

FUNDAMENTAL STUDY ON THE RECOVERY AND REMOVAL OF WHITE PHOSPHORUS FROM PHOSPHORUS SLUDGE

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Abstract : Electro-thermal production of white phosphorus(WP, P₄) generates substantial amount of highly toxic phosphy water and sludges. Because of their high phosphorus contents and lack of reliable processing technology, large tonnages of these hazardous wastes have accumulated from current and past operations in the United States. In this study, two different methods for treatment of phosphorus sludge were investigated. These were bulk removal of WP by physical separation(froth flotation) and transformation of WP to oxyphosphorus compounds by air oxidation in the sludge medium. Kerosene, among other collectors, resulted in selective flotation of WP from the associated mineral gangue. Solvent action of kerosene occurring on the WP surface(by rendering WP particles hydrophobic) might produce the high selectivity of WP. The WP recovery in the froth was 79.3% from a sludge assaying 34.2% of WP. In the oxidation study, air gas was dispersed in the sludge medium by the rapid rotation of the impeller blades. The high level of sludge agitation intensity caused a fast completion of the oxidation reactions and it resulted in the high percentage conversion of WP to PO₄³⁻ with PO₃³⁻ making up almost all portion of oxyphosphorus compounds. The WP analysis on the treated sludge showed that supernatant solution and solid residue contained an average of 4.2 μg/L and 143 ppm respectively from the sludge containing about 26 g of WP. Further investigation will be required on operational factors to better understand the processes and achieve an optimum condition.

Key Words : white phosphorus, froth flotation, hydrophobicity, wet oxidation, oxyphosphorus compound

INTRODUCTION

White phosphorus(WP, P₄) is produced by the electro-thermal reduction of phosphate rock with the presence of silica and coke. It is produced in the gaseous form which is, in turn, condensed and collected under water as common WP. The process results in the production of a significant quantity of contaminated wastewater and sludge due to the strong bondage of impurities to the phosphorus particles during the condensation process. The wastewater, commonly termed "phosphy

water" consists essentially of dissolved phosphorus, colloidal particles of phosphorus, and suspended particulates. The waste sludge, referred to as "phosphorus sludge," consists of phosphorus particles, solid impurities, and water. Exposure of WP to the atmosphere poses serious fire hazard and constitutes a potential air pollution because of its spontaneous ignition (@ 30°C) and formation of voluminous fumes of acidic oxides, primarily phosphorus pentoxide (P₂O₅). Although WP has a low solubility of about 3 ppm in water, it has been reported that WP contaminated water severely affects human and aquatic lives at concentrations below its solubility limit.^{1,2)}

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For each ton of phosphorus produced, the process generates about 5 tons of water and phosphorus sludge wastes. In the absence of reliable treatment technology to recover or remove WP from the waste stream, these sludges have been stored in specially lined ponds, containment vessels, or rail cars. Information regarding the removal of WP from phosphy water and phosphorus sludge is rather limited. Most of these processes focused on separation or oxidation of colloidal WP in phosphy water effluents to reduce its concentration.³⁻⁵⁾ Other process techniques include solid/liquid separation to recover coarse-sized WP particles for recycling^{6,7)} and in-situ contaminated site remediation.⁸⁾

The objectives of this study were to investigate processes for the recovery and removal of WP from electric-furnace sludge which hopefully render the WP sludge non-hazardous. The first method was a froth flotation technique, which had been commonly used in mineral processing industry. This technique separates minerals from waste mineral or solids of different kinds by agitating the pulverized mixture of solids with water and/or flotation reagents such as frother, collector, and surface modifier. In the process, surface of mineral particles to be recovered render hydrophobicity and the particles are separated from the liquid body by the floating air bubbles. Based on the experience in flotation separation of naturally hydrophobic elements (such as sulfur, coal and graphite), it was assumed that the covalently-bonded WP should be equally hydrophobic. The second was wet-oxidation of WP with finely dispersed air in sludge medium. The process was based on fast oxidation and conversion of insoluble WP to highly soluble oxyphosphorus compounds.

EXPERIMENTAL

Sample Preparation

The phosphorus sludge sample was obtained from Food Machine Cooperation(FMC) in Pocatello, Idaho. The as-received sludge was a mixture of relatively fine and sand like coarse-

sized particles. The pH of the sludge was about 6, indicating that it was partially neutralized prior to disposal. The as-received sludge was wet-screened at 48 mesh(300 μm) to separate the over-sized trash material. The minus 48 mesh material, representing about 98% by weight of the sample, was thoroughly mixed by agitation with the minimum contact of air. Representative split samples, weighing 180 g, were collected from the suspended solids while the sludge was mixed continuously.

