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RECOVERY OF PHOSPHATES FROM ELEMENTAL PHOSPHORUS BEARING WASTES

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ABSTRACT

A process for oxidizing aqueous elemental phosphorus containing residues (sludges) to produce orthophosphate containing slurries suitable for subsequent reaction with ammonia to produce nitrogen and phosphate containing fertilizer products. It comprises reacting aqueous elemental phosphorus containing residues with certain special mixtures of concentrated nitric acid and sulfuric acid to effect the conversion of the elemental phosphorus into mostly orthophosphoric acid and very little orthophosphorus acid with the relative ratios of the two acids being dependent upon the mole ratio of $\text{H}_2\text{SO}_4:\text{HNO}_3$ employed in the processing. The resulting aqueous reaction intermediate is neutralized with ammonia during processing to a fluid or solid fertilizer product. Prior to the conversion to products, the aqueous reaction intermediate may be subjected to a solids separation step to remove insoluble salts of certain environmentally undesirable metals, such as Pb, Cd, Ba, and Cr.

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The objective of this research was to develop an environmentally sound process to safely remediate elemental phosphorus bearing wastes by minimizing or eliminating all remediation by-products and producing a usable, and hopefully marketable, product other than elemental phosphorus. This process development study was initiated by the Tennessee Valley Authority (TVA) to develop technology for the remediation of elemental phosphorus containing by-products produced by electric furnaces operated until 1976 at Muscle Shoals, Alabama. If successfully developed, this technology would also be useful to numerous other facilities throughout the United States that once produced elemental phosphorus by the electric furnace process or utilized phosphorus as a raw material.

Background of Phosphorus Wastes

In the electric furnace process for producing elemental phosphorus, agglomerated phosphate-containing ore (apatite) is reacted with coke at temperatures of 1200 to 1500 °C. Silica is added to the reaction mixture to serve as a flux to remove calcium silicate slag. A simplified equation for the overall process is shown below.

The gaseous phosphorus and carbon monoxide, along with impurities (generally SiF_4 and dust), are passed to an electrostatic precipitator where a major portion of the dust is removed at temperatures above the dew point of phosphorus. The gaseous phosphorus and carbon monoxide then proceed to condensing columns where the phosphorus is condensed to a liquid by water sprays maintained at 45-55 °C. The uncondensed carbon monoxide exits the sprayers and may be burned as a fuel. Ferrophosphorus is tapped from the furnace as a by-product for use in steel production. The calcium silicate slag is removed as a waste product containing no elemental phosphorus.

The water-covered liquid phosphorus runs to a sump where a small amount of impurity sludge collects at the interface between the water and the liquid phosphorus. This sludge layer consists primarily of hydrated silica, fluorosilicates, dust, and emulsified phosphorus. A portion of the entrained phosphorus is recovered from the sludge by centrifugation and a limited amount of the sludge is recycled to the furnace. However, the physical and chemical properties of the residue prevent its complete recycle and the remaining sludge must be treated as a waste or processed by some other means.

Both the sludge and precipitator dust from the electric furnace process contain

small-to-moderate amounts of elemental phosphorus and can create safety and environmental hazards during handling, transporting, and storage due to the autoignition property of elemental phosphorus when exposed to air. Elemental phosphorus is also highly toxic and care must be taken to ensure that it does not enter the ecological system.

The elemental phosphorus containing sludge is a very nonhomogeneous material varying in consistency from thin slurries to thick mud to layers of hard crystalline material. Sludges that are newly formed can contain elemental phosphorus concentrations as high as 50-60% by weight. However, sludges that have settled for several years (which includes most sludges stored at the old furnace locations) will have elemental phosphorus concentrations of generally 5-15% by weight. These sludges usually contain small amounts of various heavy metals including iron, aluminum, lead, arsenic, barium, cadmium, and others. A typical analysis of phosphorus sludge located at Muscle Shoals, Alabama, is provided in Table 1.

