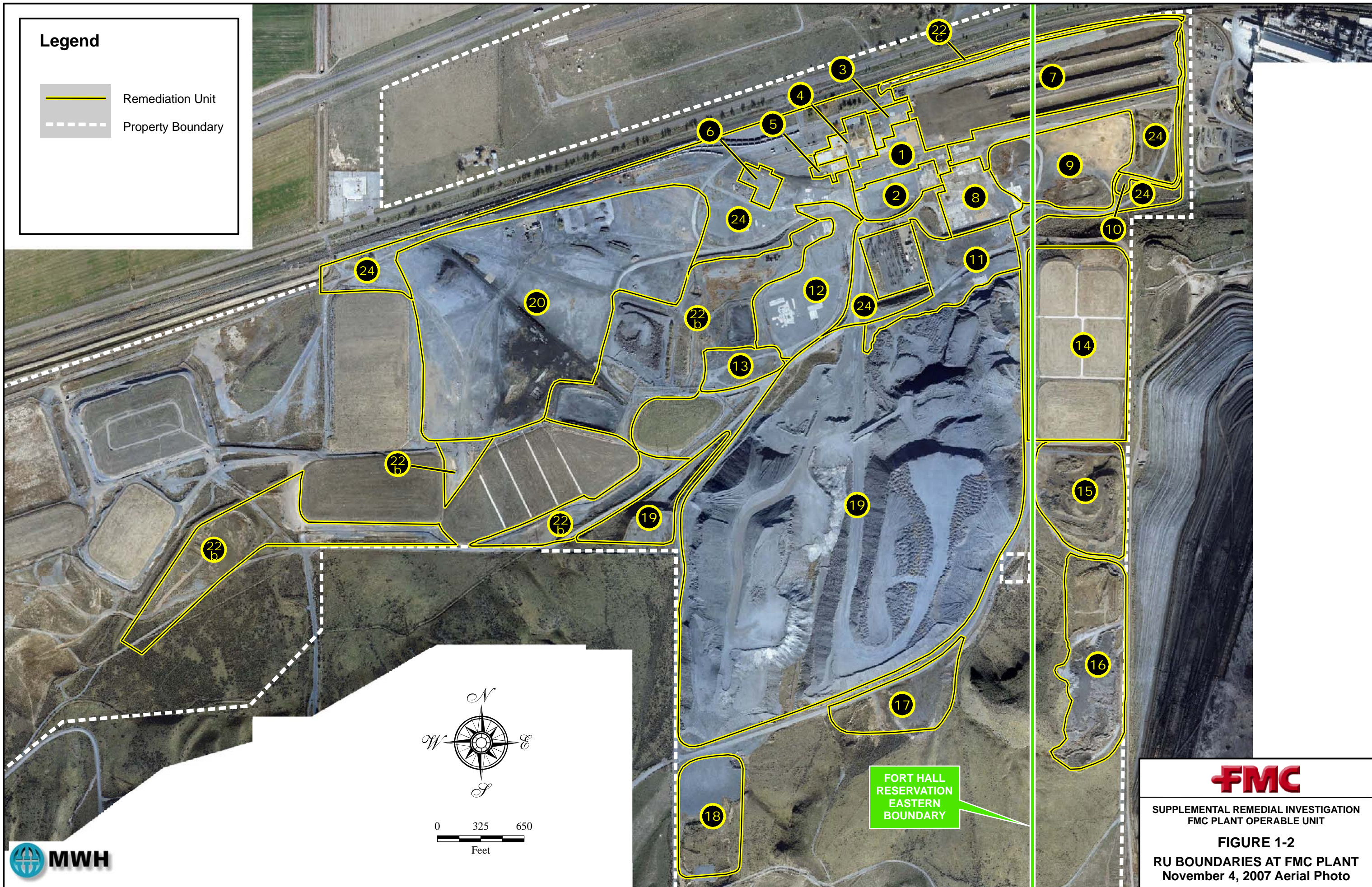
Section 5.0 – Findings - reviews the findings reached in the *2003 Treatment Technologies Report* and, considering the more recent information included in this summary report and updates those findings.

Section 6.0 - Reference List



Legend

- Remediation Unit
- - - Property Boundary



FILE Fig 1-02_RU Boundries at FMC Plant_208.mxd 4/14/08



SUPPLEMENTAL REMEDIAL INVESTIGATION
FMC PLANT OPERABLE UNIT

FIGURE 1-2
RU BOUNDARIES AT FMC PLANT
November 4, 2007 Aerial Photo

TABLE 1-1

SUMMARY OF P4 SOIL / SOLID WASTE REMEDIES– COMMERCIAL AND MILITARY SITES

COMMERCIAL P4 PRODUCT MANUFACTURING, HANDLING, and/or DISPOSAL SITES	
Name and Location	P4 soil/solid waste Remedy and oversight agency
Rhodia (fka Stauffer Chemical Company), former Elemental Phosphorus Production Plant, Silver Bow, Montana	In the RCRA corrective action process, CA not yet determined. [EPA]
Monsanto Company, former Elemental Phosphorus Production Plant, Columbia, Tennessee	Cap (design information not readily accessible) over areas contaminated with elemental phosphorus. [State]
Monsanto Company (aka P4 Production LLC), Elemental Phosphorus Production Plant, Soda Springs, Idaho	Cap (design information not readily accessible) over former ponds; operating facility subject to further remedial actions at closure. [EPA]
Tennessee Valley Authority, former Elemental Phosphorus Production Plant, Muscle Shoals, Alabama	Cap (1 foot of limestone and 6 inches of concrete) over buried sludges. [State]
Stauffer Chemical Company, former Elemental Phosphorus Production Plant, Tarpon Springs, Florida	Cap (design information not readily accessible) over unlined ponds after in situ stabilization plans abandoned due to fires and uncontrolled reactions. Groundwater remedy includes cut off wall for shallow aquifer. [EPA]
Stauffer Chemical Company (Rhone Poulenc), former Elemental Phosphorus Production Plant, Mt. Pleasant, Tennessee	Cap (design information not readily accessible) and deed restrictions. [State]
Exxon Mobile, ElectroPhos Division, former Phosphate Production Plant, Mulberry, Florida	Cap (HDPE) over former ponds. Groundwater remedy also included low permeability soil-bentonite slurry wall around the pond perimeter. [State]
Glenn Springs Holding Company (aka Hooker Chemical Co and Occidental Chemical Co), former Elemental Phosphorus Production Plant, Columbia, Tennessee ¹	Cap (design information not readily accessible) proposed as the final remedy for pond closure; formerly used alkali (i.e., lime) treatment on waste streams from P4 recovery process in active ponds. [State]
Agrifos Nichols Plant, former Phosphate Production Plant, Nichols, Florida	Cap (earthen) 2 feet of soil over closed ponds; drummed and buried P4 solids. [State]

TABLE 1-1

SUMMARY OF P4 SOIL / SOLID WASTE REMEDIES– COMMERCIAL AND MILITARY SITES

Albright and Wilson (aka ERCO), former Elemental Phosphorus Production Plant, Long Harbor, Newfoundland, Canada	Cap (design information not readily accessible) over “Mud holes” after recoverable P4 removed. [Environment Canada]
Union Pacific Railroad Company - Fairfield (aka Suisun Marsh Phosphorus Railcar Derailment), Fairfield, CA ¹	Cap (concrete) over 2 buried rail car(s). [State]
Southern Industrial Machine Company (SIMCO), former phosphorus railcar cleaning facility, Tennessee ¹	Cap (design information not readily accessible) over former ponds. [Private party voluntary]
FMC, former Phosphate Production Plant, Newark, California ¹	Cap (concrete) over closed underground P4 concrete storage tank and impacted soils. [State]
MILITARY FACILITIES WITH P4 MUNITIONS/WASTES	
Name and Location	Remedies or Partial Remedies
Defense Depot Ogden Utah (DDOU), former munitions disposal area, Ogden, Utah ¹	Thermal desorption [State and EPA]
Eagle River Flats, primary munitions impact area, Fort Richardson Army Base, Alaska	Sublimation and oxidization of P4 (max concentrations approximately 3,000 ppm) after draining ponds [EPA]
Crane Army Ammunition Activity, munitions storage site, Crane, Indiana	Incineration of WP in unexploded ordnance, capture and production of phosphoric acid [EPA]

¹ Phosphorus sites not reviewed in EPA’s 2003 *Treatment Technologies Report*.

TABLE 1-3**P4 DISTRIBUTION AND ASSOCIATED DETAILS IN REMEDIATION UNITS
FMC PLANT OU**

RU Designation	Range of P4 Concentrations	Depth of P4 Contamination (bgs)	Fill Particle Size¹	Estimated Quantity of P4 (tons)²	Total Fill (yd³)	Other COCs
RUs 1/2	0-50% 0-30% 1,000-10,000 ppm	0-10 ft 10-80 ft 83-85 ft	<1/4"- >6"	580-5,470	77,065	Rads, metals
RUs 13/22b	0-50%	0-44 ft	<1/4"- >6"	4,465-10,860	662,450	Rads, metals
RU 22C	0-10,000 ppm	0-20 ft	<1/4"- >2"	4-10	40,607	Rads, metals
Piping in RUs 1, 2, 3, 8, 12, 13, 22b, 24	0-100%	3-15 ft	unk	3-30	unk	Rads, metals

¹ Does not consider foundations and piping² Estimated minimum and maximum quantity of P4 in soils/sludges in tons

Section 2.0 P4 Technology Ancillary Process Options and Issues

2.1 INTRODUCTION

Several treatment technologies have been attempted, primarily in the laboratory, for remediation of soils and fill materials containing elemental phosphorus. These in-situ and ex-situ P4 treatment processes are discussed in Section 3.0. Ex-situ technologies require the excavation of soil and solids followed by an above-ground treatment process. Implementing ex-situ technologies requires additional process steps such as excavation and storage that are not required for in-situ technologies. Ex-situ technologies also require that a portion of the site be used and potentially impacted to implement the technology, including possible staging areas for treatment equipment and soil stockpiles. In-situ technologies require the addition (e.g., injection) of physical or chemical agents directly into the soil without removal of the soil. In-situ technologies would need to consider the effects of the treatment on the physical and chemical characteristics of the subsurface, including groundwater. Some technologies, such as stabilization and solidification, have been evaluated for both in-situ and ex-situ treatment.

Prior to any possible ex-situ treatment or disposal (on-site or offsite), P4-contaminated soils/sludges would require removal through conventional excavation or wet dredging so that the wastes could be transported for treatment. The material handling issues associated with excavation of soils containing P4 at concentrations over 1,000 ppm and preparation of those soils for treatment are documented as the most difficult issues to overcome with active treatment of P4 wastes. Various P4 handling processes that would be ancillary, but critically important to the success of the treatment technology, are introduced and discussed below. The P4 handling issues are the first step in what would be a difficult and potentially dangerous P4 treatment process train. Additional engineering and safety issues associated with all the treatment options for P4-contaminated wastes, i.e., common to both in-situ and ex-situ treatment options, are also discussed in this section.

2.2 ANCILLARY P4 TREATMENT PROCESSES AND ISSUES

It is important to recognize that a given treatment technology may require several ancillary process steps in order to be implemented. These ancillary process steps are common to many of the treatment technologies and are discussed in this section. Ancillary process steps that would be integral to the treatment process must be considered when screening/evaluating potential technologies using the standard EPA decision criteria of implementability, effectiveness, and cost.

Common ancillary P4 treatment processes for soils/fill materials include the following:

- Material/waste handling issues:
 - P4 excavation processes necessary to get P4-impacted materials to an ex-situ treatment process;
 - P4-impacted material transportation to the ex-situ treatment process, and temporary storage of such material near the treatment process to provide surge capacity;
- Treatment process feedstock preparation:
 - Sizing, such as crushing and screening, of the material to provide a consistent feed particle size to the ex-situ treatment process;
 - Blending with other extracted streams or inert materials of the feed to provide consistent P4 content to the ex-situ treatment process; and
- Management of treatment residues
 - Treatment of wastewater, further treatment and disposal of solid residues, and collection and treatment of process off-gases.

There are several engineering and safety challenges, unique to P4 waste handling and treatment, that must be identified and addressed in the overall technology treatment evaluation using the fundamental decision criteria of implementability, effectiveness, and cost. These include the following:

- Site worker health and safety;
- Public health and safety; and
- Potential environmental impacts.

2.2.1 P4-Impacted Soil Excavation and Treatment Feed Preparation

Excavation by conventional or hydraulic means would be necessary for any ex-situ treatment technology for remediation of P4-impacted soils. The following subsections discuss dry and wet excavation options and the engineering challenges associated with these ancillary process options.

2.2.1.1 Conventional Excavation

Excavating soils containing P4 greater than 1,000 to 10,000 ppm with conventional earthworking equipment (e.g., trackhoes, excavators, clam shells, draglines, etc), presents a unique challenge

in that once P4-impacted soils are exposed to ambient air, P4 oxidation (burning) is likely to occur. Without extreme measures such as covering the excavation site with an impermeable structure or keeping the area flooded with water, remediation workers and receptors located downwind the excavation could be exposed to aerosols associated with P4 combustion. In addition to the principal combustion product P_4O_{10} and its hydrolysis product orthophosphoric acid, the vapor cloud may also contain trace quantities of unreacted P4 (Van Voris et al. 1987) and/or a complex mixture of suboxides of P4 including phosphorus trioxide (P_4O_6), which reacts with water to form phosphine (PH_3) at low oxygen levels (Spangord 1985). Any conventional excavation option would need to meet the criteria of being implementable and effective at both removing the P4-containing soil and preventing worker and off-site exposures to P4 reaction products. The most immediate threat from conventional excavation would be the thermal burning of P4. Such burning would pose a significant threat to remedial workers and equipment. Extreme caution, including extraordinary procedures and PPE, would be required to prevent severe injury to remediation workers and damage to equipment. Similar to the point made above, any conventional excavation option would need to meet the criteria of being implementable and effective at both removing the P4-containing soil and preventing risks to workers and equipment from direct exposure to burning P4. Sufficient accounting also would need to be done regarding the capital and O&M costs associated with designing and operating a conventional excavation process that would prevent such exposures and resulting worker and off-site risks.

While performing conventional excavation, significant quantities of water would be needed to minimize the exposure of P4 to ambient air. The water would be used to saturate the excavation site and for equipment cleaning. Use of water in the excavation would provide hydraulic head on existing contaminants, increasing the threat to groundwater of COCs including metals, radionuclides, and P4. Hydraulic barriers could potentially be used to minimize the impacts to groundwater. Significant water use for equipment decontamination would require wastewater treatment, storage, and disposal. These water management issues would affect the evaluation of conventional excavation effectiveness, implementability, cost and other decisional criteria.

2.2.1.2 Hydraulic or Wet Dredging Excavation

Hydraulic excavation or wet dredging could be used, and has been used by FMC in the past on a limited basis at former ponds, provided the particle sizing is not too extreme (e.g., areas with pit-run slag could probably not be wet dredged.). The process involves mechanically mixing the phosphorus-rich soil/sludge with water at the point of excavation and transportation of the mixture through a pipeline to the treatment process. Since P4 is solid, but reactive, at ambient temperatures, it must either be chopped by a cutter head or melted using steam to allow pumping by a dredge. Solids in the mixture, typically ranging from 20% to 30%, are removed for treatment from the slurry by a complex process. The recovered water is returned to the excavation for reuse (Rhodia, 2007). Wet dredging has a benefit over conventional excavation in that P4-impacted soils are less likely to be exposed to ambient air, because the excavation working face is covered with water. Soil exposure to ambient air nevertheless can occur under this option. A further concern is P4 hydrolysis in the water, which would form PH_3 and create worker exposure risks. Controlling the risks from this potential PH_3 formation could require, among other actions, construction of a temporary cover structure over the excavation site.

While performing wet dredging, large quantities of water would be added to the dry soils containing P4 so that the dredging could occur and so they could be pumped to the treatment system. Wet dredging would provide significant hydraulic head on existing contaminants, significantly increasing the threat to groundwater of the site COCs including metals, radionuclides, and P4. Hydraulic barriers could potentially be used to minimize this potential impact. In addition, the slurry would have to be dewatered prior to stabilization or solidification (S/S) treatment. The use of large quantities of water would require wastewater treatment, storage, and disposal. Sufficient cost would need to be incorporated into the capital and O&M evaluation to account for the measures necessary to address wastewater management and minimize the impacts to groundwater, even if wet dredging otherwise met the remedial action decision criteria. A further and significant concern is that any wet dredging alternative would be very likely to cause migration of COCs to groundwater.

2.2.1.3 P4-Impacted Soil Transport and Storage

Following conventional or hydraulic excavation, P4-impacted materials would need to be transported, stored, sampled, sized, and blended prior to treatment. A storage area (stockpile, storage vessels, or temporary surface impoundment) would be necessary because any ex-situ treatment process would require a continuous feed stream, and therefore feed surge capacity, to allow effective and efficient treatment. The feed material for treatment would vary greatly in P4 content depending on the area of the plant from which it came. This variability is described in Section 1.3.