EXPERIMENTAL PROCEDURE

Froth Flotation

Three different types of collectors - oleic acid, n-alkylamine, and kerosene - were tested using a conventional mechanical flotation cell to selectively float WP from the sludge. Representative samples of -48 mesh were pulped in a 1.5 L Denver flotation cell and conditioned with the collector(2% by weight of dry feed). After conditioning, the pulp was diluted to about 6% solids prior to flotation, which was conducted using nitrogen as the carrier gas to collect a WP-rich froth. The flotation was conducted at an impeller speed of 1,000 rpm for 2 minutes of conditioning and flotation. The floated(froth) and un-floated material(cell product) were weighed in dry basis and analyzed for WP to determine the selectivity of collectors. No frother was used, and there were no cleaning or scavenging stages.

Wet Oxidation

A schematic diagram of the laboratory-scale phosphorus sludge treatment setup is shown in Figure 1. A representative sludge sample(180 g) was introduced in the column reactor and diluted to a total volume of one liter. The diluted sludge was agitated at 4,000 rpm and it was held constant throughout the test. Air regulated at 2 liter per minute was fed into a column reactor through a flow controller. The air was dispersed in the sludge medium by the rapid rotation of the blades. The oxygen in the dispersed air reacted fast with WP in the

high-shear agitation zone of the reactor. The phosphorus oxides were converted rapidly to phosphorus oxyacids by hydrolysis. Some of the phosphorus oxides fumes released at the surface of the slurry were drawn off from the reactor. The off-gas fume was scrubbed with potassium hydroxide in a gas scrubber. Measurements of the pulp pH and temperature were made at regular time intervals. Samples of about 10 mL were collected from the agitation zone during the progress of oxidation. The collected samples were subjected to centrifugation to analyze anionic species and WP contents in the supernatant and solid phase.

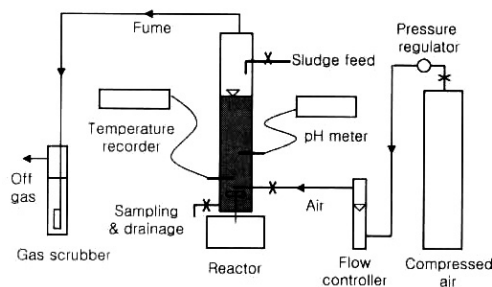


Figure 1. Schematic Diagram of Phosphorus Sludge Treatment Set-up.

Analytical Methods of WP and Oxyphosphorus Compounds

Since white phosphorus is spontaneously flammable and self-ignitable in contact with air, a weighed sludge sample was extracted with hot refluxing toluene to dissolve the phosphorus. The extracted WP was then determined quantitatively by using a HP 5890 gas chromatography equipped with a nitrogen-phosphorus detector (NPD). Details of the analytical procedure were reported elsewhere.^{9,10)} For the WP analysis of phosphy water, WP was extracted with toluene by vigorous shaking for 30 minutes in an air-tight bottle. The toluene extract then was analyzed using gas chromatography. Oxyphosphorus ionic species produced during oxidation of the WP were determined by using a Dionex 4500i ion chromatography.

RESULTS AND DISCUSSIONS

Properties of Phosphorus Sludge

Five representative sludge samples were randomly chosen to determine the WP and solid content. The analysis showed that the WP content ranged from 34.2~34.8% on a dry basis and the percent solids in the sludge was 41.7. The granulometric analysis were performed by further wet-screening -48mesh sample at 200 and 400 meshes to determine the size distribution and WP content of each size fraction. The data in Table 1 showed that a wet screening of the sludge produced WP rich coarse fractions of about 76.98% and 79.0% WP at particle size of 48 x 200 and 200 x 400 mesh, respectively. The minus 400 mesh fine fraction analyzed about 18.8% WP with a weight recovery of 73.5%. The corresponding WP distributions are 21.6% 48 x 200 mesh, 38.4% in 200 x 400 mesh, and 40.0% in the -400 mesh fines.

A quantitative analysis of the non-phosphorus sludge residue was performed to determine primarily the inorganic constituents of the sludge. The results showed that the major constituents of the solid residue were phosphate(31.58%), calcium(13.51%), zinc(10.26%), and acid insolubles (24.54%) which included silica.