Over the past 25 years the number of electric furnaces used to produce elemental phosphorus has decreased at a rapid rate. A large portion of the electric furnace phosphorus was used to produce a pure grade of phosphoric acid and munitions. With the development of improved methods of purifying wet-process phosphoric acid and the increased energy and environmental costs of operating electric furnaces, the furnaces began to close down in the 1970's and 1980's. In 1968 there were 36 furnaces in operation in the United States at 13 locations producing 655,000 t/y. By 1992 there were only eight operating furnaces in three locations with an estimated production of 265,000 t/y. Large quantities of elemental phosphorus containing sludge and precipitator dust have been stored at most locations of both nonoperational and operational phosphorus furnaces. At most nonoperational furnace locations and manufacturing facilities that have stored elemental phosphorus as a feed stock for various industrial processes, little or no expertise or equipment is available to properly handle, transport, or store the hazardous sludge. For this reason a remediation process that could be used on location to convert the elemental phosphorus first to environmentally benign phosphate compounds and then to a usable, marketable product would be beneficial.

Remediation Alternatives

TVA operated an electric furnace process producing elemental phosphorus at Muscle Shoals, Alabama, from 1934 to 1976. Although TVA made major efforts to recycle the sludge produced by its furnaces, there was still a large amount of phosphorus sludge at the time operations were terminated. In the last few years prior to the shutdown of the furnace operation, TVA stored approximately 130,000 liters of the phosphorus sludge in rail cars, tanks, and a concrete sump for future process studies. In 1990 a multidisciplinary team was established to evaluate existing processing options to utilize or convert the sludge to a useful product, as well as develop new technology alternatives. After a lengthy evaluation of all available options, it was decided that technology based on nitric acid oxidation of the sludge followed by ammonia neutralization to produce a nitrogen and phosphorus containing fertilizer was the most advantageous approach. This type process would offer the advantages of producing a safer phosphate product and would produce no by-product requiring disposal in a landfill. Also this process alternative fit the technical expertise at Muscle Shoals and offered the type of technology most likely to be accepted by environmental regulators and the public.

The methods of remediation of phosphorus sludge evaluated during this study

included incineration, distillation, air/oxygen oxidation, long-term containment, recycling into a new or existing furnace, and nitric acid oxidation. The major disadvantages associated with most of the above mentioned remediation methods included landfilling remediation by-products, incomplete remediation of the elemental phosphorus, handling and shipping hazards associated with an elemental phosphorus remediation product, high capital costs, and insufficient testing of technology. The nitric acid oxidation approach to remediation avoids most of these disadvantages and TVA was prepared to initiate a study utilizing its 130,000 liters of stored phosphorus sludge to develop and evaluate this technology.

The proposed process was based upon the assumption that the elemental phosphorus in the aqueous sludge could be oxidized with nitric acid to produce a phosphoric acid solution which in turn might be ammoniated to produce an ammonium phosphate containing mixture suitable for granulation to a fertilizer product. A simple flow diagram of the overall process proposal is shown in Figure 1. The assumed chemical reactions are shown below.

These equations assume that the phosphorus is converted to orthophosphate and that the nitric acid is reduced to nitric oxide, NO. However, in calculating the stoichiometry of this system it must be noted that the nitric acid can be reduced to one or a combination of four gaseous reduction products: nitrogen dioxide, NO₂; nitric oxide, NO; nitrous oxide, N₂O; and elemental nitrogen, N₂. Also the oxidation may not proceed all the way to the orthophosphate oxidation state and may stop at the orthophosphite (H₃PO₃) or the hypophosphite (H₃PO₂) oxidation stages. Without any quantitative information concerning the extent to which each of the mentioned reactions might occur, it was decided to base all initial calculations upon the assumption that the oxidation reaction proceeds according to eq 2.

Lab-Scale Study

In early 1991 a laboratory investigation was initiated to develop the nitric acid oxidation technology. A 55-gallon drum of representative phosphorus sludge was collected from one of the storage tanks and was found to contain 7.5-7.9% elemental phosphorus. (The nonhomogeneous nature of the sludge was responsible for the range of analysis.) The lab-scale test assembly shown in Figure 2 consisted of a reactor and a scrubber. Both vessels were cylindrical Pyrex glass 90 mm ID x 122 cm total height. Nitric acid, sludge, antifoam agent, and air were all added through glass fittings at various locations on the side of the vessel. The reactor contents were heated and agitated by means of a magnetic stirrer-heater. Reactor temperatures were measured by a type K thermocouple. The reactor was designed to process approximately 1 liter of sludge per batch. Gases evolving from the reactor were carried by 8 mm ID glass tubing to the scrubber vessel. The scrubber contained 80 cm of 1-inch stainless steel Pall packing and water which was recirculated over the packing by a peristaltic pump. Preliminary beaker tests had shown the reaction to produce large amounts of foam. For this reason the reactor was designed with a large freeboard and allowances for an antifoam agent addition.