Transport to a centralized, on-site treatment process would be by covered haul truck, tanker, or pipeline. Because P4-impacted materials are reactive, often acidic (due to the phosphoric acid generation), and can freeze during cold weather, the transporting vessels/pipelines would require significant maintenance efforts throughout the remediation process. The P4-impacted material would require blanketing by water, inert gas (e.g., nitrogen) or an air-tight mechanical enclosure to prevent exposure to oxygen during transport prior to treatment.

If ex-situ treatment were to be performed off-site (e.g., incineration), transport to the treatment facility would likely be by truck or rail. Again, as discussed above, the transporting vessels would require significant, ongoing monitoring for fire and corrosion. Ongoing maintenance would have to be performed because of the caustic and corrosive nature of the P4 wastes. There would be worker, public, and environmental dangers associated with off-site transport of wastes containing P4. Some major accidents have occurred during transportation of P4, notably train derailments at Brownston, Nebraska and Miamisburg, Ohio, both of which caused large fires (Wikipedia.com). These considerations indicate serious concerns regarding the effectiveness and implementability of an off-site shipment and treatment option which involved any significant amount of waste, e.g., a large number of truck loads would increase these risks. Cost considerations also would be significant. Sufficient cost would need to be incorporated into the capital and O&M estimates to account for equipment redundancy, specialized maintenance facilities capable of handling P4-contaminated equipment, and storage equipment needed to safely transport and store the P4-impacted materials.

2.2.1.4 P4-Impacted Soil Treatment Feed Sizing

As described above in Section 1.3, the soils and fill materials containing P4 vary greatly across the FMC Plant Site. While precipitator slurry and phosphy solids are typically fine-grained and relatively uniform, other fill materials such as slag, coke, and ore vary considerably in particle size (1/4-inch to +6 inches). In areas where crushed slag is used as cover or fill, the crushed slag over time tends to amass and form large monolithic material blocks several feet in diameter, as was observed in RU22c in the SRI, actually preventing excavation with a standard back hoe. For any treatment process to work safely and effectively, a uniform feed particle size would be required to ensure adequate mixing, complete reaction, and transfer of heat of reaction. As such the feed would require crushing and screening prior to treatment. While such equipment can be designed to operate in a “closed” manner to prevent contact with air, experience has shown that significant equipment reliability and maintenance issues will exist. In addition to determinations regarding the other decision criteria, sufficient cost would need to be incorporated into the capital and O&M estimates to account for equipment redundancy and specialized maintenance facilities that would be capable of handling P4-contaminated soils and fill equipment.

2.2.1.5 P4-Impacted Soil Treatment Feed Sampling and Blending

As described above in Section 1.3, concentrations of P4 in the soils and fill materials vary greatly across the FMC Plant Site. Soils and fill materials containing as low as 20 ppm of P4 and as high as 50% P4 may be encountered, or potentially higher in the case of piping. Any treatment process for these materials will entail specification of an effective operating range for the concentration of P4 in the feed stream (and commensurate feed of other reactants). Thus, the P4 concentration in the feed stream would have to be sampled to determine P4 concentrations and blended with other waste streams or inert materials to provide consistent feed P4 concentrations within the specified effective operating parameters. These steps would be necessary to allow for treatment process control, especially when dealing with high P4 concentration soils (e.g, feed of higher-than-specified P4 to the reaction could result in excess temperature, pressure, fire, or release). While such blending equipment can be designed to operate in a “closed” manner to prevent contact with air, experience has shown that significant equipment reliability and maintenance issues will exist. As part of the overall evaluation of any ex-situ treatment option, there would need to a consideration and quantification of the capital and O&M costs associated with equipment redundancy, specialized maintenance facilities capable of handling P4-contaminated equipment, and a process laboratory capable of providing timely P4 analysis for process control.

2.2.2 Site Worker Health and Safety

Site worker safety is one of the most difficult elements to resolve with respect to “active” ex-situ or in-situ handling and treatment of P4-contaminated soils. Skilled site workers are essential for any successful ex-situ or in-situ treatment process, because the potential processes are complex and mostly unproven. In the context of the FMC Plant Site with unproven technologies, unique site contaminants, and handling challenges associated with widely varying P4 concentrations (even within a small area), it would be difficult to build-in the proper design and operating procedures to ensure worker safety.

P4 (solid, liquid, and vapor phases) and P4 reaction products (P₂O₅, other phosphorus oxides, phosphine, and phosphoric acid) present immediate physical hazards to site workers. These have been identified in the site-specific risk assessments performed by EPA (RI Report, 1996) and FMC (SRI Report, 2007) and by numerous medical, research, and environmental agencies including the Center for Disease Control and Prevention (CDC), the USEPA Integrated Risk Information System (IRIS), and the Cold Regions Research Engineering Laboratory (CRREL). These risks have been well documented by FMC and others that manufacture or formerly manufactured P4 in a commercial/ industrial setting, including Stauffer (Rhodia), Monsanto, and Albright and Wilson.

P4 is relatively safe when maintained under water and using well-engineered process equipment, experienced operators, and established procedures. However, when not under a blanket of water or other inert material, the P4 operations and maintenance personnel necessary for the remediation activities would potentially be exposed to widely ranging physical risks due to the nature and extent of P4 throughout the FMC Plant Site area. The largely uncontrolled conditions during excavation would expose workers to fire, dermal, and respiratory hazards. Workers in enclosures would be required to wear Level A PPE, although significantly modified (if practical) to protect them from P4 thermal exposure (e.g., most Level A protective suits do not protect against P4 burns). P4 protective suits worn at most P4 manufacturing plants were constructed with an aluminum coating, designed to be immediately shed in the event of P4 exposure. This approach would not be consistent with most PPE decontamination procedures typically applied within remediation exclusion zones or contamination reduction zones. Well-designed processes, highly-trained site workers, and a comprehensive Environmental, Health, and Safety Management System (including extensive health, safety and environmental procedures) would be critical, but might not be sufficient to ensure adequate protection of site workers. Cost considerations also would be significant, requiring quantification of the capital and O&M costs associated with providing adequate site worker protective systems if indeed such systems could be designed and reliably implemented.

2.2.3 Public Health and Safety

During operation of the FMC plant, public health and exposure often were controlled by the same measures that FMC put into place to keep plant workers safe. Typical engineering controls prevented public access to hazardous areas throughout the site (e.g., fencing). Air monitoring and scrubbers were installed to meet Clean Air Act requirements to control phosphorus-related and other air emissions from the plant site. During any remedial action that involved the handling of P4-contaminated soils, engineering controls also would be in place to protect site workers. However, unlike the controlled manufacturing process, excavation and treatment of P4 wastes could cause uncontrolled releases, especially to the air, due to the widely varying site conditions and difficulty in designing appropriate engineering controls. The risk of uncontrolled air releases would increase with the quantity of P4-soils being remediated, as well as the degree of impact, e.g., active remediation of higher concentrations of P4 in impacted materials and greater quantities of impacted materials has greater risk than active remediation of lower concentrations and smaller quantities. Some of these difficulties are discussed above and in other reports (Rhodia, 2007). Short-term public exposures to airborne contaminants including

P₂O₅, phosphine gas, and phosphoric acid also might occur, due to the many unforeseen circumstances that could arise.

2.2.4 Environmental Impacts

Environmental concerns related to the handling of P₄-contaminated soils include potential impacts to air and water/groundwater. Possible worker risks from direct exposure to pure P₄, phosphorus gases, and contaminated process water and risks to the public from air emissions and impacted groundwater are described above. The following discussion addresses the release mechanisms potentially triggered by active or intrusive remediation of P₄-containing soils, which often also contain heavy metals and radionuclides, and the resulting potential on- and off-site impacts.

Air Impacts: Air impacts include those from dust and from phosphorus-related gases that any active treatment process would generate. During excavation, dust could be released from the excavation and sizing operations. The dust could contain P₄, radionuclides, and heavy metals in varying concentrations. Although dust suppression measures would be a part of any remediation alternative, it is likely that some dust would be released during these activities.

Intrusive remediation into P₄-impacted soils, including excavation, grinding, and/or sizing, would result in P₄ reaction gases including P₄ vapor, P₂O₅, and phosphine being released to the atmosphere. Their concentrations would depend in large part on the amount of P₄ contamination, the quantity of P₄-impacted soils being remediated, and the effectiveness of the engineering controls at the excavation, storage and processing areas. If these gases were to be captured and treated by a scrubber, the scrubber water would need to be treated in a waste water treatment (WWT) process. The WWT process typically would consist of neutralization (because of phosphoric acid capture by the scrubber), clarification, and sand filtration. Solids are removed by that process and consolidated by a filter press, then transported and disposed in a landfill depending on analytical testing. This material could be high in heavy metals and/or radionuclides. The water would be discharged for reuse in scrubber operations, directly discharged to the groundwater or surface water, or sent to a publicly-owned treatment works (POTW) for later discharge to surface water.

Water/Groundwater: Water would be necessary during most steps of a P₄ material handling process to prevent P₄ exposure to oxygen in the air and resulting combustion. Water also would be necessary for dust suppression during many of the material handling processes, such as mechanical excavation and material sizing.

During wet excavation, water would be added to allow excavation and transform the dry P₄-contaminated soil from a dry solid to a slurry that could be pumped to the storage area or treatment process. During conventional excavation, water would be added to each bucket load to submerge the P₄ material prior to transfer to a truck trailer. Water again would be necessary in the tank or truck trailer to prevent P₄ ignition. In the sizing and storage area, water might be used in the sizing process or used to cover the P₄-contaminated soil. Prior to the treatment process, water might be removed to provide the correct moisture in the feed stock. Water also would be used in the scrubbers that would be necessary to control emissions of P₄-related gases

at any locations in the handling process, such as the excavation and storage areas, where such emissions would occur.

Water therefore would be added to or removed from the feed stream depending upon in the process stage. Process water might be lost to the environment during any phase of the excavation, transportation, storage, and/or treatment process. If released, process water would provide hydraulic head to mobilize P4. The hydraulic head also could mobilize heavy metals and possibly radionuclides, with the potential that they could be transported to the shallow groundwater.

Section 3.0 Elemental Phosphorus Treatment Technologies – Soils and Solids

This section presents an overview of the technologies that have been identified as candidates for treatment of elemental phosphorus-contaminated soil and solids at the FMC Plant OU. It includes a description of each technology, the process steps required to implement the technology, potential factors affecting its implementability, residual and by-products created by the treatment process, and a description of the historical use of the technology for treating P4-impacted soils. (Note that for this document, “P4-impacted soils” is intended to include all soils and/or fill materials that are contaminated with elemental phosphorus).

Commercially available (e.g., off-site incineration) technologies were identified that have been used to reduce the concentration, volume, or mobility of elemental phosphorus. In addition, technologies were identified that are not commercially available for treating P4 but may have potential applicability (e.g., ex-situ stabilization/solidification). Although containment technologies such as capping have been widely used for isolating elemental phosphorus and reducing its mobility in the environment, they are not discussed because only treatment technologies are considered in this section.

Both ex-situ and in-situ technologies may be applicable for treatment of soil and fill materials containing elemental phosphorus. Ex-situ technologies require the excavation of soil and solids followed by an above-ground treatment technology. As described in Section 2, implementing ex-situ technologies requires additional process steps such as excavation and storage that are not required for in-situ technologies. Ex-situ technologies also require that a portion of the site be used and potentially impacted to implement the technology, including possible staging areas for treatment equipment and soil stockpiles. In-situ technologies require the addition (e.g., injection) of physical, chemical, or biological agents directly to the soil without removal of the soil. In-situ technologies would need to consider the effects of the treatment on the physical and chemical characteristics of the subsurface. Some technologies, such as stabilization and solidification, have been demonstrated to be performed in-situ or ex-situ although not for P4.

The following six specific treatment technologies considered for discussion utilize physical, chemical, or thermal processes to treat elemental phosphorus:

- **Solidification/Stabilization (S/S)** – S/S is a commercially available chemical fixation technology commonly used to treat heavy metals and radionuclides in matrices such as soils and sludge by the addition of cementitious material (e.g., Portland cement). While typically used ex-situ, S/S also may be implemented by injecting and mixing stabilizing agents into unexcavated soil or sludge. Ex-situ S/S was identified in the original EMF FS for the FMC Subarea as a technology but was only retained for further evaluation for treatment of non-P4-contaminated soils and solids. S/S was not retained for materials containing elemental phosphorus (e.g., the old phosphy waste ponds) due to high short-term risks and related increased costs for mitigation of these risks. For these reasons a containment remedy was selected for P4 solids. In-situ S/S was selected for the P4-

impacted soils at the Stauffer Tarpon Springs site, but upon attempted implementation it created significant short-term hazards leading to termination of that approach. A containment remedy was ultimately selected for Tarpon Springs.

- **Mechanical Aeration** – A mechanical aeration system has been suggested by the USACE that could be used to increase the exposure of elemental phosphorus to oxygen and increase the rate of oxidation. Although mechanical aeration could be used either in-situ or ex-situ, studies conducted by the United States Army Corps of Engineers (USACE) only involve ex-situ aeration. Mechanical aeration was not considered during the original EMF FS.
- **Caustic Hydrolysis** – Caustic hydrolysis was the treatment technology selected for the Land Disposal Restriction (LDR) Treatment Plant that FMC designed and constructed, but never operated due to the plant shutdown in 2001, to treat phosphorus-containing process waste streams at its Pocatello plant. Hydrolysis was identified in the original EMF FS for the FMC Subarea as a technology but was only retained for further evaluation for treatment of non-P₄-contaminated soils and solids. Hydrolysis was not retained for materials containing elemental phosphorus (e.g., the old phosphy waste ponds) due to high short-term risks and related increased costs for mitigation of these risks. The EMF FS lead to selection of a containment remedy for P₄ solids. This technology is only considered as an ex-situ treatment technology due to the reaction mechanisms of caustic hydrolysis.
- **Chemical Oxidation** – Chemical oxidation is a technology that has been implemented at the bench scale to oxidize elemental phosphorus. The Tennessee Valley Authority (TVA), the University of Alabama and the USACE have performed bench-scale and pilot scale studies on various types of oxidants for treating elemental phosphorus. Chemical oxidation was identified in the original EMF FS for the FMC Subarea as a technology, but was only retained for further evaluation for treatment of non-P₄-contaminated soils and solids. Chemical oxidation was not retained for materials containing elemental phosphorus (e.g., the old phosphy waste ponds) due to high short-term risks and related increased costs for mitigation of these. This was another factor supporting selection of a containment remedy for P₄ solids.
- **Incineration** - Incineration has been identified by the United Nations as a viable method for treating elemental phosphorus-containing waste (ARSDR, 1997). Incineration is a commercially-available thermal treatment technology that could be used to oxidize P₄ and reduce the volume of material requiring further treatment or disposal. Incineration was identified in the original EMF FS for the FMC Subarea as a technology, but was not retained for further evaluation due to high-short term risks and related increased costs for mitigation of these risks, findings that contributed to the selection of a containment remedy for P₄ solids. Off-site incineration was used to dispose of containerized P₄-containing materials generated while cleaning process equipment during FMC plant decommissioning.

- Thermal Desorption – Thermal desorption is a commercially available technology that involves heating soil to cause contaminants to volatilize and separate from the solid matrixes without combustion. Thermal Desorption was identified in the original EMF FS for the FMC Subarea as a technology but was not retained for further evaluation due to high-short term risks and related increased costs for mitigation of these risks, again supporting selection of a containment remedy for P4 solids. Thermal desorption has been used on a small volume basis for P4 associated with munitions at the Defense Depot Ogden, Utah (DDOU) site.

In this section, a screening-level evaluation of P4 treatment technologies is presented. For each technology identified, information is provided (to the extent known based upon literature research and FMC experience) on the following topics:

- Description of the treatment process as utilized in ex-situ and/or in-situ applications, as applicable.
- Description of the complete treatment process sequence. This is intended to provide information on the complete process train necessary to implement the technology. This can include steps such as excavation, storage, transportation, waste management, and use of specialized equipment. In some cases, the ancillary processes may present the biggest engineering challenges.
- Description of the engineering challenges and issues for application of the treatment technology to P4-impacted soils and fill materials.
- Description of the treatment technology performance and limitations. This is intended to provide guidance on where the treatment technology may be applicable and which site conditions would limit its potential use.
- A description of whether and how the technology has been put to actual use, including the state of its development and any actual cases where the technology has been applied to P4-impacted soils and/or fill materials. Note that no testing of technologies was performed as part of this screening evaluation.

3.1 STABILIZATION AND SOLIDIFICATION

Stabilization and solidification (S/S) is an established technology for treatment of organics, heavy metals and radionuclides (for example, see the Solidification/ Stabilization Resources Guide; EPA, 1999 and Solidification/ Stabilization Use at Superfund Sites; EPA 2000). It has been identified as a possible technology for treating P4 both in-situ and ex-situ.

