Waste Characterization and Management of the Phosphorus and Phosphoric Acid Industries

Mohammad Mahdi Rajabi[1], Mahdi Jalili Ghazizade[2*], Mohammad Esmail Ghanbari[1], Behnam Madadi[1]

[1]Department of Civil Engineering, Sharif University of Technology, Tehran, Iran

[2] Assistant Professor, Department of Environmental Pollutants, Environmental Sciences Research Institute, Shahid Beheshti University, Tehran, Velenjak, 1983963113, Iran

Abstract

The elemental phosphorus and phosphoric acid industries produce a number of hazardous waste streams that legally require a responsible disposal route. We present a review of the major waste streams of the phosphorus and phosphoric Acid industries, and show that the two most important hazardous wastes produced in these industries are: (1) arsenic filter cake which is generated from the purification process of phosphoric acid, and (2) phosphorus sludge which is an important by-product of the electro-thermal reduction of phosphate rock in the presence of silica and coke.

Large quantities of these hazardous wastes are produced each year through the world, and several studies have reported major groundwater and soil contamination events as a result of their mishandling. Our study includes the results of laboratory tests regarding these two waste streams, which aim at presenting an overview of their heavy metal concentrations. The two waste streams are then characterized based on standard methods and a comprehensive evaluation of the various alternatives for their management is presented. These alternatives include methods for material recovery, solidification, stabilization, incineration and final disposal. Finally the best methods are selected based on economic, technical and environmental criteria.

Keywords: Phosphorus Industry, Arsenic Filter Cake, Phosphorus Sludge.

[*] Corresponding Author: e-mail: ma_jalili@sbu.ac.ir; Phone No.: +98 912 7389407; Fax No: +98 21 22431972

1. Introduction

The production of elemental phosphorus and phosphoric acid, as two interrelated industries, provides the feed material for a huge array of industries, and hence, it is considered a strategic industry in the global economy [1]. Commercial production of elemental phosphorus is based on the reaction of phosphate rock with coke and silica in electric furnaces. The furnace is heated to 1500 °C by means of electric resistance. At this temperature, phosphate is reduced to P_4 which leaves the furnace as a gas. The gaseous P_4 is then condensed and collected under water as the commonly known white phosphorus [2,3]. Most of the elemental phosphorus that is mined (≈60%) is then converted into phosphoric acid [4].

Phosphoric acid is commercially produced by one the following two methods: (1) the wet process, which is the cheaper and more dominant method, and (2) the dry or thermal process which generally produces a purer product that is used for applications in the food industry [1]. In this study, we focus on the solid waste streams produced by the thermal process. By far the largest use of phosphoric acid (80~90% of the world production) is the manufacture of phosphates fertilizers. Phosphoric acid is also used in detergents, animal feed additives, pharmaceuticals, sugar refining, gelatin manufacturing, water treatment and carbonated beverages [1,4]. The main producers of phosphorus and phosphoric acid in the world are located near the large phosphate rock basins in North Africa, North America, China and Russia.

One of the principal environmental concerns of elemental phosphorus and phosphoric acid production is the solid waste streams. These industries produce large quantities of hazardous wastes each year through the world, and several studies have reported major groundwater and soil contamination events as a result of their mishandling [e.g. 5].

2. Waste Characterization

The most important solid waste stream of elemental phosphorus production, in terms of both quantity and hazardous characteristics, is phosphorus sludge. Phosphorus sludge is an important by-product of the electro-thermal reduction of phosphate rock. Phosphorus sludge mainly consisting of ore dust, coke, silica dust, slag dust, and generally includes some level of remaining P_4 which is not economically recoverable. The concentration of

P_4 in Phosphorus sludge is usually between 0 ppm to 10,000 ppm [5]. Phosphorus sludge is often maintained with a water cover to prevent oxidation of phosphorus with air. Otherwise, the remaining P_4 reacts with oxygen to form phosphorus pentoxide (P_4O_{10} or P_2O_5), which is emitted as particulate matter in the ambient atmosphere. The resulting fume is highly visible, white in color and very dense. Phosphorus pentoxide is corrosive to metal and is irritating to the eyes and respiratory tract. Phosphorus pentoxide is one of the main contributors to air pollution in the phosphorus industry. Phosphorus sludge is highly ignitable and its exposure to the atmosphere poses serious fire hazards. If phosphorus sludge is allowed to dry, black sediments will remain as a result of oxidation of the phosphorus. The studied factory produces approximately 2 tons of phosphorus sludge each day. Currently this waste is dumped in the surrounding environment.