In the initial tests, 125-150% of the stoichiometric nitric acid was fed to the reactor using both 57% and 70% HNO₃. The large excess of nitric acid was to ensure the complete oxidation of the elemental phosphorus and to compensate for other

impurities in the sludge that might compete for the oxidizer. The earliest tests of this series showed that the foaming problem was more easily controlled when the batch reactor was precharged with the nitric acid and the sludge was metered into the acid over a 30-45 minute period. Reaction temperatures ranged from 102-110 °C and resulted in continuous boiling of the reaction solution, with the evolution of large quantities of NOx gases. After all the sludge was fed, the reactor temperature was held at the reaction temperature for a retention time of 2 hours. Results of this first group of tests are shown in Table 2. The product slurry contained only 5-10 ppm of elemental phosphorus; however, the orthophosphate was only 47-57% of the total phosphorus and the remaining phosphorus analyzed was orthophosphite. No hypophosphite was identified. These levels of orthophosphites presented a problem in converting the oxidized slurry to a fertilizer. Unlike orthophosphates, orthophosphites are toxic to plants at high concentrations and at the above mentioned levels, they would nullify the effect of the plant nutrient properties of the orthophosphates.

In the next series of tests varying amounts of sulfuric acid were added to the 125-150% stoichiometric equivalent of 56% nitric acid in the reactor. These acid mixtures were used in hopes of increasing the oxidation level of the phosphorus and reducing the orthophosphites to levels that would not adversely effect the plant nutrient value of the product. Weight ratios of H₂SO₄ (93%) to HNO₃ (56%) were tested at 1:3, 2:3, 1:1, and 3:2. Results of these tests are shown in Table 3. The mixed acids reduced levels of elemental phosphorus (0.8-3.2 ppm) at all acid ratios and resulted in a substantial increase in the production of orthophosphates relative to orthophosphites when the acid weight ratio was above 1:1. Figure 3 shows a graphical representation of the effect that the ratio of sulfuric to nitric acids had on the conversion of elemental phosphorus to orthophosphates.

The results of the lab-scale study proved that the elemental phosphorus in the sludge could be effectively oxidized using a mixture of sulfuric and nitric acids with a weight ratio of 1:1 or higher and a 25-50% excess of nitric acid. The reactor design requires a 300% freeboard to adequately control the foaming even with the use of a foam retardant. The reaction can be controlled at the boiling point of the solution (105-115 °C), thereby allowing evaporative cooling to remove excess heat from the reaction. Based on these results it was decided to build a bench-scale plant (20:1 scale-up) to further optimize the oxidation process, evaluate the effects of scale-up, and produce enough product to evaluate the production of a nitrogen and phosphate fertilizer product.

Bench-Scale Development

In mid-1992 a bench-scale facility designed to process approximately 20 liters of phosphorus sludge per batch was constructed and successfully operated. The facility consisted primarily of a phosphorus sludge feed tank, a feed pump, and a reactor. The sludge feed tank was a 316 stainless steel cylindrical cone bottom tank, 66 cm in diameter by 100 cm high, containing a turbine-type agitator. The feed pump was a peristaltic metering pump. The reactor was constructed of 316 stainless steel with dimensions of 25 cm inside diameter by 182 cm high. The lower 30 cm of the reactor was jacketed for heating and cooling. The reactor was baffled and fitted with a turbine type agitator and had J-type thermocouples located throughout the reaction zone. No scrubbing system was added to this facility due to the expected short duration of the tests. However, an exhaust system was designed to allow for air sampling that would be necessary to design an adequate scrubber system for any additional testing or scale-up. A diagram of the bench-scale oxidation plant is

shown in Figure 4. The process procedures were designed after the optimum results of the lab study with minor modifications to adjust for scale-up and potential industrial applications.

In the lab-scale tests the feed rates were based on the assumption that all phosphorus was oxidized to orthophosphates and all the nitric acid was reduced to nitric oxide (eq 2). For the bench-scale tests the assumption that all phosphorus would be completely oxidized to orthophosphates was accepted. However, it was now believed that a mixture of the four nitric acid reduction products mentioned previously is formed. Therefore, an equally weighted average of the four nitric acid reduction stoichiometries was used to determine feed rates. Based on this assumption, the mole ratio of $\text{HNO}_3:\text{P}_4$ was calculated to be approximately 8.9. When an excess of 25-50% nitric acid is incorporated into the formulation, the $\text{HNO}_3:\text{P}_4$ mole ratio is set for a range of 11.1 to 13.4. The sulfuric acid feed rate was based on the results correlated in Figure 3 and set at a range of 1.1 to 1.3 mole ratio of sulfuric acid to nitric acid.