3.1.1 S/S Treatment Process

S/S involves mixing a waste with binding agents (i.e., pozzolanic materials), such as Portland Cement or fly ash, to create a slurry, paste, or semi-liquid and then providing curing time and

conditions for the mixture to set into a solid form. Although generally performed ex-situ in a pug mill, S/S can be performed in-situ using augers or backhoes to inject and mix the stabilizing agent in place.

S/S reduces the mobility of contaminants in a matrix through chemical or physical processes. The S/S process physically binds or encapsulates contaminants using a pozzolanic material within a stabilized mass to prevent further migration. It also chemically converts the contaminants into less soluble, mobile, or toxic forms.

3.1.2 Complete S/S Process Treatment Sequence

The complete ex-situ S/S treatment sequence as applied at the FMC Plant Site would be a complex process operation involving: 1) the excavation (or wet dredging) of the P4-impacted material, 2) transport of the material to the treatment location, 3) storage of the excavated material to provide feed surge to the treatment process, 4) sizing (e.g., crushing and screening) of the material to provide a consistent feed particle size to the treatment process, 5) sampling and blending with other extracted streams or inert materials of the feed to provide consistent P4 content, 6) S/S treatment, 7) curing to allow time for solidification, 8) transportation to the final disposal site, and 9) landfill disposal.

The complete in-situ S/S treatment sequence would involve injecting the cementitious material and water into the contaminated soil while providing mechanical mixing in place.

In the case of applying S/S treatment technology to P4-impacted materials, the mobility of P4 would be reduced in some part due to the hydrolysis reaction of P4 with the alkali admix and in some part due to encapsulation of P4 within the hardened concrete. Off-gassing of PH_3 will result from that portion of the P4 which undergoes caustic hydrolysis. For both in-situ and ex-situ S/S, phosphorus off-gas capture, scrubbing, and wastewater treatment systems would likely be necessary at the point of treatment and likely at the point of excavation and temporary storage for ex-situ treatment, dependent on the quantity of waste being managed as well as the P4 concentration in the waste.

3.1.3 Engineering Challenges/Issues for S/S

The following discussions provide preliminary analysis of the engineering challenges and issues if S/S were applied to P4-impacted soils at the FMC Plant Site.

3.1.3.1 Ex-Situ S/S Treatment As Applied to P4-Impacted Soils

Ancillary process options associated with S/S ex-situ treatment: If ex-situ S/S treatment were performed, the engineering considerations with respect to S/S applied to P4-contaminated soil would include one or more of the following ancillary process options (and associated engineering challenges/issues):

- Conventional excavation of soils (see Section 2.2.1.1);
- Wet dredging/hydraulic pumping excavation of soils (see Section 2.2.1.2);
- Excavated soil transport and storage (see Section 2.2.1.3);
- Treatment feed sizing (see Section 2.2.1.4); and
- Treatment feed sampling and blending (see Section 2.2.1.5).

Ex-situ S/S treatment: The ex-situ treatment process would also present some significant engineering challenges, even with a consistent feed particle size and P4 concentration. The reaction of P4 with alkaline cementitious materials will result in significant releases of reaction products (i.e., P4 vapor, P₂O₅, PH₃, phosphorus oxides, and H₃PO₄). These reactions would have to be carefully controlled in the process and the resulting emissions would have to be captured using the appropriate air pollution control and ancillary equipment. The remedial alternative evaluation would need to include consideration of the capital and O&M costs for equipment redundancy, specialized maintenance facilities capable of handling P4-contaminated equipment, and air pollution control equipment and operation.

3.1.3.2 *In-Situ S/S Treatment As Applied to P4-Impacted Soils*

If in-situ S/S treatment were performed, the engineering issues with respect to S/S applied to P4-contaminated soil would include the following:

Control of P4 reactions during injection or mixing: One of the critical process controls necessary for S/S treatment of P4 is the control of the P4 reaction, both in terms of an overly rapid reaction that results in a P4 fire, or having insufficient mixing that results in un-reacted P4. This type of process control during in-situ treatment is likely to be impossible due to a range of factors such as the variability of the P4 concentrations, the soil or fill matrix in which the P4 is located, and the difficulty of controlling in-situ reactions. In-situ S/S at the FMC Plant Site could result in one or more of the following scenarios:

- Uncontrolled excessive reaction of P4 with alkaline cementitious material, resulting in a fire and threat of release of reaction products (i.e., P4 vapor, P₂O₅, PH₃, phosphorus oxides, and H₃PO₄) and/or thermal burns to remediation workers and equipment; and/or
- Incomplete mixing of cementitious material with contaminated soils such that P4 is not completely reacted (i.e., it remains as P4) in the resulting solidified mass.
- Loss of free liquids that could transport other site COCs, including metals and radionuclides, to shallow groundwater.

Without extreme measures such as covering the in-situ treatment area with an impermeable structure, receptors downwind of the in-situ treatment could potentially be exposed to aerosols associated with P₄ combustion.

The most immediate threat for in-situ S/S treatment would be the thermal burning of P4 in the event of uncontrolled P4 reactions, which would pose a threat to remedial workers and

equipment. Extreme caution, including extraordinary procedures and PPE, would be required to prevent severe injury to remediation workers and damage to equipment. Evaluation of this technology as a remedial option would have to take into account the cost and other factors associated with taking the measures necessary to prevent direct exposure of remediation workers and equipment to burning P4.

Increased hydraulic head in contaminated soils: During the initial solidification process, free water is typically generated in the treated mass. This free water would likely provide a temporary hydraulic head that could carry COCs, including metals and radionuclides to groundwater. A hydraulic barrier could potentially be used to partially mitigate this impact.

3.1.4 S/S Treatment Performance and Limitations

Given the engineering challenges and issues associated with ex-situ and/or in-situ S/S treatment, the following are the limitations, advantages, and potential applications of this technology for treating P₄ contaminated soils at the FMC Plant Site:

Limitations:

- Generally not applicable for soil depth over 15 feet for ex-situ application and 20 feet for in-situ application due to limitations of construction excavation equipment and mixing auger limitations;
- Generally not applicable for large volumes such as in RUs 1, 2, 13, or 22b (both ex-situ and in-situ) due to the significant volume increase (as much as 30 %) in total waste to be managed after S/S;
- Difficult to control P₄ reactions (in-situ and ex-situ) because of widely varying P₄ concentrations;
- Very complex complete treatment sequence (ex-situ) due to feed material sizing, blending and off-gas management;
- P₄ associated with UG Piping could not easily be processed, as metal piping would not allow for in-situ treatment and would make wet-dredging, pumping, sizing, blending and treatment impossible. Special handling of piping containing P₄ would be required; and
- Significant variation in soil particle size and P₄ concentration as found in most RUs containing P₄ would make the ex-situ handling process extremely complex and difficult to operate and maintain. For in-situ treatment, the particle size variation would very likely result in inadequate/incomplete mixing.

Advantages:

- Also stabilizes metals and radionuclides present in the soil/fill matrix (both in-situ and ex-situ) although would not likely be effective at addressing gamma.
- Ex-situ process would recover free water during processing, and thus would not present the risk associated with in-situ S/S treatment of creating a hydraulic head and adding contamination to underlying soils and groundwater, assuming risks associated of using water during excavation were otherwise addressed

Potential applicability:

- Shallow soils with low concentration P₄ (< 10,000 ppm);
- Shallow soils with consistent material sizing and concentration of P₄; and
- Relatively low volumes of wastes.

3.1.5 By-Products and Residuals

In any treatment process, the by-products and residuals must be addressed in the feasibility evaluation and cost. The following by-products and residuals would be expected from the S/S treatment process:

Ex-situ:

- Solidified mass consisting of other fill materials (containing bound metals, radionuclides, and inert materials), unreacted cementitious material, and insoluble calcium phosphate;
- P₄ reaction air emissions including PH₃, P₂O₅, H₃PO₄, and H₂;
- Contaminated water used for storing and transporting recovered soils, dewatering, and air pollution control that would require treatment; and
- Air pollution control system sludges.

In-situ:

- Solidified mass consisting of other fill materials (containing bound metals, radionuclides, and inert materials), unreacted cementitious material, and insoluble calcium phosphate;
- P₄ reaction air emissions including PH₃, P₂O₅, H₃PO₄, and H₂;
- Free liquids potentially containing metals, radionuclides and dissolved/particulate P₄.
- Air pollution system control wastewaters and sludges.

3.1.6 History of Use

S/S is a widely used treatment for the management/disposal of a broad range of contaminated media and wastes including metals and radionuclides (Wilk, 2004). However, there has only been one documented case of using S/S on soils contaminated with elemental phosphorus. S/S was selected along with excavation and consolidation as the recommended remedial alternative for the Stauffer Management Company (SMC) Superfund site. The SMC superfund site was the former location of a WP manufacturing site in Tarpon Springs, Florida.

At the Tarpon Springs site, a two-stage process was performed involving the identification of a S/S mix design and implementation of an in-situ S/S. In February 2006, SMC conducted a full-scale field study for in-situ solidification and stabilization within a former pond containing sludge and soil containing elemental phosphorus. An 8.5 foot auger was used to inject and mix a cement slurry into contaminated soil and materials to a depth of 20 feet. As a result of the cement curing, the elemental phosphorus ignited and created a persistent fire that was eventually

extinguished. The fire caused the generation of PH_3 gas, though the levels were not high enough to warrant evacuation of nearby residents. Because of the violent and poorly controllable chemical reactions the field-scale study was discontinued. EPA issued an Explanation of Significant Differences (ESD) documenting its decision to abandon in-situ S/S at that site and replace it with capping and a hydraulic barrier. The ESD approved the construction of a cut-off wall and cap as replacement for the in-situ S/S remedy (FDEP, 2006).

3.2 MECHANICAL AERATION

Mechanical Aeration has been identified as a possible technology for treatment of P_4 in soil. The process could potentially be performed both in-situ and ex-situ.

3.2.1 Mechanical Aeration Treatment Process

Mechanical aeration involves the use of physical equipment, such as a mixer, to agitate a solid or slurry material and expose the material to the atmosphere, causing ambient oxygen to react with the P_4 contained in the solid matrix and oxidize the P_4 . Mechanical aeration would convert P_4 to various phosphate compounds. Aeration also would convert P_4 to phosphine and P_2O_5 (EPA, 2003). Mechanical aeration would involve exposing P_4 particles in the soil to oxygen.

The USACE indicated that a mechanical aeration system could be used ex-situ or in-situ to expose elemental phosphorus to oxygen (Rivera, 1996). However, further studies would be required to determine how the degradation of elemental phosphorus is affected by concentrations of dissolved oxygen, mixing rate, matrix characteristics, depth of material, temperature, and pH. An in-situ mechanical aeration system could be used to increase the dissolved oxygen (DO) in the soil. This would result in increasing the oxygen availability to the P_4 in the soil, accelerating the degradation rate of P_4 . Mechanical aeration would not be effective at treating radionuclides and heavy metals.

3.2.2 Complete Mechanical Aeration Process Treatment Sequence

The complete ex-situ mechanical aeration sequence would be a complex process operation that would involve: 1) the excavation (or wet dredging) of the P_4 -impacted material, 2) transport of the material to the treatment location, 3) storage of the excavated material to provide feed surge to the treatment process, 4) sizing (e.g., crushing and screening) of the material to provide a consistent feed particle size to the treatment process, 5) sampling and blending with other extracted streams or inert materials of the feed to provide consistent P_4 content (i.e., percentage of P_4), 6) mechanical aeration treatment, 7) transportation to the final disposal site, and 8) landfill disposal. In addition, soils treated with mechanical aeration likely would require further treatment for radionuclides and metals prior to disposal.

The complete in-situ mechanical aeration treatment sequence would involve injecting air into the contaminated soil while providing mechanical mixing in place.

For both in-situ and ex-situ mechanical aeration, phosphorus off-gas capture, scrubbing, and wastewater treatment systems would be necessary at the point of treatment and likely at the point of excavation and temporary storage for ex-situ treatment.

3.2.3 Engineering Challenges/Issues for Mechanical Aeration

The following discussions provide a preliminary analysis of the engineering challenges and issues if mechanical aeration were applied to P₄-impacted soils.

3.2.3.1 Ex-Situ Mechanical Aeration Treatment As Applied to P₄-Impacted Soils

Ancillary process options associated with mechanical aeration ex-situ treatment: If ex-situ mechanical aeration treatment were performed on P₄-impacted materials, the ancillary process options (and associated engineering challenges/issues) would include the following:

- Conventional excavation of soils (see Section 2.2.1.1);
- Wet dredging/hydraulic pumping excavation of soils (see Section 2.2.1.2);
- Excavated soil transport and storage (see Section 2.2.1.3);
- Treatment feed sizing (see Section 2.2.1.4); and
- Treatment feed sampling and blending (see Section 2.2.1.5).

Ex-situ mechanical aeration treatment: The ex-situ treatment process would also present some significant engineering challenges, even with a consistent feed particle size and P₄ concentration. The reaction of P₄ with air will result in significant releases of reaction products (i.e., P₄ vapor, P₂O₅, PH₃, phosphorus oxides, and H₃PO₄) and possibly result in combustion of P₄. These reactions would have to be carefully controlled in the process and the resulting emissions would have to be captured and controlled using the appropriate air pollution control and ancillary equipment. The remedial alternative evaluation would have to account for needed equipment redundancy, specialized maintenance facilities capable of handling P₄-contaminated equipment, and air pollution control equipment.

3.2.3.2 In-Situ Mechanical Aeration Treatment As Applied to P₄-Impacted Soils

If in-situ mechanical aeration treatment were applied to P₄-contaminated soil, the engineering issues would include the following:

Control of P₄ reactions during injection or mixing: One of the critical process controls necessary for mechanical aeration treatment of P₄ is the control of the P₄ reaction, both in terms of an overly rapid reaction that results in a P₄ fire or having insufficient injection and mixing of air that results in un-reacted P₄. This type of process control during in-situ treatment is likely to be impossible, resulting in one or both of the following scenarios:

- Uncontrolled excessive reaction of P₄ with air, resulting in a fire and the threat of release of reaction products (i.e., P₄ vapor, P₂O₅, PH₃, phosphorus oxides, and H₃PO₄) and/or thermal burns to remediation workers and equipment; and/or

- Incomplete mixing of air with contaminated soils such that P₄ is not completely reacted (i.e., it remains as P₄) in the soil.

Without extreme measures such as covering the in-situ treatment area with an impermeable structure, receptors downwind of the in-situ treatment could be exposed to aerosols associated with P₄ combustion. The remedial alternative evaluation would need to consider the measures necessary to prevent exposure of P₄ reaction products to remediation workers and the public.

The most immediate threat for in-situ mechanical aeration treatment would be the thermal burning of P₄ in the event of uncontrolled P₄ reactions, which would pose a threat to remedial workers and equipment. Extreme caution, including extraordinary procedures and PPE, would be required to prevent severe injury to remediation workers and damage to equipment. Evaluation of this remedial option would need to address the measures necessary to prevent direct exposure of burning P₄ to remediation workers and equipment.

3.2.4 Mechanical Aeration Treatment Performance and Limitations

Given the engineering challenges and issues associated with ex-situ and/or in-situ mechanical aeration treatment, the following limitations, advantages, and potential applications are identified for P₄-contaminated soils at the FMC Plant Site:

Limitations:

- Generally not applicable for soil depth over 15 feet for ex-situ application and 20 feet for in-situ application due to limitations of construction excavation equipment and mixing auger limitations.
- Generally not applicable for large volumes such as in RUs 1, 2, 13, or 22b (both ex-situ and in-situ) due to the material handling challenges on that scale.
- Difficult to control the P₄ reactions (in-situ and ex-situ) because of widely varying P₄ concentrations.
- Significant variation in soil particle size and P₄ concentration as found in most RUs containing P₄ would make the ex-situ handling process extremely complex and difficult to operate and maintain. For in-situ treatment, the particle size variation would result in inadequate/incomplete mixing.
- Would not treat metals and radionuclides that are present in the P₄-contaminated soils.

Advantages:

- Does not require the injection of costly additives, potentially making it easier to implement in low porosity material.

Potential applicability:

- Shallow soils with low (< 10,000 ppm) and generally uniform levels of P4.
- Shallow soils with consistent material sizing.

3.2.5 By-Products and Residuals

In any treatment process, the by-products and residuals must be addressed in the feasibility evaluation including cost analysis. The following by-products and residuals would be expected from the mechanical aeration treatment process:

Ex-situ:

- Soil potentially requiring additional treatment for metals and radionuclides prior to disposal;
- P4 reaction emissions including PH₃, P₂O₅, H₃PO₄, and H₂;
- Contaminated water used for storing and transporting recovered soils, dewatering, and air pollution control; and
- Air pollution control system sludges.