In this study phosphorus sludge was analyzed for the presence of heavy metals, and the results are illustrated in **Table 1**. The analysis shows that phosphorus sludge contains high concentrations of zinc, mercury, cadmium and lead. This is an important characteristic of phosphorus sludge that has been mostly neglected in the relevant literature. It is common practice in the phosphorus industry to use this waste as a fertilizer additive due to its high Zinc content. However, the results of our analysis shows that this practice is not warranted, because the waste stream also contains relatively high concentrations of lead, mercury and cadmium.

Table 1. Concentration of heavy metals in phosphorus sludge

Parameter	Concentration	Unit
Zinc (Zn)	1120	mg/kg
Copper (Cu)	146	mg/kg
Mercury (Hg)	48	mg/kg
Arsenic (As)	12	mg/kg
Cadmium (Cd)	34	mg/kg
Nickel (Ni)	84	mg/kg
Lead (Pb)	840	mg/kg

The most significant solid waste generated from the purification process of phosphoric acid is arsenic filter cake [4]. In the thermal process, phosphoric acid is produced by burning elemental phosphorus in air and hydrating the resulting P_4O_{10} vapor to form the acid. In order to produce food-grade phosphoric acid, arsenic impurities should be removed from the resulting acid. This is accomplished by adding hydrogen sulfide, sodium hydrogen sulfide or sodium sulfide, to precipitate arsenic as arsenic sulfides, which is then removed from the phosphoric acid by pressure filtration. Some form of filter aid such as diatomaceous earth, is often used is this process [6]. The arsenic filter cake produced during the filtration is mainly composed of the filter aid material, arsenic sulfide and residue phosphoric acid. Arsenic filter cake is a yellow colored semi-solid sludge with a sulfur odor. Due to the residue phosphoric acid, arsenic filter cake is also corrosive.

The studied factory produces approximately 5 tons of arsenic filter cake each year. The filter cake is stored in plastic barrels, which has resulted in the development of a large stockpile of these containers over the years. **Table 2** demonstrates the results of laboratory analysis of heavy metal concentrations in the arsenic filter cake. As expected, the filter cake includes a very high concentration of arsenic. The waste also has significant concentrations of zinc, copper and lead.

Table 2. Concentration of heavy metals in arsenic filter cake

Parameter	Concentration	Unit
Zinc (Zn)	316	mg/kg
Copper (Cu)	208	mg/kg
Mercury (Hg)	9.3	mg/kg
Arsenic (As)	4410	mg/kg
Cadmium (Cd)	18	mg/kg
Nickel (Ni)	6	mg/kg
Lead (Pb)	316	mg/kg

The studied facility also produces a considerable amount of wastewater treatment sludge (approximately 500 kilograms per week) in an on-site wastewater treatment plant. This sludge is the product of wastewater neutralization by lime and the subsequent sedimentation of the resulting colloidal particles. The wastewater treatment sludge is a relatively uniform, fine-grained, grey-colored solid waste with a slight odor of phosphorus. The sludge is periodically removed from the wastewater system and dumped in the surrounding environment.

Amongst the described solid waste streams, Phosphorus sludge and Arsenic filter cake are characterized as hazardous waste according to definitions of EPA and the Basel convention. **Table 3** presents the EPA and Basel convention waste codes pertaining to these two waste streams. The wastewater treatment sludge is not characterized as hazardous waste. Note that EPA has also identified the wastewater treatment sludge of phosphoric acid producing factories (using the same thermal process) as non-hazardous [4].

Table 3. Characterization of the main hazardous waste streams of the phosphorus and phosphoric acid industries according to the EPA and Basel convention waste codes.