An X-ray diffraction analysis was performed on the WP extractable sludge residue, and a qualitative analysis indicates that major mineral constituents of the non-phosphorus residue are fluorapatite($\text{Ca}_5(\text{PO}_4)_3\text{F}$), fluorite(CaF_2), sphalerite (ZnS), quartz(SiO_2) and cole(C).

Table 1. Granulometric WP analysis of the aludge

Size Fraction mesh	Weight gram	Weight %	Analysis %, WP	Distribution %, WP
48 x 200	7.3	9.7	76.9	21.6
200 x 400	12.6	16.8	79.0	38.4
-400	55.2	73.5	16.8	40.0
Composite	75.1	100.0	34.6	100.0

Froth Flotation

Table 2 is the result of the WP recovery for different collector types. The froth products using oleic acid and n-alkylamine were lower in WP than the cell product and the selectivity of

separation was incomplete indicating that the surface of the WP was more hydrophilic than hydrophobic. Based on the very limited information about the surface properties of WP, it was expected to be naturally hydrophobic and floatable like other covalently-bonded elements such as sulfur and carbon (graphic, coal). However, as shown in Table, the floatability of WP by common anionic collector(oleic acid) was poor. The poor floatability of WP might be related to a high polarity of its negatively-charged surface. The cationic flotation of WP by reagents(such as long chain K-amylxanthate) was possible, but the separation was poor due to co-flotation of inert minerals along with the WP in the sludge. Unlike carbon or sulfur, WP is highly unstable under ambient conditions. It reacts with dissolved oxygen in the pulp to produce high concentrations of oxy-phosphorous ionic species at the WP/water interface. This might cause the formation of a highly-structured water layer around the particles.

On the other hand, kerosene resulted in selective flotation of WP from the associated mineral gangue. The data show that the WP-rich froth(containing about 85% WP) was produced at a WP recovery rate of 79.3% from a sludge assaying 34.2% WP. The choice of hydrocarbon oil (for use in rendering the WP surface hydrophobic) was based on the fact that WP was significantly more soluble in mineral oils (>14,500 ppm) than in water (<3.3 ppm).¹¹⁾ Thus, the high selectivity to their compatibility

and strong affinity of WP toward mineral oils might be related to their compatability and to solvent action occurring on the phosphorous surface. The use of other hydrocarbon solvents (such as toluene or xylene) may also give good results. However, kerosene appeared to be the most cost effective. More detailed experiment was required on the factors affecting the flotation process - collector type and dose, pulp pH and solid content - to optimize the operation.

Oxidation Studies

The Flotation of WP from the sludge(with kerosene) recovered considerable amount of WP as high grade concentrates suitable for recycling. Although the cell product was relatively low in WP, their contents were still inadequate for safe environmental disposal. The possible reason for not achieving complete flotation of WP was the untrapped particulates form an emulsion with WP during condensation of WP, which made for some WP particles unable to contact with kerosene.

Therefore, in this part of the investigation, efforts were made to develop a method for removal of colloidal WP contaminants by oxidation. When air was injected and dispersed in the reactor by mechanical agitation, white fumes started to appear at the sludge surface. The evolution of the fumes became intensive with the progress of reaction. The termination of the oxidation reaction was accompanied by a decrease of the white fumes, which ceased

Table 2. Flotation response of phosphorus sludge for different collector types

Collector Type	Product	Weight %	WP analysis %	WP distribution %
Oleic acid	Froth	64.9	20.2	37.9
	Cell product	35.9	58.3	62.1
	Composite	100.0	34.6	100.0
n-alkylamine	Froth	54.9	25.8	41.1
	Cell product	45.1	44.9	58.9
	Composite	100.0	34.4	100.0
Kerosene	Froth	31.9	85.0	79.3
	Cell product	68.1	10.4	20.7
	Composite	100.0	34.2	100.0

completely at the end of the experiment.