In-situ:

- P4 reaction air emissions including PH₃, P₂O₅, H₃PO₄, and H₂;
- Air pollution system control wastewaters and sludges.

3.2.6 History of Use

The USACE has stated that mechanical aeration has not been field tested, and that the feasibility of applying this to WP-contaminated sediments would need additional research and experimental work. It has not suggested a design for in-situ mechanical aeration treatment (Rivera, 1996). However, several bench scale studies have been conducted to relate the amount of dissolved oxygen (DO) to the degradation of WP. Lai (1979b) conducted a study to evaluate the degradation rate of WP in solutions by manipulating the amount of DO in the samples. The study indicated that mechanical aeration would reduce the concentration of WP in aqueous solution from near 1,000 µg/L to less than 10 µg/L in 60 days. However, these studies were performed on aqueous solutions containing a generally low and homogenous concentration of WP. Attempting to treat P4-contaminated soil with mechanical aeration may produce different results.

3.3 CAUSTIC HYDROLYSIS

Caustic Hydrolysis is a chemical process in which elemental phosphorus is dissociated and reacts with hydrogen and/or hydroxyl ions in solution. Hydrolysis reactions are typically catalyzed with acids or bases. In addition, increased temperature and pressure typically increase the rate of reaction. FMC previously identified and used caustic hydrolysis (using slaked lime) to treat P₄-containing production waste streams (specifically precipitator slurry). Hydrolysis of P₄ produces various forms of phosphorus compounds (i.e., phosphites and phosphates), as well as phosphine gas. Because the P₄ hydrolysis reaction rate is significantly higher at elevated temperatures, caustic hydrolysis is only considered as an ex-situ treatment technology.

3.3.1 Caustic Hydrolysis Treatment Process

Contaminated P₄ soils would be transferred to a stirred batch reactor and heated to a temperature greater than 140°F. A source of hydroxide ion (typically lime) and water then are added, while continuing to stir the reactor contents. A pH of approximately 11 is maintained. Caustic hydrolysis would convert P₄ in soil to various phosphite and phosphate compounds, and heavy metals to metal oxides and hydroxides. The phosphine and hydrogen gas produced by this process are typically combusted in a thermal oxidizer, forming water vapor and P₂O₅. The P₂O₅ is then scrubbed with water, producing a phosphoric acid stream which can be neutralized or potentially sold as product.

3.3.2 Complete Caustic Hydrolysis Process Treatment Sequence

The complete ex-situ caustic hydrolysis sequence would be a complex process operation involving: 1) the excavation (or wet dredging) of the P₄-impacted material, 2) transport of the material to the treatment location, 3) storage of the excavated material to provide feed surge to the treatment process, 4) sizing (e.g., crushing and screening) of the material to provide a consistent feed particle size to the treatment process, 5) sampling and blending with other extracted streams or inert materials of the feed to provide consistent P₄ content, 6) caustic hydrolysis treatment, 7) transportation to the final disposal site, and 8) landfill disposal. In addition, soils treated with caustic hydrolysis may require further treatment for radionuclides prior to disposal.

For caustic hydrolysis treatment, phosphorus off-gas capture, scrubbing, and wastewater treatment systems would be necessary at the batch reactor and likely at the point of excavation and temporary storage.

3.3.3 Engineering Challenges/Issues for Caustic Hydrolysis

The following discussions provide a preliminary analysis of the engineering challenges and issues if mechanical aeration were applied to P₄-impacted soils.

3.3.3.1 Caustic Hydrolysis Treatment As Applied to P4-Impacted Soils

Ancillary process options associated with caustic hydrolysis ex-situ treatment: If ex-situ caustic hydrolysis treatment were performed on P4-impacted materials, the ancillary process options (and associated engineering challenges/issues) would include the following:

- Conventional excavation of soils (see Section 2.2.1.1);
- Wet dredging/hydraulic pumping excavation of soils (see Section 2.2.1.2);
- Excavated soil transport and storage (see Section 2.2.1.3);
- Treatment feed sizing (see Section 2.2.1.4); and
- Treatment feed sampling and blending (see Section 2.2.1.5).

Caustic hydrolysis treatment: The treatment process would also present some significant engineering challenges, even with a consistent feed particle size and P4 concentration. The reaction of P4 with a caustic solution will result in significant releases of reaction products (i.e., P4 vapor, P₂O₅, PH₃, phosphorus oxides, and H₃PO₄). The resulting emissions would have to be captured and controlled using the appropriate air pollution control and ancillary equipment, including a thermal oxidizer for phosphine and hydrogen conversion and a scrubber for capturing the resulting P₂O₅ and producing phosphoric acid. Evaluation of this technology as a remedial option would have to take into account cost and other factors associated with the needed equipment redundancy, specialized maintenance facilities capable of handling P₄-contaminated equipment, and air pollution control equipment.

3.3.4 Caustic Hydrolysis Treatment Performance and Limitations

Given the engineering challenges and issues associated with ex-situ caustic hydrolysis, the following limitations, advantages, and potential applications are identified for P4- contaminated soils at the FMC Plant Site:

Limitations:

- Generally not applicable for soil depth over 15 feet for ex-situ application due to limitations of construction excavation equipment.
- Extremely complex complete treatment sequence including all the ancillary treatment processes (feed preparation, reactant preparation, waste slurry management, air emissions management).
- Difficult to supply consistent (size and concentration) P4 feed stream and therefore control P4 reactions.
- Significant variation in soil particle size and P4 concentration, as found in most P4-containing RUs, would make the handling process extremely complex and difficult to operate and maintain.

- Requires additional treatment for radionuclides at a minimum, but possibly the metal oxides and hydroxides as well.

Advantages:

- Converts heavy metals in process feed material to metal oxides and hydroxides that may not require additional treatment. Bench scale testing of treatment sludges would be necessary to evaluate if additional treatment is necessary for metal and radionuclides present in process sludges.

Potential Applicability:

- Shallow soils with low concentration P4 (< 10,000 ppm).
- Shallow soils with consistent material sizing and concentration of P4.

3.3.5 By-Products and Residuals

In any treatment process, the by-products and residuals must be addressed in the feasibility evaluation including the cost analysis. The following by-products and residuals would be expected from the caustic hydrolysis treatment process:

- Slurry/solid residue in the hydrolysis reactor bottoms stream, consisting primarily of inert dirt, un-reacted lime, and insoluble calcium phosphite (CaHPO_3) would require further stabilization;
- The wastewater generated from the caustic hydrolysis treatments would contain suspended solids and soluble calcium hypophosphite that would require treatment and disposal;
- Gases produced during hydrolysis include phosphine (PH_3), hydrogen (H_2), and water; and
- Air pollution control system sludges.

3.3.6 History of Use

A full-scale caustic hydrolysis system has been in operation since 2000 at the GSHI facility in Columbia, Tennessee to treat a low concentration P4 furnace production process waste stream (Rhodia, 2007).

Beginning in the mid-1990s, FMC began using lime treatment of precipitator slurry in the furnace precipitator dust "slurry pots" principally to increase the pH of the precipitator slurry and decrease the solubility of metals within the precipitator solids. The lime treatment was termed Non-hazardous Slurry Assurance Project or "NOSAP." The lime addition also catalyzed

hydrolysis of P4 within the precipitator solids causing generation of PH3 from the lime-treated precipitator slurry. Under the RCRA Consent Decree, certain operating criteria, including volume of lime addition, temperature, final pH and retention time, were established that constituted "on-specification" NOSAP precipitator slurry. However, the RCRA Consent Decree required the development and implementation of a more rigorous treatment process for the precipitator slurry and phosphy water/solids from the plant due, in part, to EPA's position that the NOSAP process did not meet EPA's treatment objectives. EPA's conclusion that additional treatment was required led to the RCRA Consent Decree requirement that FMC design, construct and operate what was referred to as the LDR Treatment Plant to more thoroughly treat the plant process wastes. Although the LDR Treatment System was not completed or ever operated, the LDR system was intended to replace and improve upon the NOSAP process for the treatment of precipitator slurry from ongoing P4 production.

The main objective of the LDR treatment system was to treat the waste stream slurries from the furnace production process containing low levels of elemental phosphorus (less than 2% P4 and particle size less than U.S. Standard Sieve Mesh # 60) to reduce the P4 concentration. The treated, filtered and dewatered waste solids then would have undergone cement stabilization to stabilize metals and meet RCRA LDR requirements prior to disposal in an on-site landfill. As stated in Section 4.2, the LDR treatment system would have had narrow operational parameters (e.g., injection rates, particle size cutoffs, and P4 feed concentrations). It also would have involved numerous operational steps. These would have included the following: slurry feed processing in a ball mill to achieve less than 60 mesh particle size; collection and piping of the considerable amount of off-gas the caustic hydrolysis process would have generated; lime reactant preparation; chemical hydrolysis in reactor columns; reacted solids dewatering and stabilization; treatment of the off-gas management in a thermal oxidizer unit; oxidizer emissions scrubbing; and scrubber water treatment. The process was developed based on bench and pilot testing. It was never operated or demonstrated to be successful at full-scale even on the specific type of waste for which it was designed. A major process engineering review and design effort would be required in any to attempt to modify and expand that process to treat varying soil matrices that contain varying levels of P4.

3.4 CHEMICAL OXIDATION

Chemical oxidation involves the addition of chemical agents to react with COCs in the soil to form oxidized by-products. Chemical oxidation could potentially be used to treat P4 as an in-situ application or an ex-situ application.

3.4.1 Chemical Oxidation Treatment Process

Chemical oxidation involves adding uniformly sized feed material to a batch reactor where air, oxygen or acid (often nitric or sulfuric) is added, depending on the process, to react with and oxidize the P4 in the soils. In all but the High Speed Air Dispersion (HSAD) chemical oxidation process, the reaction vessel is heated to between 100 and 400°F during the batch treatment. A variety of waste streams are created depending on the type of oxidants used for the reaction. A scrubber would be needed to treat phosphorus gas emissions, and liquid wastes (scrubber water/wastewater) would need treatment or processing prior to on/off-site disposal or sale. In

general, chemical oxidation would convert P4 to various phosphate compounds. However, it would not be effective at treating metals and radionuclides.

Chemical oxidation could be performed ex-situ in a reactor vessel. Several ex-situ oxidation processes have been identified for possibly oxidizing P4, including High-Speed Air Dispersion (HSAD) for Wet Oxidation, the Praxair Oxidation Process, the Zimpro/Wet Air Oxidation Hybrid process, and nitric/sulfuric acid oxidation. The possibility has been suggested of performing chemical oxidation in-situ using a flushing process (Rhodia, 2007). Chemical oxidants would be added to the P4-contaminated soils either through injection or another method for distributing the oxidants through the contaminated medium. Although this has been used for a variety of chemicals, no information is available regarding in-situ chemical oxidation of P4-contaminated soils, and EPA did not discuss it further in the report prepared for the FMC historic ponds containing P4 in pond sediments (EPA, 2003). As with any in-situ injection technology, the effectiveness is largely dependent on the soil matrix constraints affecting the treatment criteria for physical contact and residence time between the oxidizing liquor and the targeted reactant. Given the mixed particle size in the fill materials, two issues arise. First, injection would likely take preferential pathways and not adequately contact the P4. Second, recovery of any reacted liquor likely would not be sufficient to prevent migration to groundwater.

3.4.2 Complete Chemical Oxidation Process Treatment Sequence

The complete ex-situ chemical oxidation treatment sequence would be a complex process involving: 1) the excavation (or wet dredging) of the P4-impacted material, 2) transport of the material to the treatment location, 3) storage of the excavated material to provide feed surge to the treatment process, 4) sizing (e.g., crushing and screening) of the material to provide a consistent feed particle size to the treatment process, 5) sampling and blending with other extracted streams or inert materials of the feed to provide consistent P4 content (i.e., percentage of P4), 6) chemical oxidation treatment, 7) additional treatment of solids for metals and radionuclides, 8) transportation to the final disposal site, and 9) landfill disposal. Both the wastewaters and gases from the process would need additional treatment processes before being disposed of, sold or otherwise released.

The complete in-situ chemical oxidation treatment sequence would involve injecting chemical oxidants into the contaminated soil and extraction of reacted liquor

For both in-situ and ex-situ chemical oxidation, phosphorus off-gas capture, scrubbing, and wastewater treatment systems would be necessary at the point of treatment and likely also at the point of excavation and temporary storage for ex-situ treatment.

3.4.3 Engineering Challenges/Issues for Chemical Oxidation

The following discussions provide a preliminary analysis of the engineering challenges and issues if chemical oxidation were applied to P4-impacted soils.

3.4.3.1 *Ex-Situ Chemical Oxidation Treatment As Applied to P4-Impacted Soils*

Ancillary process options associated with chemical oxidation ex-situ treatment: If ex-situ chemical oxidation treatment were performed on P4-impacted materials, the engineering considerations would include one or more of the following ancillary process options (and associated engineering challenges/issues):

- Conventional excavation of soils (see Section 2.2.1.1);
- Wet dredging/hydraulic pumping excavation of soils (see Section 2.2.1.2);
- Excavated soil transport and storage (see Section 2.2.1.3);
- Treatment feed sizing (see Section 2.2.1.4); and
- Treatment feed sampling and blending (see Section 2.2.1.5).

Ex-situ chemical oxidation treatment: Ex-situ chemical oxidation might be implemented by construction of a chemical reactor and ancillary treatment units using one of the processes mentioned above. Extensive development testing in a bench- or pilot- scale facility would be needed prior to construction of a full-scale treatment facility.

The ex-situ treatment process would present some significant engineering challenges, even with a consistent feed particle size and P4 concentration. The reaction of P4 with oxidizing agents can, depending on the chemical oxidation process and oxidant used, result in significant releases of various reaction products including H₂, P₄ vapor, P₂O₅, PH₃, phosphorus oxides, and H₃PO₄. These reactions would have to be carefully controlled in the process and the resulting emissions would have to be captured and controlled using the appropriate air pollution control and ancillary equipment (see Section 2.x above). The remedial option evaluation would have to take into account the cost and other factors associated with the needed equipment redundancy, specialized maintenance facilities capable of handling P4-contaminated equipment, and air pollution control equipment.

3.4.3.2 *In-Situ Chemical Oxidation Treatment As Applied to P4-Impacted Soils*

If in-situ chemical oxidation treatment were performed on P4-contaminated soil, the engineering issues would include the following:

Control of P4 reactions during injection: One of the critical process controls necessary for chemical oxidation treatment of P4 is the control of the P₄ reaction. Insufficient mixing results in un-reacted P4. This type of process control during in-situ treatment is likely to be impossible, resulting in one or all of the following scenarios:

- Incomplete mixing of chemical oxidant with contaminated soils, such that P4 is not completely reacted (i.e., it remains as P4) in the soil;
- Uncontrolled excessive reaction of P4 with air, resulting in a fire and threat of release of reaction products (i.e., P₄ vapor, P₂O₅, PH₃, phosphorus oxides, and H₃PO₄) and/or thermal burns to remediation workers and equipment; and/or

- Release of free liquids during the injection process (depending on the oxidant) that could transport other site COCs including metals and radionuclides to shallow groundwater.

Without extreme measures such as covering the in-situ treatment area with an impermeable structure, receptors downwind of the in-situ treatment could be exposed to aerosols associated with P4 combustion.

The most immediate threat for in-situ chemical oxidation treatment would be the thermal burning of P4 in the event of uncontrolled P4 reactions, which would pose a threat to remedial workers and equipment. Extreme caution, including extraordinary procedures and PPE, would be required to prevent severe injury or death to remediation workers and damage to equipment. Evaluation of this technology as a remedial option would have to consider cost and other factors associated with the measures necessary to prevent direct exposure of remediation workers and equipment to burning P4.

3.4.4 Chemical Oxidation Treatment Performance and Limitations

Given the engineering challenges and issues associated with ex-situ or in-situ chemical oxidation treatment, the following limitations, advantages, and potential applications are identified for P₄ - contaminated soils at the FMC Plant Site:

Limitations:

- Very complex complete treatment sequence.
- Generally not applicable for soil depth over 15 feet for ex-situ and 20 feet for in-situ.
- Generally not applicable for large volumes such as in RUs 1, 2, 13, or 22b (both ex-situ and in-situ).
- Difficult to control P4 reactions (in-situ and ex-situ) because of widely varying P4 concentrations.
- In-situ process would involve free liquids within the soil/fill material matrix thus creating a hydraulic head resulting in potential contamination of underlying groundwater.
- Significant variation in soil particle size and P4 concentration as found in most RUs would make the process extremely complex and difficult to operate and maintain.
- Does not treat metals and radionuclides associated with P4-contaminated soils and some processes even concentrate metals in the reactor sludges.

- Generation of phosphorus related gases that need to be treated and sludges disposed.
- Liquid and solid process streams would need secondary treatment prior to disposal.

Advantages:

- None.