The results of the bench-scale tests confirmed the results obtained in the earlier lab-scale tests, and process procedure modifications were developed that would assist in further scale-up of the process. Oxidation of the phosphorus sludge was excellent with the product containing 0.3-3.0 ppm elemental phosphorus and 97-99% of the total phosphorus was in the form of orthophosphate. The bench-scale oxidation results are given in Table 4. The scale-up of the reactor created a decrease in the ratio of surface area to volume and caused the reaction temperature to increase to 120-124 °C in some of the tests. Reaction temperatures above 120 °C produced excessive volatilization and/or thermal reduction of the nitric acid and reduced the oxidizing capacity of the reactor. To control the reactor temperature, many procedures were attempted or theorized that would correct this problem. These included reducing the sludge feed rate; reducing the concentration of the elemental phosphorus in the sludge by dilution; adding a portion of the nitric acid feed (10-15%) after the completion of the sludge feed; installing a cooling jacket or coils to control the reaction temperature; and adding a condenser to the reactor vent to return the volatilized nitric acid to the reactor. The two procedures found to be most practical for this test series were slowing the feed rate of sludge and splitting the nitric acid feed. A reactor freeboard of 300% was again demonstrated to be necessary to control the foam. Also the use of an antifoam agent (sulfonated oleic acid) or increased agitator speed was shown to significantly aid foam control. During these bench-scale tests, no supplemental heat was needed during the 2-hour reaction time after the sludge addition was complete. After reaching a reaction temperature of 110-120 °C, the reactor cooled to 85-95 °C during this retention time without any noticeable reduction in the oxidation of the elemental phosphorus.

A portion of the oxidized sludge produced in the bench-scale oxidation facility was used as a feed to an ammoniator granulator to produce a fertilizer product. These test were made on a bench-scale granulation plant utilizing a 30-cm-diameter by 30-cm-long rotary drum granulator, followed by a 30-cm by 90-cm rotary dryer and a sizing screen. Ammonia was introduced in the granulator to neutralize and solidify the sludge and produce granules sized to approximately 2.4-3.4 mm size. The granulation facility was operated at 6.8 kg/h and produced a product with a fertilizer grade of 17-13-0-5S. The product had an average pH of 5.0, and all the TCLP metals were analyzed and found to be below the regulatory levels. Table 5 shows a listing of these results from the granulation tests. Physical properties, storage, and greenhouse studies on the product all showed satisfactory results. The greenhouse tests showed the product to be at least as effective for plant growth as

analogous rates of MAP (monoammonium phosphate) and no adverse effects of heavy metals were detected. Because of the success of the granulation study and the simplicity of the ammoniation/granulation process, scale-up to a standard granulation pilot plant (0.5-1.0 t/h) should be routine.

These bench-scale tests successfully demonstrated the oxidation of elemental phosphorus containing sludge using mixed nitric and sulfuric acids and the conversion of the oxidation product into a usable granular nitrogen-phosphate fertilizer product. These tests further verified the process dependence on the molar ratios of sulfuric acid to nitric acid and nitric acid to elemental phosphorus and confirmed earlier lab-scale tests. Based on these test results, a patent application was submitted in March 1993. At this stage in the project, scale-up of the oxidation and granulation processes to pilot-plant scale was considered to be highly feasible and would provide an opportunity to complete the development of this technology while providing a technology demonstration with the remediation of the approximately 130,000 liters of elemental phosphorus containing sludge currently in storage at TVA's Muscle Shoals facility.

Pilot Plant Construction

Design and construction of a nitric acid oxidation pilot plant to process phosphorus sludge was started in early 1993. Completion and startup of the facility is scheduled for early fall 1993. The oxidation pilot plant is a scale-up of approximately 20:1 over the bench-scale plant and will process up to 380 liters of sludge per batch. An existing granulation facility will be used for the pilot granulation work. Preferred operating parameters developed during the bench-scale tests will be used for startup of the pilot plant and are listed in Table 6.