In the process of oxidation, WP reacted with dissolved oxygen to produce various oxides which were hydrolyzed subsequently in the sludge medium. The major compounds formed during oxidation were PO_4^{3-} and PO_3^{3-} . Trace amount of PO_2^{3-} was also detected in the solution. Figure 2 shows the rate of PO_4^{3-} and PO_3^{3-} ion formation during oxidation. The reaction kinetic curves show an initial slow reaction region followed by a fast oxidation region in which the PO_4^{3-} and PO_3^{3-} forming increased linearly with time to reach limiting values in the plateau region after the fast reaction. The initial slow reaction region indicates the presence of an initial mass transfer reaction which depends, among other factors, on the kinetic energy provided to the system, oxygen dissolution in the aqueous phase, temperature, and the reactive surface area at the solid-liquid-gas interfaces. The existence of two parallel reactions for PO_4^{3-} and PO_3^{3-} indicate that major reactions occurring in the system seemed to be greatly dependent on the concentration of dissolved oxygen as shown in the following series of reactions.

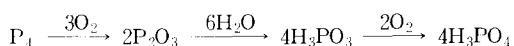
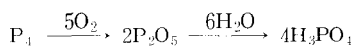


Figure 3 shows the sludge temperature and pH as a function of time. The data show that the pulp temperature increases steadily with agitation time to reach maximum values in the region of termination of the fast oxidation reaction then declines in the plateau region (see figure 2). The rising parts of the curves shows a change in the slope (break point) when the pulp temperature approaches a critical value of about 44°C (melting point of WP). This occurs after 90 minutes of agitation. The time to reach the critical temperature was found to correspond to that required for initiation of the fast oxidation. Thus, at higher temperature the solid WP particles in the sludge were transformed to the

more disordered liquid state and become highly dispersed in the aqueous medium. This results in a higher contact area with dissolved oxygen and acceleration of the oxidation reaction.

Oxidation of WP and subsequent hydrolysis of oxophosphorus compounds were the major source for the decrease in pH of the sludge. The initial sludge pH of 6 decrease to a limiting value of about 1.7. Figure shows a fast drop of pH, which corresponds to the fast formation of phosphoric acid.

The separated solid and liquid products were analyzed for residual WP. The result of WP analysis in solid residue and supernatant solution revealed that there was no WP detected in the off-gas scrubber solution tested. Extremely low concentration of $4.2 \mu\text{g/L}$ was detected in the supernatant solution, indicating complete oxidation of all dissolved or dispersed colloidal phosphorus in the solutions. On the other hand, relatively high residual WP of 143 ppm, was detected in the residue. This amount of residual WP appears not to be accessible to oxidation due to encapsulation or absorption in the clay or other solid particles. The chemical analysis of solid residue and supernatant solution of treated and untreated sludge are summarized in table 3.

Further studies are needed to better understand the mechanisms and factors controlling the oxidation of WP. These may include oxygen content in the dispersed gas, agitation intensity, initial reaction temperature, sludge pH, and solid content etc.

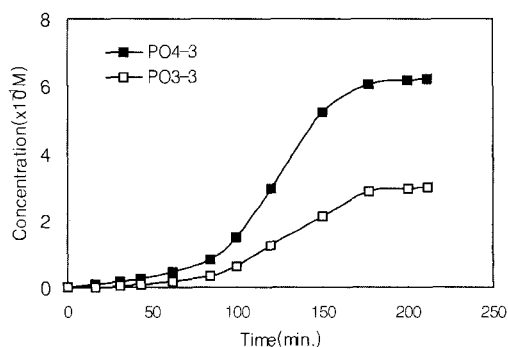


Figure 2. Formation of PO_4^{3-} and PO_3^{3-} During Air Oxidation.

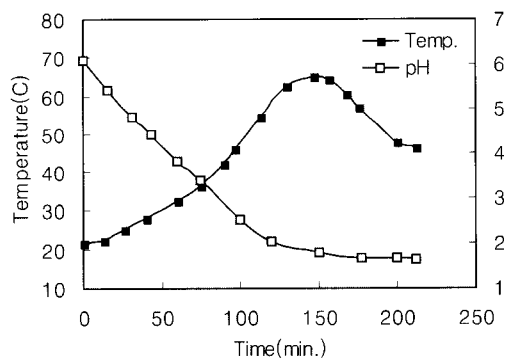


Figure 3. Change of Sludge Temperature and pH During Air Oxidation.