Potential applicability:

- Soils with low concentration P^4 ($< 10,000$ ppm). HSAD bench scale testing were conducted using 180 gram samples of “filtered sludge” at 3.75, 7.5, and 15 percent solids, oxygen concentrations of 20, 50, and 80 percent, and agitation intensities between 4,000 and 8,000 rpm. The sludge contained P^4 at 4.4% ppm (EPA,2003).
- Soils with consistent material sizing.

3.4.5 By-Products and Residuals

In any treatment process, the by-products and residuals must be addressed in the feasibility evaluation and cost. The following by-products and residuals would be expected from a chemical oxidation treatment process:

Ex-situ:

- Sludge residues, which would require dewatering and treatment for metals and radionuclides; and
- Contaminated water generated from storing and transporting recovered soils, dewatering, and controlling air pollution during several steps in the process.

In-situ:

- Soil mass with radionuclides and elevated metals;
- P^4 reaction air emissions including PH_3 , P_2O_5 , H_3PO_4 , and H_2 ;
- Air pollution control system wastewaters and sludges; and
- In-situ process would involve free liquids within the soil/fill material matrix that would have to be managed.

3.4.6 History of Use

Chemical oxidation of soils and solids containing P₄ has only been conducted at bench and pilot scale. Two types of ex-situ oxidation technologies have been identified as potential candidates to treat elemental phosphorus; nitric/sulfuric acid oxidation and the HSAD process. The acid oxidation technology was developed and tested (pilot-scale) by the Tennessee Valley Authority (TVA) on sludge containing elemental phosphorus. The effluent from this process was then reacted with ammonia to produce a nitrogen and phosphate containing plant nutrient. The HSAD technology was developed and tested by researchers at the University of Alabama on sludge from Astaris (previously FMC), TVA, and Occidental Chemical. These processes are based on chemical transformation by oxidation.

Although the acid oxidation pilot scale study conducted by the TVA was capable of reducing the concentrations of P₄, operational concerns included sludge granulation and the generation of relatively large amounts of fertilizer and nitrogen oxide gases that would require further management or disposal. In addition, the pilot plant was only capable of processing the 30,000 lbs of P₄ sludge at 380 liters per batch. Tests using the HSAD chemical oxidation process were conducted using 180 gram samples of filtered sludge (4.4 % P₄), oxygen (at 20, 50 and 80 percent), and agitation intensities of 4K, 6K, and 8K revolutions per minute (rpm). The results show marked decrease in P₄ concentrations, but also increases in heavy metals (Jefcoat et. al., 1995). Therefore, additional treatment for metals would likely be required prior to disposing of the waste.

Any ex-situ chemical oxidation would require the excavation and preprocessing for granulation of P₄. This would result in significant short-term health and safety risks.

3.5 INCINERATION

Incineration is a proven technology that is commercially available to treat hazardous wastes. Mobile incinerators also are available for use at treatment sites. Typically, the technology is used for the destruction of organic compounds such as hydrocarbons and to reduce waste volume (Cost and Performance Remediation Case Studies [FRTR, 2001]). At least two commercial incinerators are licensed to treat P₄ in 55 gallon drums; no commercial incinerator has been identified which would accept P₄-contaminated soils in bulk. Relative to the FMC Plant Site wastes, radionuclides and metals would be concentrated in the incinerator ash and would require S/S before disposal. There are no in-situ incineration technologies due to the high heat requirements.

3.5.1 Incineration Treatment Process

Incineration is a thermal process where soil, sludge and other wastes are treated at high temperatures (1,400 to 2200°F) in a kiln, often a rotary kiln, to volatilize and combust contaminants. Incinerators typically are constructed using primary and secondary combustion chambers. They also use a variety of off-gas treatment processes and equipment, including filtration, wet-scrubbers, electrostatic precipitators, baghouses, vapor-phase carbon adsorption, and thermal oxidation.

Incineration would reduce the concentration of elemental phosphorus and volume in soil. Elemental phosphorus would be oxidized and natural organic matter in the soil would be converted to carbon dioxide. Oxidized elemental phosphorus would be captured by off-gas treatment systems such as scrubbers and treated further or discharged as a by-product. Most of the heavy metals and radionuclides would not be oxidized and would be concentrated in the residual ash.

3.5.2 Complete Incineration Process Treatment Sequence

The complete incineration treatment sequence would be a complex process operation that would involve the excavation (or wet dredging) of the P4-impacted material and transport of the material to the treatment location either on- or off-site. If conducted on-site, the treatment train also would require storage of the excavated material to provide feed surge to the treatment process, sizing (e.g., crushing and screening) of the material to provide a consistent feed particle size to the treatment process, incineration, treatment of ash for metals and radionuclides, transportation to the final disposal site, and landfill disposal.

3.5.3 Engineering Challenges/Issues for Incineration

The following discussions provide a preliminary analysis of the engineering challenges and issues if incineration were applied to P4-impacted soils.

3.5.3.1 On-Site Incineration Treatment As Applied to P4-Impacted Soils

Ancillary process options associated with incineration ex-situ treatment: If on-site incineration treatment were performed on P4-contaminated soil, the ancillary process options (and associated engineering challenges/issues) would include the following:

- Conventional excavation of soils (see Section 2.2.1.1);
- Wet dredging/hydraulic pumping excavation of soils (see Section 2.2.1.2);
- Excavated soil transport and storage (see Section 2.2.1.3);
- Treatment feed sizing (see Section 2.2.1.4); and
- Treatment feed sampling and blending (see Section 2.2.1.5).

Incineration: If conducted on-site, the incineration treatment process itself would present some significant engineering challenges, even with a consistent feed particle size and P4 concentration. The soils at the site would most likely have a low BTU value and therefore would require large amounts of fuel. Further, assuming that on site incineration would be based on bulk feed; the water in the slurried feed would also consume excess energy to combust. In addition, the elevated concentrations of inorganic contaminants and minerals in the soil may result in slagging, which would be retained in the incinerator ash and reduce output (EPA, 1998a). Incineration would result in the volatilization of some metals and the generation of PH₃ gas. These gas streams would require treatment by an off-gas treatment system involving a scrubber. Before the incinerator could be operated at full scale, a trial burn would be necessary to optimize

the treatment process and ensure that emissions and operating conditions were consistent with those specified under applicable permit programs.

3.5.3.2 Off-Site (Commercial) Incineration Treatment As Applied to P4-Impacted Soils

Ancillary process options associated with incineration ex-situ treatment: If off-site incineration treatment were performed on P4-contaminated soil, the engineering considerations would be more limited because several of the processes necessary for on-site incineration would be conducted by the commercial incinerator. Ancillary process options (and associated engineering challenges/issues) nevertheless would still exist with off-site incineration, specifically those associated with material handling:

- Conventional excavation of soils (see Section 2.2.1.1);
- Wet dredging/hydraulic pumping excavation of soils (see Section 2.2.1.2); and
- Excavated soil transport and storage (see Section 2.2.1.3). However, storage requirements might be reduced by placing soils directly in 55-gallon barrels using the proper precautions (i.e., nitrogen blanket, cooling of the containers, use of water, etc.) to eliminate spontaneous combustion of P4. An additional issue associated with this option would be public safety concerns from transportation of many loads P4-contaminated soils to the selected off-site commercial incinerator.

The commercial off-site incinerator would be responsible for these other necessary processes steps including:

- Treatment feed sampling and blending (see Section 2.2.1.5); and
- Ash S/S and disposal.

Incineration: For off-site incineration, issues surrounding the required sizing and physical composition of the feed stream, P4 concentration in the feed stock, BTU value of the feed stock, gas and wastewater treatment systems (i.e., air scrubber and waste water treatment plant [WWTP]), and ash disposal would be the responsibility of the commercial incinerator.

3.5.4 Incineration Treatment Performance and Limitations

Given the engineering challenges and issues associated with incineration, the following limitations, advantages, and potential applications are identified for P₄-contaminated soils at the FMC Plant Site:

Limitations:

- Generally not applicable for soil depth over 15 feet due to limitations of excavation equipment.

- High energy requirements.
- Requires obtaining air permit if conducted on-site.
- Does not treat all metals and radionuclides, which instead are concentrated in the ash.
- Some metals would be volatilized, requiring those volatiles and gases from the P4 reaction processes to be removed by an air scrubber connected to the rotary kiln.
- High cost and, for on-site incineration, extended time required for design, construction, trial burns and demonstration of compliance with operational and emission requirements under applicable permit programs.

Advantages:

- Robust technology that can handle larger variations in P4 concentrations.
- Significant variation in soil particle size may not prevent processing.
- Commercially available with necessary permits.

Potential Applicability:

- Soils with wide range of P4 concentrations.

3.5.5 By-Products and Residuals

In any treatment process, the by-products and residuals must be addressed in the feasibility evaluation and cost. The following by-products and residuals would be expected from the incineration treatment process:

- Off-gases consisting of P_2O_5 , phosphine, and some metals, which would require further treatment;
- Ash, potentially containing concentrated levels of metals and radionuclides that would require further treatment before disposal; and
- Wastewater from scrubber and waste dewatering would require WWTP. Sludges from the WWTP likely would contain metals and radionuclides that would require further treatment prior to disposal.

3.5.6 History of Use

Commercial incinerators are available for treating P4-contaminated soils. During the FMC Plant decommissioning from 2002 to 2006, offsite incineration was used for disposal of residual P4 removed from process tanks, sumps and aboveground piping and for a limited amount of P4-contaminated equipment that could not be effectively cleaned (e.g., small diameter heat transfer coils) and that could be reduced in dimensions to fit into 55-gallon drums.

A full-scale incinerator has been developed for P4 in munitions at the Crane Army Ammunition Activity (CAAA), in Crane, Indiana. The facility is referred to as the WP to Phosphoric Acid Conversion (WP-PAC). The furnace was designed to treat small quantities of elemental phosphorus contained in bombs. At the WP-PAC facility, a hole is punched in ordinance using a 115 ton hydraulic press at ambient temperatures, exposing the WP in the ordinance to oxygen. The ordinance items are then pushed into the first section of a rotary kiln furnace to melt the WP, which flows out of the punched hole. The WP is then burned in an oxygen-rich furnace to form P₂O₅. At full-scale level since 1989, the facility at maximum capacity can process up to 11,500 pounds of WP, which is extracted from munitions, per day. In a 24-hour period, the facility produces 48,000 pounds of phosphoric acid with 75% concentration (http://www.crane.army.mil/caaa/WhitePhosphorus/WhitePhosphorus_pg.htm). Information was not provided regarding the current status of the WP-PAC facility and whether it might be available for use by commercial companies such as P4 manufacturers (EPA, 2003).

3.6 THERMAL DESORPTION

Thermal desorption is much like the incineration process in that it uses heat to volatilize (oxidize) the COCs. However the temperatures in the rotary furnace under this process are much lower (on the order of 200 to 600°F instead of 1,400 to 2,200°F). Thermal desorption is used to treat soil and sludge by heating (directly or indirectly) to volatilize contaminants and separate them from the solid matrix without combustion. Radionuclides and metals would be concentrated in the solid residues of the treatment unit and would require S/S before disposal. There are no in-situ incineration technologies due to the high heat requirements. Thermal desorption is considered only as an ex-situ treatment technology.

3.6.1 Thermal Desorption Treatment Process

The common configuration for the thermal desorption process includes a rotary kiln, thermal screw, or infrared (IR) exposure. With IR treatment, the contaminated soil/sludge is typically placed in 5 cubic yard trays for processing. The rotary kiln and thermal screw operate on a continuous basis, with heat applied by combustion of natural gas, while the IR system is a batch process (EPA, 2003). The temperatures used in a thermal desorber are lower than in an incinerator, generally on the order of 200 to 600 °F. The volatilized contaminants (vapors) are collected and generally treated by one or more off-gas treatment technologies. Off-gas treatment equipment might include filtration, wet scrubbers, electrostatic precipitators, baghouses, vapor-phase carbon adsorption, and thermal oxidation. Thermal desorption would reduce the concentrations of P4 through volatilization. The P4 vapors would be recovered by treatment of the off-gas.

3.6.2 Complete Thermal Desorption Process Treatment Sequence

The complete thermal desorption treatment sequence would be a complex operation involving: 1) the excavation (or wet dredging) of the P4-impacted material, 2) transport of the material to the treatment location, 3) storage of the excavated material to provide feed surge to the treatment process, 4) sizing (e.g., crushing and screening) of the material to provide a consistent feed particle size to the treatment process, 5) sampling and blending with other extracted streams or inert materials of the feed to provide consistent P4 content, 6) thermal desorption treatment, 7) treatment of the solid residues from the process, 8) transportation to the final disposal site, and 9) landfill disposal.

3.6.3 Engineering Challenges/Issues for Thermal Desorption

The following discussions provide a preliminary analysis of the engineering challenges and issues if thermal desorption were applied to P4-impacted soils.

3.6.3.1 Thermal Desorption Treatment As Applied to P4-Impacted Soils

Ancillary process options associated with thermal desorption treatment: If thermal desorption treatment were performed for P4-impacted materials, the ancillary process options (and associated engineering challenges/issues) would include the following:

- Conventional excavation of soils (see Section 2.2.1.1);
- Wet dredging/hydraulic pumping excavation of soils (see Section 2.2.1.2);
- Excavated soil transport and storage (see Section 2.2.1.3);
- Treatment feed sizing (see Section 2.2.1.4); and
- Treatment feed sampling and blending (see Section 2.2.1.5).

Thermal Desorption Treatment: The treatment process would present some significant engineering challenges, even with a consistent feed particle size and P4 concentration. Operational concerns include the quantity of fuel needed to sustain desorption, and possible fire and explosion hazards. The soils at the FMC Plant Site have relatively low BTU values; therefore, thermal desorption would likely require significant consumption of fuel in order to reach and maintain treatment temperatures (EPA, 2003). Further, bulk feed stock would be wetted or in a slurry form, further increasing energy requirements to evaporate the water. Hot spots of WP contamination also present a safety hazard due to the possibility of spontaneously combusting during the thermal desorption process. In addition, the solid residue from the process would require further treatment for metals and radionuclides.

3.6.4 Thermal Desorption Treatment Performance and Limitations

Given the engineering challenges and issues associated with thermal desorption, the following limitations, advantages, and potential applications are identified for P₄-contaminated soils at the FMC Plant Site:

Limitations:

- Generally not applicable for soil depth over 15 feet due to limits of excavation equipment.
- High energy requirements.
- Might have difficulties treating highly-concentrated P4 (explosions) as might be found in many of the site soils.
- Requires obtaining air permit and time necessary to demonstrate and achieve compliance with operational and emission requirements under applicable permit programs.
- Does not treat metals and radionuclides.

Advantages:

- Lower energy requirements than incineration.
- Lower treatment temperatures would limit or eliminate the volatilization of metals that occurs during incineration.

Potential applicability:

- Soils with a relatively wide range of P4 concentrations.

3.6.5 By-Products and Residuals

In any treatment process, the by-products and residuals must be addressed in the feasibility evaluation including the cost analysis. The following by-products and residuals would be expected from the thermal desorption treatment process:

- Off-gases consisting of P_2O_5 , phosphine, and some metals that might be volatilized would require further treatment;
- Wastewater from scrubber and waste dewatering (if applicable) would require WWTP. Sludges from the WWTP likely would contain metals and radionuclides that would require further treatment prior to disposal; and
- Solid residue from the process would contain concentrated levels of metals and radionuclides that would require further treatment before disposal.

3.6.6 History of Use

This process has been used at full scale for the volatilization of P4. As described in EPA's *2003 Treatment Technologies Report*, the USACE reported that a patented infrared system, operating on a batch basis, was used to treat 300 tons of WP-contaminated soil in DDOU. The treatment system was provided by ENSR (fka McLaren-Hart Environmental Engineering Corporation). The treatment rates for this system were reported to average 1 hr and 40 minutes for each 5 yd³ batch, for a total treatment time for the 300 tons of 4 days. Assuming a similar treatment time it would take approximately 30 years to treat all of the impacted soils in RUs 1, 2, and 22b using a similar process. The USACE reported that one instance of auto-ignition of P4 was detected inside the desorber, which was controlled. Information was not provided specifying the concentrations of WP or other contaminants in the soil before or after treatment, or about the disposition of treatment residuals (USACE, 1996). It is assumed that the technology was used to treat relatively low concentrations of P4 in soils as is typically found in military sites, e.g., <1,000 ppm P4. ENSR personnel were not familiar with the current availability of the infrared desorption unit (Stewart, 2001).

Section 4.0 Elemental Phosphorus Treatment Technologies – Groundwater

This section presents an overview of the technologies that were identified and screened for treatment of elemental phosphorus-contaminated groundwater at the FMC Plant OU.