A basic flow diagram of the phosphorus sludge oxidation pilot plant is shown in Figure 5. Phosphorus sludge to be processed in the oxidation pilot plant will be removed from the storage vessels into a large sump. In the sump the sludge will be recirculated through a chopper-type pump for size reduction and slurried for pumping to the pilot-plant feed tanks. It should be noted that removal of any phosphorus sludge from its containment under water is an extremely hazardous operation. The sludge should be kept wet or preferably under water while it is being handled. Personnel working with the sludge should be dressed in fire protective suits and supplied with personnel protective respirators designated for the copious amounts of P_2O_5 smoke that is produced by the oxidation of the phosphorus with air. Tanks will be available at the pilot plant to adjust the elemental phosphorus concentrations before feeding to the reactor. The reactor is a brick-lined cylindrical vessel with a 0.76 m inside diameter and 3.35 m high. A natural gas thermal NO_x reducer was purchased for the pilot plant that is designed to reduce 90-95% of the NO_x produced to CO_2 , H_2O , and N_2 .

The first several months of pilot-plant operation will be dedicated to developing operating procedures and performing variable studies to further optimize the process technology. Beginning in early 1994, plans are to have the pilot plant operating on a 24-hour schedule with project completion targeted for August 1994.

TABLE 1
TYPICAL ANALYSIS OF PHOSPHORUS SLUDGE

	Concentration	
	Mean	Range
Total P, wt %	20.2	6.1 - 37.5
Elemental P, wt % P_4	11.0	0.7 - 32.9
Fe, wt %	2.6	1.0 - 5.5
C, wt %	2.0	0.9 - 3.4
Al, wt %	0.2	0.1 - 0.4
Pb, ppm	310	70 - 600
As, ppm	42	20 - 70
Ba, ppm	19	0 - 40
Cd, ppm	30	0 - 60
Hg, ppm	<1	<1

FIGURE 1
TVA REMEDIATION PROCESS

FIGURE 2
LAB-SCALE BATCH OXIDATION REACTOR

TABLE 2
RESULTS OF LAB-SCALE TESTS

	57% NITRIC ACID	70% NITRIC ACID
SLUDGE		
P_4 , wt %	7.9	7.5
Total P, wt %	9.8	9.0
OXIDATION PRODUCT		
P_4 , ppm	5.9	9.9
Total P, wt %	4.9	6.3
Orthophosphate, wt % of total P	57	47
HNO_3 , wt %	21	12

TABLE 3
LAB RESULTS USING
SULFURIC / NITRIC ACID MIXTURES

WEIGHT RATIO OF H_2SO_4 : HNO_3 *	1:3	2:3	1:1	3:2
OXIDATION PRODUCT				
P_4 , ppm	1.3	3.2	0.8	1.8
TOTAL P, wt %	5.2	4.6	4.5	3.7
ORTHOPHOSPHATE, wt % of total P	50	53	93	98

* H_2SO_4 - 96% HNO_3 - 56%

FIGURE 3
CONVERSION TO ORTHOPHOSPHATE

FIGURE 4
BENCH-SCALE PHOSPHORUS SLUDGE OXIDATION PLANT
(BATCH OPERATION)

TABLE 4
BENCH-SCALE OXIDATION RESULTS

FEED

SLUDGE

P₄, wt %	6.4
Total P, wt %	7.5
ACID RATIO, H₂SO₄: HNO₃	1.1

OXIDATION PRODUCT

P₄, ppm	0.3 - 3.0
Total P, wt %	4.4 - 4.6
Orthophosphate, wt % of total P	97 - 99

TABLE 5

BENCH-SCALE GRANULATION RESULTS

PRODUCTION RATE, kg/h	6.8
PRODUCT	
Total N, wt %	17.3
Total P ₂ O ₅ , wt %	13.9
Total K ₂ O, wt %	0.5
Total S, wt %	5.7
Total H ₂ O, wt %	0.9
pH	5.0
TCLP Metals	(All Below Regulatory Levels)

TABLE 6

PREFERRED OPERATING PARAMETERS

HNO ₃ Feed, % of stoichiometric	125 - 150
Molar Ratio of H ₂ SO ₄ : HNO ₃	1.1 - 1.3
Nitric Acid Concentration, wt %	56 - 70
Sulfuric Acid Concentration, wt %	93 - 98
Phosphorus Sludge Concentration, wt % P ₄	5 - 11
Reaction Temperature, °C	100 - 115
Reaction Time, h	1.5 - 3.0

FIGURE 5
PHOSPHORUS SLUDGE OXIDATION PILOT PLANT