Table 3. Chemical analysis of toluene-extracted residue and supernatant solution

Constituent	Toluene-extracted Residue Wt. %	Supernatant mg/L
Aluminum	2.50	ND
Arsenic	0.06	4.60
Carbon	2.49	ND
Cadmium	0.73	0.13
Calcium	13.51	61.00
Chloride	0.97	1485.00
Chromium	0.04	0.04
Copper	0.03	0.09
Fluoride	0.81	578.00
Iron	0.75	2.23
Hydrogen	0.93	—
Lead	0.11	0.30
Nitrogen	0.22	—
Magnesium	0.58	28.50
Phosphate	31.58	2961.00
Potassium	4.50	5740.00
Selenium	ND	ND
Sulfate	—	240.20
Sulphur, total	3.09	—
Zinc	10.26	7.60
Acid Insolubles	24.54	—
Phosphorus	143*	4.2**

ND: not detected, *: ppm, **: $\mu\text{g/L}$

CONCLUSIONS

Based on the results obtained in this investigation, the following conclusion can be made:

1. In the separation of WP from other sludge constituents, anionic and cationic collectors tested were poorly selective. Selectivity in direct flotation of WP from the electric

furnace sludge was achieved with minimal quantities of kerosene as the WP collector. Selectivity may be attributed to WP being significantly more soluble in mineral oils than in water, thereby enabling kerosene to "solution coat" WP particles in preference to other sludge constituents.

2. Oxidation kinetics studies showed that the process involved three major reactions: initial slow reaction, fast oxidation, and final slow reaction. The initial slow reaction was a mass transfer controlled reaction with an induction period representing the energy barrier for reaching the transition state of the reaction. The fast oxidation reaction was achieved after reaching the melting point of WP. In the fast oxidation region, PO_4^{3-} and PO_3^{3-} formation increased linearly with time indicating the presence of zero-order reaction. Another slow reaction occurred in the plateau region after termination of the fast oxidation reaction.
3. Oxidation of WP and subsequent hydrolysis of oxyphosphorus compounds were the major source for the decrease in pH of the sludge.
4. Test showed an increase in sludge temperature during treatment. This indicated that the oxidation reactions were exothermic. The temperature profiles showed a break in the temperature rise at the initiation of the fast oxidation reaction at a critical temperature corresponding to the melting point of WP.
5. The WP analysis demonstrated that practically 100% of the WP removal was accomplished from the sludge by dispersed air oxidation. Treatment of sludge containing about 26g/L of WP produced a WP analysis 4.2 $\mu\text{g/L}$ in the supernatant solution of treated sludge and 143 ppm in the solid residue.

REFERENCES

1. Davidson, K. A., Hovtter, P. S., and Sigmon, C. F., Water quality criteria for white phosphorus, Oak Ridge National Laboratory, Final Report ORNL-6336. DE88-000645, NTIS ADA186613, (1987).

2. U. S. EPA, Summary review of health effects associated with elemental and inorganic phosphorus compounds: Health issue assessment. EPA 500/89/072. Washington, D> C.: Office of Health and Environmental Assessment, U.S. Environmental Protection Agency. (1989).
3. Campbell, D. L., Oxidation of phossey water by ozone, Technical report, ARCSL- TR-77060, Chemical systems laboratory, Aberdeen Proving Ground, MD., pp. 1-19 (1977).
4. Koon, J. H., Davis, G. M., and Knowlson, P. D., "Development of a wastewater management system for an elemental phosphorus production plant," Proceedings, The 35th Industrial waste conference, Purdue University, pp. 550-559 (1980).
5. Barber, J. C., Processes for the disposal and recovery of phossey water, U. S. Patent 5,549,878 (1996).
6. Crea, D. A., Recovery of phosphorus from waste ponds, U. S. Patent 4,492,627 (1985).
7. Beck, S. M. and Cook, E. H., Phosphorus recovery from phosphorus-containing pond sludge, U. S. Patent 4,717,558 (1988).
8. Richardson, S. M. and Weston, R. F., "White phosphorus contamination of wetlands: Effects and options for restoration," in Proceedings of the Federal Environmental Restoration, Vienna, VA, April, pp. 186-189 (1992).
9. Anazia, I., Jung, J., Removal of Elemental Phosphorus from Electric Furnace Sludge Using Froth Flotation, first year progress report, Mineral Waste Treatment and Recovery Generic Center, University of Nevada-Reno, Reno, NV. October (1989).
10. Walsh, M. E., "Analytical method for white phosphorus in water," *Bulletin of Environmental Contamination and Toxicology* **54**(3), 432-439 (1995).
11. Kirk-Othmer Encyclopedia of chemical technology, 4th ed. New York, NY Raven Press, pp. 164 (1994).