As described in the Groundwater Current Conditions Report for the FMC Plant OU, the primary site-related groundwater COC is arsenic and the extent of site-related groundwater impacts can effectively be delineated by arsenic concentrations above the representative concentration. Within the overall area of arsenic-impacted groundwater, site-related groundwater COCs include metals (e.g., manganese, selenium and vanadium), nutrients (primarily total phosphorus in orthophosphate form and nitrogen primarily as nitrate), fluoride, total cyanide and elemental phosphorus. The SFS Report will present the identification and screening of technologies for groundwater based on the full suite of groundwater COCs. Remedial technologies for the overall site-impacted groundwater will be identified, screened and evaluated in the SFS Report for the FMC Plant OU.

This section focuses on technologies that may be effective for treatment of P4 in groundwater that has been detected downgradient from RUs 1 and 2, specifically at wells 108 and 122. The groundwater P4 remedial technologies may or may not be effective for the treatment of other groundwater COCs.

Several process options / technologies have been identified that will be evaluated as options and/or as components of an overall groundwater remedial alternative for the site. These options will not be discussed here because they would not likely be applied solely to P4-containing groundwater:

- Deed (Groundwater Use) Restrictions
- Groundwater Monitoring
- Source controls
- Cut-off (e.g., slurry or grout) walls

The ancillary process steps associated with the in-situ and ex-situ technologies that may represent treatment options for site-impacted groundwater, including P4-containing groundwater, are not discussed in detail in this section. The ancillary process steps associated with in-situ technologies relate to the injection wells and systems necessary for addition (e.g., injection) of physical and/or chemical agents directly into groundwater. Ex-situ technologies require additional process steps such as groundwater extraction (pumping), either for hydraulic control or for mass removal, storage prior to and potentially after the treatment process, and use/disposal of the treated water. These ancillary process steps will be evaluated in the SFS Report but are not discussed below because these steps are not unique to treatment of P4-containing groundwater.

The following technologies have been identified for potential treatment of P4-containing groundwater:

- Oxidation – Chemical or physical oxidation could be effective as an ex-situ and in-situ treatment technology for dissolved-phase P4-containing groundwater.
- Hydrolysis – Chemical hydrolysis could be effective as an ex-situ treatment technology for dissolved and particle-phase P4-containing groundwater.
- Reverse osmosis – Reverse osmosis could be effective as an ex-situ treatment technology for dissolved and particle-phase P4-containing groundwater.

A screening-level evaluation of treatment technologies for P4-containing groundwater is presented below. For each technology identified, information is provided (to the extent known based upon literature research and FMC experience) on the following topics:

- Summary description of the technology and its potential applicability, ex-situ or in-situ, at the FMC Plant OU, and
- Preliminary evaluation of the effectiveness of the technology and potential engineering and operational challenges associated with implementation.

4.1 Oxidation

4.1.1 Summary Technology Description

Ex-situ or in-situ oxidation technologies involve the addition of chemical oxidants, ultraviolet light (UV), ozonation and/or mechanical addition of oxygen (air) to the aqueous solutions to promote oxidation of reduced inorganic elements or to create an oxidizing reaction with organic compounds. Chemical oxidants for treatment of aqueous solutions include the following:

- Hydrogen peroxide
- Potassium permanganate
- Calcium hypochlorite
- Persulfate (Potassium, sodium, ammonium)

Physical oxidation involves the use of UV light irradiation and/or introduction of oxygen, ozone or air by diffusion (e.g., sparging) into the aqueous solution.

As described in the Groundwater Current Conditions Report for the FMC OU, elemental phosphorus is detected in groundwater at wells 108 and 122 downgradient from RUs 1 and 2, but not at wells 111, 146 and 110 that are further downgradient from wells 108 and 122. Although the reduction in P4 concentrations could be due in part to advective mixing, oxidation and hydrolysis of P4 in groundwater are likely the primary mechanisms whereby the P4 is converted to phosphorus compounds (e.g., orthophosphate) as groundwater migrates downgradient from

these wells. Chemical or physical oxidation would be utilized to accelerate (increase the rate) of natural oxidation of P4 in water.

Ex-situ treatment would involve extracting (pumping) groundwater and routing the water to a storage tank(s) and then feeding the water into a reactor tank(s) where the selected oxidizing chemical(s) would be added and/or physical oxidation would be performed.

In-situ treatment would involve injection of the selected oxidizing chemical(s) and/or use of physical oxidation techniques within groundwater wells located to effectively deliver the oxidant within the zone of P4-containing groundwater.

4.1.2 Preliminary Evaluation of Effectiveness

Laboratory testing, pilot-scale and/or full scale application of chemical and/or physical oxidation technologies found from the literature and information search is focused on treatment of P4 production waste streams (e.g., phosphy water and P4 sludge). The literature indicates chemical and/or physical oxidation (including wet air oxidation) are not very effective for treating solid phase P4 (either as particles, particle-sorbed or as a P4/water emulsion).

The technology identification search did not reveal any information specific to the testing of oxidation technologies on relatively low concentrations of dissolved P4 in water (i.e., water with P4 concentrations less than the solubility limit of 3 mg/l). However, based on the literature and research into the fate of P4 in aqueous systems, oxidation would be expected to be effective for accelerating the natural oxidation of P4 in water and conversion of the P4 to oxidized phosphorus compounds (e.g., orthophosphate).

Chemical/physical oxidation for treatment of P4 would also oxidize metals (e.g., As⁺³ to As⁺⁵) and nutrients (e.g., ammonia to nitrate) and potentially make these groundwater COCs more amenable to treatment using other technologies. However, oxidation would not be effective as a stand-alone overall groundwater treatment technology. This limits its potential utility as an in-situ technology. In addition, adequate delivery and mixing of the oxidant into groundwater could be difficult to implement.

4.2 Hydrolysis

4.2.1 Summary Technology Description

Hydrolysis is a chemical reaction during which water molecules are split into hydrogen and hydroxide ions, which may go on to participate in further reactions. Generally, strong acids or bases must be added to achieve hydrolysis. The acid or base is considered a catalyst and aid in increasing the rate of the reaction.

As described in the Groundwater Current Conditions Report for the FMC Plant OU, elemental phosphorus is detected in groundwater at wells 108 and 122 downgradient from RUs 1 and 2, but not at wells 111, 146 and 110 that are further downgradient from wells 108 and 122. Although the reduction in P4 concentrations could be due in part to advective mixing, oxidation and hydrolysis of P4 in groundwater are likely the primary mechanisms whereby the P4 is converted

to phosphorus compounds (e.g., orthophosphate) as groundwater migrates downgradient from these wells. Chemical catalyzed hydrolyses would be utilized to accelerate (increase the rate) of natural hydrolysis of P4 in water.

Ex-situ treatment would involve extracting (pumping) groundwater and routing the water to a storage tank(s) and then feeding the water into a reactor tank(s) where the selected acid- or base-catalyzed hydrolysis would be performed.

In-situ chemical catalyzed hydrolysis would involve injection of the selected acid/base within groundwater wells located to effectively deliver the reagent within the zone of P4-containing groundwater.

4.2.2 Preliminary Evaluation of Effectiveness

Laboratory testing, pilot-scale and/or full scale application of base (caustic) catalyzed hydrolysis technologies found from the literature and information search is focused on treatment of P4 production waste streams (e.g., precipitator slurry and phosphy water). The literature indicates that caustic hydrolysis is effective for treating wastewater and non-wastewater wastes (e.g., phosphy water and precipitator slurry) containing P4 concentrations in the range of 1 to 2 percent.

The technology identification search did not reveal any information specific to the testing of hydrolysis technologies on relatively low concentrations of dissolved P4 in water (i.e., water with P4 concentrations less than the solubility limit of 3 mg/l as observed in wells 108 and 122). However, based on the literature and research into the fate of P4 in aqueous systems, chemical-catalyzed hydrolysis would be expected to be effective for accelerating the natural hydrolysis of P4 in water and converting the P4 to phosphorus compounds (e.g., phosphorus acids and phosphine).

Chemical-catalyzed hydrolysis treatment of P4 would not be effective for treatment of other groundwater COCs. However, the use of lime (calcium oxide) or slaked lime (calcium hydroxide) for catalyzed caustic hydrolysis would also be expected to precipitate other cations and anions. Precipitation, in conjunction with filtration technology, will be evaluated as a remedial technology the overall groundwater remedy.

In-situ hydrolysis of P4-containing groundwater would have similar challenges to chemical/physical oxidation, i.e., effective delivery and coverage. It also would have the negative effect of adding salts (TDS) to the groundwater system.

4.3 Reverse Osmosis

4.3.1 Summary Technology Description

Reverse osmosis is physical treatment process in which pressurized water passes through a semi-permeable membrane. The applied pressure to the waste stream is greater than the osmotic pressure of the feedwater. As water passes through the membrane, dissolved constituents in the water are concentrated on the feed side of the membrane to form the waste brine and a purer, more dilute product water is formed on the permeate side of the membrane. Depending upon the

feedwater concentrations, the waste brine may be as much as 15-percent to 25-percent of the total feedwater flow. The brine would require further handling and/or treatment prior to disposal.

Ex-situ treatment would involve extracting (pumping) groundwater and routing the water to a storage tank(s) and then feeding the water into a reverse osmosis system(s). Reverse osmosis is not applicable as an in-situ technology.

4.3.2 Preliminary Evaluation of Effectiveness

The technology identification search did not reveal any information specific to the testing of reverse osmosis technologies on dissolved P4 in water (i.e., water with P4 concentrations less than the solubility limit of 3 mg/l). However, based on literature and research of reverse osmosis, the technology would be effective at removing dissolved constituents (including P4) from site groundwater. However, reverse osmosis produces a concentrated brine stream that would likely require further treatment prior to disposal. In addition, reverse osmosis has high energy requirements and the waste brine would require pretreatment, making it much more costly than other effective ex-situ treatment technologies.

Section 5.0 Findings

This report provides a summary and evaluation of available information regarding “active” or “intrusive” remedial technologies, both in-situ and ex-situ, that have the potential to treat soils (including fill materials) and groundwater at areas within the FMC Plant OU that are known or suspected to have P4 contamination. The approach taken here regarding the identification and evaluation of potential treatment technologies is similar to that taken by the EPA Office of Solid Waste and Emergency Response in its 2003 report entitled “*Treatment Technologies for Historical Ponds Containing Elemental Phosphorus – Summary and Evaluation.*” While this report focuses on treatment technologies, it is recognized that the SFS Report will also evaluate all remediation technologies that potentially could treat all the site COCs, including heavy metals, radionuclides (including gamma), and organics in addition to P4, where those COCs are detected in soils and groundwater above RAOs.

This section is organized into two subsections. The first subsection (Section 5.1) summarizes the findings of EPA’s 2003 *Treatment Technologies Report* referenced above, and updates those findings to reflect developments since the date of that report and the evaluations presented here. The second subsection (Section 5.2) presents the general findings of this report and lists for reference, the remedial technologies that this report has identified and evaluated. Both subsections discuss the relevant findings of the *SRI Report* to specifically evaluate the technologies against the actual conditions at the site including the potential application of these technologies to the Remedial Units containing P4 in the FMC Plant OU.

5.1 UPDATES TO THE OVERALL FINDINGS OF EPA’S 2003 TREATMENT TECHNOLOGIES REPORT

EPA’s 2003 *Treatment Technologies Report* was specifically focused on treatment of P4-containing sludges within ponds at the FMC Plant Site. Thus it is worthwhile to re-examine the general findings of that report.

Six technologies were identified in the 2003 *Treatment Technologies Report* as potentially applicable: solidification/stabilization (S/S); caustic hydrolysis; chemical oxidation; mechanical aeration; incineration; and thermal desorption. The following is a summary, discussion and update of the key findings in that report.

EPA Report Finding No. 1: No technology has been used at full-scale to treat waste material similar to that found at the FMC Plant Site.

Summary of EPA finding No. 1: Only limited information is available in the literature covering the remediation of WP, with fewer than 10 studies identified that discuss the potential use of treatment technologies for WP. This primarily includes studies performed at WP manufacturing facilities and at military facilities. While technologies have been used to treat WP in bench- and pilot-scale studies, no technologies were identified as having been used for full-scale treatment.

Current Update to EPA Finding No. 1: Based upon the review of internal FMC technical documents related to P4, discussions with personnel at other P4 manufacturing facilities, review

of technical information from these sources related to P4 treatment, and search of the Internet for technical documents related to P4 treatment, there have been no significant developments in P4 treatment technologies since 2003.

EPA Report Finding No. 2: No new treatment technologies have emerged as potentially applicable since the EMF Feasibility Study.

Summary of EPA Finding No. 2: The six technologies in the 2003 EPA report had been identified in the Feasibility Study for the FMC Subarea prepared in 1996.

Current Update to EPA Finding No. 2: Again, no new treatment technologies have emerged as potentially applicable to the FMC Plant Site.

EPA Report Finding No. 3: Other WP manufacturing facilities primarily used capping as the remedy for similar waste.

Summary of EPA Finding No. 3: Eight other WP manufacturing sites were identified that have similar contaminated historical ponds as those at the FMC Plant OU. Six of the eight sites have installed or plan to install caps. For the two remaining sites, one (Rhodia, located at Silver Bow, Montana) indicated that the ponds are not under corrective action or closure programs that would require capping, and the other (Stauffer, located at Tarpon Springs, Florida) is evaluating a remedy of in situ S/S.

Current Update to EPA Finding No. 3: EPA's finding regarding the WP manufacturing sites that have installed or plan to install caps as soil/solid waste remedies remains valid, although additional WP sites have been identified where the final remedy also has included capping / containment. Updates regarding the Rhodia-Silver Bow and Stauffer-Tarpon Springs sites are provided below.

The Rhodia, Inc. phosphorus manufacturing facility in Silver Bow, Montana is currently evaluating treatment technology for waste in a process clarifier consisting of solidified, phosphorus-rich (20%) sludge. Rhodia is conducting this evaluation under the RCRA corrective action program. The clarifier is 100 feet in diameter, 12 feet deep, open-topped, with reinforced concrete walls and base. It contains 8 to 9 feet of phosphorus-rich waste, covered by more than 2 feet of water. To date, this evaluation has not yielded a selected corrective action.

The Stauffer site in Tarpon Springs, Florida completed a treatability study after the 2003 EPA Report that evaluated in-situ S/S. In-situ S/S has since been rejected as not being viable and a capping remedy has been selected. See the June 2007 Explanation of Significant Differences for this site and discussion below.

EPA Report Finding No. 3: Minimal performance data currently exist for use of the six technologies to treat similar waste material as found at EMF.

Summary of EPA finding No. 3: Performance data were identified for treatment of WP using chemical oxidation, mechanical aeration, and incineration. However, these data are not for treatment of wastes in historical ponds at a WP manufacturing facility. Performance data for

chemical oxidation and mechanical aeration are for work at bench- and pilot-scale, while data for incineration are for ordnance wastes with a higher percentage of WP than found in the FMC historical ponds. Thermal desorption was used for the treatment of WP in contaminated soil. Recent attempts to obtain specific information on the project revealed that the technology vendor was sold to another company. Personnel at this company were not familiar with the current availability of the technology. Therefore, it is unknown if the WP-contaminated soil was similar to waste material as found at the FMC Plant OU and no specific performance data were available for review. No performance data were identified for treatment of WP using S/S and caustic hydrolysis. Both technologies have been considered for the treatment of similar waste material at WP manufacturing sites.

The Stauffer site in Tarpon Springs, Florida is planning to test in situ S/S in 2003. Although the information from this test program could be used to evaluate the effectiveness of S/S at the FMC Plant OU, the test program at Tarpon Springs may not be an accurate predictor of performance for the FMC Plant OU waste. Reasons for this include: the type of phosphate ore used at Tarpon Springs is different from that used at EMF, elemental phosphorus is not a primary contaminant at Tarpon Springs, and the scale of the Tarpon Springs site is smaller. Caustic hydrolysis was considered for use at the Rhodia site in Silver Bow, Montana. In addition, caustic hydrolysis was identified as the Land Disposal Restrictions treatment technology for process waste streams from the FMC plant, but construction of that treatment system was halted with the plant shutdown.

Current Update to EPA Finding No. 3: In February 2006, Stauffer initiated the field-scale studies for in-situ solidification and stabilization within Pond 48. As a result of the cement curing, the elemental phosphorous ignited and created a persistent fire. The Field Scale study was discontinued due to the fire, resulting phosphorus gas generation, and uncertainty regarding the potential locations of buried elemental phosphorous that could create additional fires. In May 2007, a modified remedy was selected consisting of the construction of a groundwater cut-off wall and cap as a replacement for the planned in-situ stabilization remedy.

EPA Report Finding No. 4: Additional testing would be necessary to assess whether treatment technologies could perform adequately across a range of contaminant concentrations and properties of the waste material as found at EMF.

Summary of EPA finding No. 4: Limited site characterization data are available and the historical ponds are assumed to be heterogeneous in physical and chemical composition. Therefore, extensive site assessment and treatability testing would be needed to verify the potential for any technology to treat the soil and sludge at the FMC Plant OU. Treatability tests would include evaluating how the technology would perform for the specific matrices in the different ponds, and the variations in performance across the range of concentrations and physical properties.