Waste type	EPA waste code	Basel convention		
		Annex I	Annex III	Annex VIII
Arsenic filter cake	D002 D004 D006 D008 D009	Y22 Y23 Y24 Y26 Y29 Y31 Y34	H 6.1 H 8 H 11 H 12	A4090 A1030
Phosphorus sludge	D001 D004 D006 D008 D009	Y22 Y23 Y24 Y26 Y29 Y31 Y34	H 4.2 H 10	A1030

3. Waste Management

3.1. Phosphorus sludge

Currently there is no reliable processing technology for handling phosphorus sludge, and hence, large quantities of this waste have accumulated in some of the major phosphorus producing factories around the world [3]. This study includes the identification, screening and evaluation of methods for the disposal of phosphorus sludge. The identified methods are briefly described in the following:

(a) Incineration: Incineration can reduce both the volume of the waste and the concentration of elemental phosphorus in the phosphorus sludge. The system would require an off-gas treatment system (such as scrubbers) to capture the resulting oxidized elemental phosphorus [5], which in turn would produce a significant amount of wastewater. The residual ash likely contains elevated levels of heavy metals and should be treated as hazardous waste. Moreover, phosphorus sludge has a low BTU and high moisture content, and considering the relatively high rate of its production, large amounts of fuel would be required for its incineration. Overall, incineration is not an attractive option for the treatment of phosphorus sludge.

(b) Methods based on reducing the P_4 content of phosphorus sludge: A number of methods are available for reducing the P_4 content of phosphorus sludge, with the intention of mitigating its hazardous characteristics prior to transport and Landfilling. These methods include mechanical aeration, caustic hydrolysis, chemical oxidation and thermal desorption. Details of these methods can be found in [5]. There are several key considerations regarding these methods: (1) they often fail to sufficiently treat the heavy metal concentrations present in the phosphorus sludge, and so, the output may still be classified as hazardous waste. (2) These methods frequently exhibit operational complexities due to the formation of toxic off-gases, fire hazards and the potential for reduced efficiency. The varying particle size and P_4 concentrations of phosphorus sludge adds to the complexity of operations.

(c) Stabilization + Landfilling: Phosphorus sludge can be stabilized by a number of methods including the addition of Portland cement. However, the large volume of the generated phosphorus sludge creates two setbacks for the stabilization procedure: (1) it requires a huge amount of cement or other reagents, which makes it an expensive option, and (2) stabilization further increases the volume of the waste, which would also add to the cost of transport and disposal.

(d) Landfilling: Landfilling of phosphorus sludge must include the following considerations: (1) preventing the Leachate (which contains high concentrations of heavy metals such as lead and mercury) from polluting the underlying soil and aquifer system, (2) preventing the exposure of phosphorus sludge to the atmosphere which creates both air pollution problems and fire hazards.

In this study the selection of an appropriate method for disposal of phosphorus sludge has been formulated as a multi-criteria decision making problem. The main criteria are the costs of disposal, the technical complexities of the design, construction and operation of the required facilities, and the level of environmental risk associated with the disposal option. Based in this analysis, Landfilling of phosphorus sludge has been chosen as the best option for the studied factory.

3.2. Arsenic filter cake

Arsenic filter cake is composed of three key components: residue phosphoric acid, filter aid and arsenic compounds. A considerable portion of the residue phosphoric acid can be recovered by simple physical processes such as centrifugal or compressed filtration. The filter aid can also be recovered by employing a chemical process which involves treating the filter cake with sufficient amount of a base (e.g. soda ash) to dissolve the contaminating arsenic compounds into the solution, and then separating and recovering the filter media from the arsenic-containing solution by filtration [6]. The process renders the filter aid suitable for reuse. Besides the economic value gained from the recovery of residue phosphoric acid and filter aid media, these processes result in tremendous reduction in the volume of the arsenic filter cake, which makes the subsequent handling and disposal of the remaining waste much easier. Recovery of arsenic from arsenic filter cake is not economically viable, because of the relatively low cost of arsenic in the global market and the fact that the concentration of arsenic in the waste stream is not high enough to validate the costs of its recovery [7]. Moreover, Arsenic filter cake contains impurities such as lead, zinc and copper which are uneconomic to remove.

A comprehensive survey of potential methods for the disposal of arsenic filter cake has been done in this study. The identified methods are briefly reviewed in the following:

(a) Incineration: Arsenic filter cake can potentially be treated by on-site or off-site incinerators. However, the incineration of arsenic filter cake has two important setbacks: (1) it has a low BTU value and therefore would require large amounts of fuel, and (2) the resulting volatilization of arsenic compounds creates technical complexities in the handling of the off-gas, and it also poses environmental risks.

(b) Concentration and containment: The studied factory currently uses this method for handling of arsenic filter cake. However, long-term stockpiling of arsenic containing wastes poses safety and environmental risks due to the potential for accidental spills [7].

(c) Dilution: Dilution involves combining numerous waste streams together, so as to dilute the hazardous contaminants (in this case arsenic compounds). Dilution is an economically attractive option, but the carcinogenic nature of arsenic and the risks associated with long-term exposure to low concentrations of arsenic, prohibits the use of this option [8].

(d) Landfilling of raw waste material: Arsenic filter cake is semi-solid and has a high leaching rate of arsenic compounds. So the Landfilling of raw arsenic filter cake highly increases the costs of implementing an appropriate liner and Leachate collection system, and also poses environmental risks. Solidification/stabilization prior to Landfilling provides both a cost saving and an environmental risk mitigation solution to these problems.

(e) Solidification/stabilization + Landfilling: Solidification option for arsenic filter cake include cementitious solidification [9], vitrification [10], and a process in which the waste is heated to a temperature sufficient to volatilize the heavy metals, and the metal vapors are subsequently contacted with a sorbent which sequesters them into a non-leachable complex [11].

Based on multi-criteria decision analysis, cementitious solidification has been chosen as the optimal method for the disposal of arsenic filter cake in the current study.

4. Summary and conclusion

The two major hazardous waste streams of the elemental phosphorus and phosphoric acid industries are phosphorus sludge and arsenic filter cake. In this study we have presented the results of laboratory tests regarding these two waste streams, which show that phosphorus sludge contains relatively high concentrations of lead, mercury and cadmium. The study also shows that arsenic filter cake contains high concentrations of zinc, copper and lead. These two waste streams were then characterized based on the classifications of EPA and the Basel convention. A review and evaluation of potential strategies for handling these wastes was also presented. The evaluations show that the best method of handling phosphorus sludge is Landfilling through surface impoundments. For arsenic filter cake the best method, based on multi-criteria decision analysis, is cementitious solidification prior to Landfilling.

5. References

[1] Hocking, M. B.: Handbook of chemical technology and pollution control, Elsevier (2013).

[2] Schipper, W. J., Klapwijk, A., Potjer, B., Rulkens, W. H., Temmink, B. G., Kiestra, F. D. G., LIMBACH, A.: Phosphate recycling in the phosphorus industry, Phosphorus Research Bulletin, 15(0), 47-51 (2004)

[3] Jung, J. O.: Fundamental study on the recovery and removal of white phosphorus from phosphorus sludge, Environmental Engineering Research (EER), 10(1), 38-44 (2005).

[4] U.S. Environmental Protection Agency: Phosphoric acid listing background document for the inorganic chemical listing determination, http://www.epa.gov/osw/hazard/wastetypes/wasteid/inorchem/docs/phosphor.pdf (2000) Accessed 20 April 2015

[5] MWH: Identification and evaluation of P_4 treatment technologies, http://www.sbtribes-ewmp.com/documents/FMC-OU_documents/Treatment%20options/P4%20Treatment%20Technologies_FMC%20SFS%20july2010.pdf (2009) Accessed 16 April 2015

[6] Wheeler, D. R.: U.S. Patent No. 4,652,380. Washington, DC: U.S. Patent and Trademark Office (1987)

[7] Leist, M., Casey, R. J., & Caridi, D.: The management of arsenic wastes: problems and prospects. Journal of Hazardous Materials, 76(1), 125-138 (2000)

[8] S.M. Naqvi, C. Vaishnavi, H. Singh, in: J.O. Nriagu, Ed.., Adv. Environ. Sci. Technol. vol. 27 Wiley, New York, 1997, pp. 556–604.

[9] Singh, T. S., & Pant, K. K: Solidification/stabilization of arsenic containing solid wastes using portland cement, fly ash and polymeric materials. Journal of Hazardous Materials, 131(1), 29-36 (2006).

[10] Wheeler, D. R.: U.S. Patent No. 4,820,325. Washington, DC: U.S. Patent and Trademark Office (1989).

[11] Srinivasachar, S., Morency, J.: U.S. Patent No. 5,245,120. Washington, DC: U.S. Patent and Trademark Office (1993).