Although the six technologies are at various stages of commercial development, the technologies would all require testing to establish that they could perform reliably for the waste material in the historical ponds. S/S, chemical oxidation, incineration, and thermal desorption have been applied commercially at full-scale for site remediation, but have not been used to treat WP pond material. Caustic hydrolysis and mechanical aeration have not been used extensively for site

remediation, and significant developmental testing would be required for scale-up along with treatability testing. Developmental and treatability testing for the six technologies would require additional time and resources to undertake.

Current Update to EPA Finding No. 4: No additional input to this finding.

EPA Report Finding No. 5: A series of technologies may be necessary to collectively treat all the types of contaminants.

Summary of EPA finding No. 5: *The soil and sludge in the historical ponds contain multiple types of contaminants that all may require treatment. For example, incineration, thermal desorption, mechanical aeration, and chemical oxidation show potential to treat WP, but would not be able to treat heavy metals or radionuclides. In these cases, an additional treatment process would likely be needed, such as S/S, using what is often referred to as a “treatment train.”*

Current Update to EPA finding No. 5: No additional input to this finding.

EPA Report Finding No 6: Of the six technologies, only S/S and caustic hydrolysis have the potential to be effective for treatment of heavy metals and radionuclides.

Summary of EPA finding No. 6: *S/S is applied frequently at full-scale to reduce the mobility of heavy metals (radionuclides are expected to behave in a manner similar to heavy metals) at contaminated sites. Caustic hydrolysis would convert heavy metals to metal oxides and hydroxides, which generally are less soluble than the metal compounds, and could be removed by filtration or settling processes.*

Current Update to EPA Finding No. 6: It is not clear that caustic hydrolysis would treat waste streams containing metals or radionuclides to levels that would not require further treatment. At a minimum, treatability studies would be necessary to evaluate effectiveness of caustic hydrolysis in treating all COCs at the site..

EPA Report Finding No 7: Residuals from treatment, such as solid, liquid, or gaseous materials, would require further management.

Summary of EPA finding No 7: *Residual management may include characterizing and transporting these residuals to a storage or disposal facility (on- or off-site), or performing further treatment (such as for off-gases) prior to release to the environment.*

Current Update to EPA finding No. 7: Management of residuals likely would have significant implementability and cost impacts, and could pose significant potential environmental, site worker safety and public safety issues. The remedial alternative evaluation including the cost analysis would have to consider the capital and O&M costs and other factors associated with implementing the measures that would be needed to manage residuals.

EPA Report Finding No 8: Soil and sludge may require pre-processing to homogenize the material for use by treatment technologies.

Summary of EPA finding No. 8: Pre-processing may include crushing, grinding, or milling, to break up large masses of soil and sludge. For both ex-situ and in-situ technologies, pre-processing may be necessary depending on the distribution of contaminants in the ponds and the methods used to implement the treatment technologies.

Current Update to EPA finding No. 8: As discussed in this report, ancillary processes: 1) are integral to the overall remedial alternative, 2) present engineering challenges as difficult as the treatment process itself, 3) will have major cost impacts, and 4) pose significant potential environmental, site worker safety and public safety issues. The remedial action evaluation would need to consider the capital and O&M costs and other decisional criteria with respect to the measures that would be required to safely pre-process the soils, sludges, and fill materials before implementing treatment technologies.

EPA Report Finding No. 9: The estimated volume of waste material to treat (500,000 cubic yards) would entail a large remediation project, including significant engineering issues.

Summary of EPA finding No. 9: The physical layout of the site, where historical ponds are located near RCRA ponds, structures, and slag piles, may impact the implementation of a treatment technology, including the need for space to stage equipment or to store material before or after treatment.

Current Update to EPA Finding No. 9: Based upon the current estimates for RUs 1, 2, 13, 22b, and 22c and areas with underground piping containing P4, the total volume of materials to be treated in areas impacted by P4 is estimated at 780,122 yd³. The total amount of P4 within this volume is estimated to range from 5,050 to 16,380 tons.

EPA Report Finding No. 10: Site workers would need to follow stringent health and safety precautions for handling soil or sludge containing WP.

Summary of EPA finding No. 10: WP is an inorganic compound that ignites spontaneously in warm air. It is toxic by ingestion and inhalation, and skin contact with WP causes burns. Site workers would likely need to use Level C personal protective equipment (respiratory and skin contact protection) when conducting work on the soil or sludge in the historical ponds. In addition, health and safety precautions related to metals and radionuclides would also have to be considered.

Current Update to EPA Finding No. 10: Although neither the EPA 2003 Treatment Technologies Report nor this paper was intended as a full evaluation of the health and safety precautions necessary for site remediation workers, very stringent worker protection measures certainly would be required. It is clear that Level C PPE would not be sufficient or adequate to protect against thermal burn hazards and/or gas generation associated with P4 reactions (which could include PH₃). For any work inside enclosures where P4 gases were present, as discussed in Section 2.0, supplied air would be necessary (Level A PPE) in addition to aluminum gear to

prevent direct dermal exposure to P4. The remedial action evaluation would need to address the capital and O&M costs and other factors associated with the needed health and safety precautions, protections, and procedures.

EPA Report Finding No. 11: The cost to implement any of the six treatment technologies would be high, based on the criteria used to identify high cost projects by EPA's National Remedy Review Board (NRRB).

Summary of EPA finding No. 11: The NRRB identifies high cost remedial actions as those that cost more than \$30 million, or more than \$10 million and 50 percent greater in cost than the least costly cleanup alternative. Although the technology cost estimates in this report could be above or below the actual costs, the actual total treatment costs are likely to be higher. Specifically, the technology costs estimates do not include costs for associated project components, such as excavation (if required), preprocessing of waste material, health and safety (such as ambient gas control), and residual management, which could be integral parts of a remediation project at the FMC Plant OU using any of the six technologies.

Current Update to EPA Finding No. 11: This paper did not review costs associated with these technologies and does not provide any additional input to this finding.

5.2 GENERAL FINDINGS P4 TREATMENT TECHNOLOGY SCREENING FOR FMC PLANT OPERABLE UNIT

The following are the general findings of this report:

- When screening and evaluating remedial technologies for P4-impacted materials, it is very important to consider the ancillary process options that would be necessary to complete the overall P4 treatment train. While some components of these ancillary process options have been used in other settings, none have been applied directly to materials representing a combination of P4/soil/fill materials like those present at the FMC Plant Site. Ancillary process options, especially those associated with ex-situ treatment, may present greater challenges for implementability than the treatment technology itself.
- Treatability studies for one or more of the ancillary and treatment processes likely would be required before categorizing any of the P4 treatment technologies as viable remedial options.
- EPA's 2003 *Treatment Technologies Report* appears to have been a complete and accurate evaluation of the availability of treatment technologies, the level of development, and the challenges of implementing a full-scale treatment system.
- Ex-situ oxidation or hydrolysis and in-situ oxidation have been identified as potentially effective treatment technologies for P4-containing groundwater although no specific information was found regarding the implementation of these technologies for P4-contaminated water at full scale.

The following is a brief summary of the P4 treatment technologies identified and evaluated in this report as applied to the types of soils and fill materials found at the FMC Plant OU.

5.2.1 Stabilization and Solidification (S/S)

S/S is potentially applicable, either in-situ or ex-situ, to areas with metals and radionuclides (but without P4 contamination) although would not likely be effective at addressing gamma. S/S might also be potentially applicable ex-situ to small volumes of shallow soils with low P4 impacts, e.g., soils around P4 piping that may have leaked, although likely not for the piping itself. S/S is likely not applicable for in-situ application for P4-impacted soils due to the inability to control mixing and reaction in variable P4 concentrations within the soils, similar to the experience at Tarpon Springs.

5.2.2 Mechanical Aeration

While aeration has been used successfully applied at a site where relatively shallow, low-concentration P4 exists in soils (Eagle River Flats), in-situ aeration or mechanical aeration is likely not applicable for P4-impacted soils at the FMC Plant OU due to the inherent safety risks of controlling P4 burning and gas generation rates in soils with highly, locally variable levels of P4 impact. Also, ex-situ mechanical aeration is likely not applicable due to lack of performance testing: even if excavation, feed material sizing, and blending challenges were overcome, alternative technologies have been identified as potentially more effective means to reduce P4 mobility and toxicity. Mechanical aeration also does not address radionuclides and metals and would require combination with other remedial technologies to address all co-located COCs.

5.2.3 Caustic Hydrolysis

Caustic hydrolysis is likely not applicable for in-situ application due to the inherent safety risks of controlling P4 burning and gas generation rates in soils with highly, locally variable levels of P4 impact. It may be applicable for ex-situ treatment of shallow P4 impacted soils where P4 concentrations are generally < 2 % in a matrix without significant amounts of larger particles (e.g., slag). Those parameters are necessary to provide some assurance of overcoming feed material sizing and blending challenges, above and beyond the excavation challenges that also would have to be met. To the extent that RU 13, 22b and 22c contain some portions of P4-impacted soils that meet these parameters, caustic hydrolysis, in combination with other technology (treatment or containment) for the generally much larger portion of those RUs where this technology would not be applicable, may warrant further evaluation. EPA (2003) indicates that caustic hydrolysis may convert some heavy metals present in process feed material (from site soils) to metal oxides and hydroxides. These metal oxides and hydroxides may not require additional treatment, although further testing would be required in this regard. The fate of radionuclides in the caustic hydrolysis process would also have to be determined.

5.2.4 Chemical Oxidation

Chemical oxidation is likely not applicable for in-situ application for P4-impacted soils due to the inherent safety risks of controlling gas generation rates in soils with highly, locally variable

levels of P4 impact. Chemical oxidation is also likely not applicable for ex-situ application due to lack of performance testing. This means that even if excavation, feed material sizing, and blending challenges were overcome, alternative technologies are potentially more effective in reducing P4 mobility and toxicity.

5.2.5 Incineration

Incineration is an ex-situ treatment technology only. Use of off-site incineration is potentially applicable to small volumes of shallow soils with low P4 impacts, e.g., soils around P4 piping that may have leaked. Off-site incineration is likely not applicable for large volumes due to transportation risks inherent with the total number of truck loads required and the packaging requirements (containers of 55 gallons or less). On-site incineration is likely not applicable due to the inability to treat other co-located COCs. Even if excavation, feed material sizing, and blending challenges were overcome, alternative technologies have been identified as potentially more effective means to reduce P4 mobility and toxicity as well as metals and radionuclides. On-site incineration also is likely not applicable due to the stringent permit design, environmental evaluation and operational requirements that would have to be met.

5.2.6 Thermal Desorption

Thermal desorption is an ex-situ treatment technology that is similar to incineration, but the treatment temperatures are much lower. Unlike offsite incineration, there are no known commercial offsite thermal desorption systems in operation so the system would have to be built on-site. Use of thermal desorption is potentially applicable to small volumes of shallow soils with low to moderate P4 impacts, e.g., soils around P4 piping that may have leaked. Thermal desorption is likely not applicable due to the inability to treat other co-located COCs (i.e., metal and radionuclides). Alternate technologies have been identified as potentially more effective means to reduce P4 mobility and toxicity as well as metals and radionuclides, again assuming that excavation, feed material sizing, and blending challenges could be overcome.

Table 5-1

Summary of Elemental Phosphorus Treatment Process Options

ELEMENTAL PHOSPHORUS TREATMENT TECHNOLOGIES - SOILS AND SOLIDS

Process Option	Process Description	Limitations	Safety During RA		History of Technology Field Use for P4 Contaminated Soils/Solids?
			Remedial Site Worker	Public	
Removal Process Options					
Conventional Excavation	Excavation of contaminated soils using conventional earthworking equipment sized appropriately for the volume of material to be removed. Conventional excavation would be used to excavate the contaminated soil and transfer to other material handling steps prior to delivery to the treatment technology (process). With careful operation, soils containing phosphorus might be transferred with a water cover in the bucket to minimize mass burning, but there likely will be some level of smoking or fires from unintended, occasional spills or material above the water cover. Excess water in the excavation could result in mobilization of other COCs and potential groundwater impacts. Judicious water use may be better managed in small areas; risk of fire and/or excess water in the excavation would increase with the size of excavation area. Excavation might be combined with an enclosed temporary structure to minimize uncontrolled release of P4 combustion products and exposure to other site workers or the public, but would also include air pollution control device for vented air and treatment and/or disposal of APC media.	<ul style="list-style-type: none"> Depth of excavation, no greater than 15 feet below ground surface (bgs) Handling of P4 soils would require addition of water to prevent combustion or temporary cover to capture phosphorus combustion offgases Scrubber sludges would likely require treatment prior to disposal PPE would require aluminum suit and possibly supplied air to prevent exposure to burning P4 (modified Level A) 	Moderate to high hazard associated with excavating and handling P4 in widely varying concentrations in the subsurface as of result of potential direct exposure (burns) and exposure to oxidation/reaction products.	Low to moderate hazard associated with removing soils with P4 due to potential release should significant oxidation occur.	During the construction of the LDR system, a small quantity of P4-contaminated soils were encountered. The P4-containing soils were excavated, containerized, and disposed off-site at an incinerator (the total quantity of excavated soil was less than 20 55-gallon drums).
Wet Dredging	Using a conventional dredge, wet materials would be excavated. Since the material is semi solid, it must be chopped up or melted into a slurry to allow pumping through a pipeline to the treatment process. For this process, solids are removed from the slurry with a complex treatment system, and the water is returned to the excavation site for reuse. This process was used by FMC in former phosphorus-laden ponds (i.e., phossey ponds). However, none of these semi-liquid phosphorus-bearing wastes remain at the site, and this process would require introduction of a significant volume of water to soils or solids (to create a slurry) that could result in mobilization of other COCs and potential groundwater impacts.	<ul style="list-style-type: none"> Only dry P4 soils exist at the FMC Plant OU, would have to be flooded before process could work Free water might transport soil COCs to the underlying groundwater 	Low to moderate hazard during wet dredging and material handling of slurried soils/solids with widely varying P4 concentrations in the subsurface due to potential direct exposure (burns) and exposure to oxidation/reaction products.	Low to moderate hazard associated with removing soils with P4 due to potential release should significant oxidation occur.	Yes. Wet dredging has been used in the past at the FMC facility to remove P4 contaminated sludges in active phossey ponds (during plant operations). However, none of these semi-liquid phosphorus-bearing wastes remain at the site and for this process to work water would have to be added to the ground surface without protection of the underlying groundwater. Note wet dredging has not been used at any P4 remediation sites to excavate dry materials.
Ex-Situ Treatment					
All ex-situ technologies would require the excavation or dredging of soil/solids and material handling steps: 1) transport within the site and 2) on-site storage. On-site ex-situ treatment technologies would also require the material handling steps: 1) sizing and blending of soil/solids to provide a uniform feed to the treatment process and 2) disposal of treated solids. Off-site ex-situ treatment (incineration) would also require the material handling steps: 1) containerization (and potentially sizing to enable containerization) and 2) off-site transport.					
Stabilization/Solidification	Stabilization involves the addition of a cementitious material that reacts with the contaminated soils to reduce the mobility of the contaminants. It is widely used for wastes containing metals prior to landfilling and in some cases Type C fly ash is used to replace or supplement Portland cement. The types of stabilization agents used depend on the chemical composition of the material being stabilized. Stabilization and solidification has been shown to be effective for reducing the leachability of heavy metals, however, its effectiveness for treating elemental phosphorus containing wastes and potential for unintended reactions during the curing process is not well understood.	<ul style="list-style-type: none"> Generally not applicable for soil depth over 15 feet Generally not applicable for large volumes such as in RUs 1, 2, 13, or 22b Very complex complete treatment sequence P4 associated with UG Piping could not easily be processed using S/S and Significant variation in soil particle size and P4 concentration as found in most RUs would make the ex-situ handling process extremely complex. 	Moderate to high hazard associated with excavating and handling P4 in widely varying concentrations in the subsurface as of result of potential direct exposure (burns) and exposure to oxidation/reaction products. For ex situ treatment, handling necessary for feed material sizing and blending of spontaneously combustible material increases these risks.	Low to moderate hazard associated with removing soils with P4 due to potential release should significant oxidation occur.	No. There is no history of laboratory or field testing has been identified for ex-situ S/S.
Mechanical Aeration	Mechanical aeration involves the use of physical equipment, such as a mixer to agitate a solid or slurry material and expose the material to the atmosphere where ambient oxygen would react with the elemental phosphorus contained in the solid matrix. The United States Army Corps. Of Engineers (USACE) indicated that a mechanical aeration system could be used ex-situ or in-situ to expose elemental phosphorus to oxygen. However, further studies would be required to determine how the degradation of elemental phosphorus is effected by concentrations of dissolved oxygen, mixing rate, matrix characteristics, depth of material, temperature, and pH.	<ul style="list-style-type: none"> Generally not applicable for soil depth over 15 feet; Generally not applicable for large volumes such as in RUs 1, 2, 13, or 22b; Difficult to control of P4 reactions because of widely varying P4 concentrations. Very complex complete treatment sequence (ex-situ); and Significant variation in soil particle size and P4 concentration as found in most RUs containing P4 would make the ex-situ handling process extremely complex and difficult to operate and maintain. Would not treat metals and radionuclides that are present in the P4-contaminated soils 	Moderate to high hazard associated with excavating and handling P4 in widely varying concentrations in the subsurface as of result of potential direct exposure (burns) and exposure to oxidation/reaction products. For ex situ treatment, handling necessary for feed material sizing and blending of spontaneously combustible material increases these risks.	Low to moderate hazard associated with removing soils with P4 due to potential release should significant oxidation occur.	No. Has only been implemented in bench-scale studies. System has not been identified to effectively oxidize large amounts of soils with P4.

Table 5-1

Summary of Elemental Phosphorus Treatment Process Options

<p>Caustic Hydrolysis</p>	<p>Caustic Hydrolysis is a chemical process where P4 reacts with lime and water at elevated temperature and pressure to form various phosphate compounds, as well as phosphine. This technology uses complex processing equipment operated by personnel with a relatively higher level of training. Key operating parameters include the amount of lime and water added, reaction pH, as well as the reactor temperature and pressure. Caustic hydrolysis would reduce the concentration of P4 and results in the generation of significant amounts of phosphine gas as a by-product that would require subsequent treatment. This technology would not be appropriate for metals or radionuclides.</p>	<ul style="list-style-type: none"> • Generally not applicable for soil depth over 15 feet. • Very complex complete treatment sequence including all the ancillary treatment processes; • Difficult to supply consistent (size and concentration) P4 feed stream and therefore control P4 reactions. • Significant variation in soil particle size and P4 concentration as found in most RUs containing P4 would make the handling process extremely complex. • Requires additional treatment for radionuclides at a minimum, but possibly the metal oxides and hydroxides 	<p>Moderate to high hazard associated with excavating and handling P4 in widely varying concentrations in the subsurface as of result of potential direct exposure (burns) and exposure to oxidation/reaction products. For ex situ treatment, handling necessary for feed material sizing and blending of spontaneously combustible material increases these risks.</p>	<p>Low to moderate hazard associated with removing soils with P4 due to potential release should significant oxidation occur.</p>	<p>No, but has been used on slurried P4 production wastes. FMC used lime (caustic hydrolysis) treatment of precipitator slurry in the "slurry pots" during plant operation. Lime was used to treat a slurried process waste with low concentrations of P4 at GSHI facility in Columbia, TN. High concentrations of P4 have not been treated using this process. The LDR system formerly located at the FMC facility required a feed of slurried fine-grained process waste with low percentage of P4. The LDR systems was not completed; however it was not designed to handle feeds of varying P4 concentrations or high concentrations of P4. Designed feed rate would require an extremely long treatment time-frame for the amount of soil requiring treatment.</p>
<p>Chemical Oxidation</p>	<p>Chemical oxidation involves the addition of chemical agents to react with COCs in the soil to form oxidized by-products. Several types of ex-situ oxidation technologies have been identified to treat elemental phosphorus including nitric/sulfuric acid and oxygen (using high speed air dispersion (HSAD) process). The acid oxidation technology was developed and tested by the Tennessee Valley Authority (TVA) on sludge containing elemental phosphorus. The effluent from this process was then reacted with ammonia to produce a nitrogen and phosphate containing plant nutrient. Not effective for metals and rads, limited effectiveness for P4.</p>	<ul style="list-style-type: none"> • Generally not applicable for soil depth over 15 feet • Very complex complete treatment sequence ; • Generally not applicable for large volumes such as in RUs 1, 2, 13, or 22b (both ex-situ and in-situ); • Difficult to control P4 reactions (in-situ and ex-situ) because of widely varying P4 concentrations; • Significant variation in soil particle size and P4 concentration as found in most RUs would make the process extremely complex and difficult to operate and maintain. • Does not treat metals and radionuclides associated with P4-contaminated soils and some processes even concentrate metals in the reactor sludges • Generation of phosphorus related gases that need to be treated and sludges disposed. • Liquid and solid process streams would need secondary treatment prior to disposal. 	<p>Moderate to high hazard associated with excavating and handling P4 in widely varying concentrations in the subsurface as of result of potential direct exposure (burns) and exposure to oxidation/reaction products. For ex situ treatment, handling necessary for feed material sizing and blending of spontaneously combustible material increases these risks.</p>	<p>Low to moderate hazard associated with removing soils with P4 due to potential release should significant oxidation occur.</p>	<p>No. However, it has been testing in the laboratory. Two types of ex-situ oxidation technologies have been identified to treat P4 including nitric/sulfuric acid and oxygen, using high speed air dispersion (HSAD) process. FMC and TVA have conducted tests in the laboratory using these processes with P4 sludge. Acid oxidation technology was developed by the TVA on sludge containing P4. However, homogenous application of chemical oxidation agents at the FMC plant OU may be extremely difficult in-situ due to the varying concentrations of P4 in the soil and the heterogeneous nature of the subsurface soil matrix.</p>
<p>Incineration</p>	<p>Incineration is a thermal process where soil, sludge and other wastes are treated at elevated temperatures (1,400 to 2200 °F) to volatilize and combust contaminants. Incineration would reduce the concentration of elemental phosphorus and volume in soil. Elemental phosphorus would be oxidized and natural organic matter in the soil would be converted to carbon dioxide. Oxidized elemental phosphorus would be captured by off-gas treatment systems such as scrubbers and treated further or discharged as a by-product. Heavy metals and radionuclides in the soil would not be oxidized and would mainly be concentrated in the residual ash from the incinerator. These ashes would require proper disposal.</p>	<ul style="list-style-type: none"> • Generally not applicable for soil depth over 15 feet; • High energy requirements • Requires obtaining air permit (if conducted on-site). • Does not treat all metals and radionuclides (i.e., they are concentrated in the ash) • Some metals would be volatilized and these metals along with P4 reaction processes would have to be scrubbed from the air leaving the rotary kiln • Can only be shipped in 55 gallon containers for off-site commercial incinerator 	<p>Moderate to high hazard associated with excavating and handling P4 in widely varying concentrations in the subsurface as of result of potential direct exposure (burns) and exposure to oxidation/reaction products. For ex situ treatment, handling necessary for feed material sizing and blending of spontaneously combustible material increases these risks.</p>	<p>Low to moderate hazard associated with removing soils with P4 due to potential release should significant oxidation occur.</p>	<p>Yes. Off-site commercial incinerators are available and can handle widely varying concentrations of P4 but only in (up to 55-gallon) drums. The US Army has constructed and operated a facility at Crane Army Ammunition Activity (CAAA) to convert WP contained within ordnance to phosphoric acid using a rotary kiln furnace. On-site incineration would require construction of an incineration unit with ancillary feed preparation process(es) and air and wastewater treatment systems.</p>
<p>Thermal Desorption</p>	<p>Thermal Desorption is used to treat soil and sludge by heating (directly or indirectly) to volatilize contaminants and separate them from the solid matrix without combustion. The temperatures used in a thermal desorber are lower than in an incinerator, generally on the order of 200 to 600 °F. The volatilized contaminants (vapors) are collected and generally are treated by one or more off-gas treatment technologies. Thermal desorption would reduce the concentrations of P4 through volatilization, and P4 vapors would be recovered by treatment of the off-gas. Thermal desorption would not reduce concentrations of heavy metals or radionuclides in the solids. The solids would require proper disposal with elevated metals and rads.</p>	<ul style="list-style-type: none"> • Generally not applicable for soil depth over 15 feet; • High energy requirements • Might have difficulties treating highly concentrated P4 as might be found in many of the site soils (e.g., explosions); • Requires obtaining air permit; and • Does not treat metals and radionuclides 	<p>Moderate to high hazard associated with excavating and handling P4 in widely varying concentrations in the subsurface as of result of potential direct exposure (burns) and exposure to oxidation/reaction products. For ex situ treatment, handling necessary for feed material sizing and blending of spontaneously combustible material increases these risks.</p>	<p>Low to moderate hazard associated with removing soils with P4 due to potential release should significant oxidation occur.</p>	<p>Yes. Has been used on a limited basis in the field for a small quantity of P4 contaminated soils. A thermal desorption system was used for treatment of WP-contaminated soil in Ogden Utah. However, only 300-tons of material was processed and the concentration of P4 in the wastes was not disclosed.</p>

Table 5-1

Summary of Elemental Phosphorus Treatment Process Options

In-Situ Treatment					
Stabilization/Solidification (S/S)	Stabilization/Solidification is a technology in which cementitious material that reacts with the contaminated soils to reduce the solubility or mobility of the COCs. In-situ stabilization generally involves mechanical mixing of the solids in-place with stabilization agents. Various types of stabilization agents are available, including cement, fly ash, silica, bentonite, and various polymers. The types of stabilization agents used depend on the chemical composition of the material being stabilized.	<ul style="list-style-type: none"> • Generally not applicable for soil depth over 20 feet • Generally not applicable for large volumes such as in RUs 1, 2, 13, or 22b • Difficult to control P4 reactions because of widely varying P4 concentrations; • Difficult to get complete mixing in-situ • In-situ process would require no free water during treatment. Might result in contamination of underlying groundwater. • Liquid and solid process streams (air scrubber) would need secondary treatment prior to disposal. 	Moderate to high hazard during intrusion into and reaction kinetics with soils/solids with widely varying P4 concentrations in the subsurface due to potential exposure to oxidation/reaction products.	Low to moderate risk from potential uncontrolled releases due to exposure to oxidation/reaction products.	No. However, in-situ S/S was chosen at Tarpon Springs, Florida as the remedy for pond material and contaminated soil containing P4, heavy metals, and radionuclides. A brief pilot study at Tarpon Springs indicated that reactions of P4 with S/S additives were extremely violent and resulted in discontinuation of study. S/S has since been removed as remedy at Tarpon Springs and capping is the preferred alternative.
Mechanical Aeration	As described above in Ex-Situ treatment, mechanical aeration involves the use of physical equipment, in this case, such as a tiller to break up or agitate a solid material and expose the material to the atmosphere where ambient oxygen would react with (oxidize) elemental phosphorus contained in the solid matrix. The process would generate P4 oxidation/reaction off-gases during treatment that would need to be collected and treated.	<ul style="list-style-type: none"> • Generally not applicable for soil depth over 20 feet; • Generally not applicable for large volumes such as in RUs 1, 2, 13, or 22b; • Difficult to control of P4 reactions because of widely varying P4 concentrations. • Inadequate/incomplete mixing because of widely varying particle size. • Would not treat metals and radionuclides that are present in the P4-contaminated soils • Liquid and solid process streams (air scrubber) would need secondary treatment prior to disposal. 	Moderate to high hazard during intrusion into and reaction kinetics with soils/solids with widely varying P4 concentrations in the subsurface due to potential exposure to oxidation/reaction products.	Low to moderate risk from potential uncontrolled releases due to exposure to oxidation/reaction products.	No. No system has been identified to effectively oxidize large amounts of soils with P4 in situ. Requires mechanical mixing or aeration equipment to provide continuous supply of ambient air/oxygen to the soils with P4. Aeration of P4 would likely generate hazardous off gases, such as phosphine, during treatment that would require collection and treatment.
Chemical Oxidation	Oxidation involves the addition of chemical agents through subsurface injection points to react oxidant with COCs in the soil to form oxidized by-products. Can be used with organics, but typically not used for inorganics.	<ul style="list-style-type: none"> • Generally not applicable for soil depth over 20 feet • Very complex complete treatment sequence ; • Generally not applicable for large volumes such as in RUs 1, 2, 13, or 22b; • Difficult to control P4 reactions (in-situ and ex-situ) because of widely varying P4 concentrations; • In-situ process would require no free liquids during processing. Might result in contamination of underlying groundwater. • Significant variation in soil particle size and P4 concentration as found in most RUs would make the process extremely complex and difficult to operate and maintain. • Generation of phosphorus related gases that need to be treated and sludges disposed. • Liquid and solid process streams (air scrubber) would need secondary treatment prior to disposal. 	Moderate to high hazard during intrusion into and reaction kinetics with soils/solids with widely varying P4 concentrations in the subsurface due to potential exposure to oxidation/reaction products.	Low to moderate risk from potential uncontrolled releases due to exposure to oxidation/reaction products.	No. Has only been implemented in bench-scale studies. No history of treatability studies on other sites containing P4 in soils. System has not been identified to effectively oxidize large amounts of soils with P4. Homogenous application of chemical oxidation agents at the FMC plant OU may be extremely difficult in-situ due to the varying concentrations of elemental phosphorus in the soil and the heterogeneous nature of the subsurface

ELEMENTAL PHOSPHORUS TREATMENT TECHNOLOGIES - GROUNDWATER

Process Option	Process Description	Limitations	Safety During RA		History of Technology Field Use for P4 Contaminated Groundwater?
			Remedial Site Worker	Public	

Ex-Situ Treatment

All ex-situ technologies require additional process steps including groundwater extraction (pumping), either for hydraulic control or for mass removal, storage prior to and potentially post treatment, and use/disposal of the treated water.

Oxidation	Oxidation involves the addition of chemical oxidants, ultraviolet light (UV), ozonation and/or mechanical addition of oxygen (O3, O2 or air) to the aqueous solutions to promote oxidation of reduced inorganic elements or to create an oxidizing reaction with organic compounds.	Oxidation would not be effective for removal of other groundwater COCs.	Low to moderate hazard due to potential exposure to subsurface soils during installation of extraction wells. Low to moderate during system construction and O&M.	Low	No information was found specific to the testing or application of oxidation technologies on relatively low concentrations of dissolved P4 in water. Based on the literature and research into the fate of P4 in aqueous systems, oxidation would be expected to be effective for accelerating the natural oxidation of P4 in water and conversion of the P4 to oxidized phosphorus compounds (e.g., orthophosphate).
Hydrolysis	Hydrolysis generally involves the addition of a strong acid or base as a catalyst to increase the hydrolysis reaction rate in aqueous solutions.	Hydrolysis would not be effective for removal of other groundwater COCs.	Low to moderate hazard due to potential exposure to subsurface soils during installation of extraction wells. Low to moderate during system construction and O&M.	Low	No information was found specific to the testing or application of hydrolysis technologies on relatively low concentrations of dissolved P4 in water. Based on the literature and research into the fate of P4 in aqueous systems, chemical-catalyzed hydrolysis would be expected to be effective for accelerating the natural hydrolysis of P4 in water.

Table 5-1

Summary of Elemental Phosphorus Treatment Process Options

Reverse Osmosis	Reverse osmosis is physical treatment process in which pressurized water passes through a semi-permeable membrane. The applied pressure to the waste stream is greater than the osmotic pressure of the feedwater. As water passes through the membrane, dissolved constituents in the water are concentrated on the feed side of the membrane to form the waste brine and a purer, more dilute product water is formed on the permeate side of the membrane.	Reverse osmosis produces a concentrated brine stream that would likely require further treatment prior to disposal. In addition, reverse osmosis has high energy requirements making it much more costly than other effective ex-situ treatment technologies.	Low to moderate hazard due to potential exposure to subsurface soils during installation of extraction wells. Low to moderate during system construction and O&M.	Low	No information was found specific to the testing or application of reverse osmosis on relatively low concentrations of dissolved P4 in water.
In-Situ Treatment					
Oxidation	Oxidation involves the injection of chemical oxidants and/or mechanical addition of oxygen (O3, O2 or air) to groundwater to promote oxidation of reduced inorganic elements or to create an oxidizing reaction with organic compounds.	Oxidation would not be effective for removal of other groundwater COCs and adequate delivery and mixing of the oxidant into groundwater could be difficult to implement.	Low to moderate hazard due to potential exposure to subsurface soils during installation of injection wells. Low to moderate during system construction and O&M.	Low	No information was found specific to the testing or application of oxidation technologies on relatively low concentrations of dissolved P4 in water. Based on the literature and research into the fate of P4 in aqueous systems, oxidation would be expected to be effective for accelerating the natural oxidation of P4 in water and conversion of the P4 to oxidized phosphorus compounds (e.g., orthophosphate).
Hydrolysis	Hydrolysis involves the injection of a strong acid or base as a catalyst to increase the hydrolysis reaction rate in groundwater.	Hydrolysis would not be effective for removal of other groundwater COCs; adequate delivery and mixing of the acid/base catalyst into groundwater could be difficult to implement and would have the negative effect of adding salts (TDS) to the groundwater system.	Low to moderate hazard due to potential exposure to subsurface soils during installation of injection wells. Low to moderate during system construction and O&M.	Low	No information was found specific to the testing or application of hydrolysis technologies on relatively low concentrations of dissolved P4 in water. Based on the literature and research into the fate of P4 in aqueous systems, chemical-catalyzed hydrolysis would be expected to be effective for accelerating the natural hydrolysis of P4 in water.

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