Production of Alum from Spent Phostoxin

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Abstract: Alum was produced from spent phostoxin—an agricultural waste—using sulphuric acid. The optimum conditions for the reaction were determined as 40 wt%, 70°C and 30 minutes of sulphuric acid concentration, reaction temperature and time, in that order. A kinetic model, \( \frac{dA_2}{dt} = 2.9885 (\text{Al}_2\text{O}_3)^{1.453} (\text{H}_2\text{SO}_4)^{0.2846} \), was developed for the reaction.

Key words: alum, spent phostoxin, aluminium phosphide

INTRODUCTION

Nigeria is undeniably blessed with rich arable and fertile land for farming. Agriculture is the dominant economic activity, in terms of employment and linkages with the rest of the economy. This vital sector, mostly small-scale, low input subsistence farming, contributes about 40% of the GDP, 90% of the non-oil export earnings, and provides employment to about 70% of the adult labour force \(^1\). Traditional food crops are sorghum, millet, beans and maize in the north, and cassava, yam, plantain, maize and sorghum in the central and southern regions.

In recent years, food production management has failed to keep up with population growth, making food imports necessary. Lack of sufficient investment in new technologies, research and extension, as well as poor storage technique are reflected in continuing need for food importation \(^2\). To attain food sufficiency, the government encourages farmers to use improved seeds, fertilisers, irrigation and pesticides.

Pesticides are vital in controlling the destructive tendencies of insect pests like weevil, moth, beetle, cadelle, etc and their preadult stages- eggs, larvae and pupae. However, in off-setting the benefits of the application of pesticide are many problems identified with the use: unsafe use; persistence in the environment; toxicity to bees, fish and wildlife; contamination of water sources; persistent pesticides accumulating in the food chain; impact on earthworms and other beneficial organisms. In developing countries, pesticides are routinely used in unsafe conditions, and farmers lack training and resources at a detriment to their own safety and health and the environment \(^3\). Common pesticides used in Nigeria are karate, cymbush, nuvacroon 40EC, furadan, primextra, lindane and phostoxin. Some of these pesticides are highly hazardous, widely banned and environmentally persistent.

**Aluminium Phosphide:** Aluminium phosphide is a widely used pesticide which comes in different commercial names; celphide, celphine, delicia, phosfume, phostek, phostoxin etc with varying concentration. Phostoxin contains 55% aluminium phosphide as its active ingredient and 45% inert. This inert is mainly alumina, used as a carrier of the active ingredient. When exposed phostoxin, reacts with moisture to liberate phosphine as shown in Equation 1 \(^5\). The gas is the poison used in controlling insects and the aluminium hydroxide left behind is called phostoxin ash (spent aluminium phosphide). This reaction may be incomplete, possibly owing to the formation of a protective layer of aluminium hydroxide on the surface.

\[
\text{AlP} + 3\text{H}_2\text{O} \rightarrow \text{Al(OH)}_3 + \text{PH}_3
\]

Phosphine is a colourless gas which is odourless when pure, but the technical product usually has foul odour, because of the presence of substituted phosphines and diphosphines. It is flammable and explosive in air and can autoignite at ambient temperature. However, the commercial aluminium phosphide contains ammonium carbamate which liberates non-flammable and inert agents to reduce fire hazards. Phosphine gas is highly toxic to insects, burrowing pests, humans, and other forms of animals. In addition to its toxic properties, the gas will corrode certain metals \(^4,5\).

Phosphine in air can be detected by the discolouration of silver nitrate or indicator papers impregnated with mercury (II) chloride, and can be measured by flame photometry, infrared spectroscopy, mass spectroscopy or gas chromatography. Samples are taken on solid adsorbents and desorbed for analysis \(^4\).

**Effects of Aluminium Phosphide Waste on Human and Environment:** In Nigeria, the Federal Ministry of Environment (FMEnv) and the National Environmental
Protection Management of Solid and Hazardous Wastes Regulation, 1991, have classified aluminium phosphide and phosphine as extremely hazardous wastes because of the toxic level and reactivity\[^6\]. In spite of this, knowledge of proper standards and procedures of the use of the fumigant and the disposal present the most potent problem. Most Nigerian farmers are uneducated and with the poor extension services available, these farmers can hardly differentiate a fresh, partial or spent aluminium phosphide. The common practice by farmers is the mixing of the phostoxin tablet with grains. When the grains are removed, high velocity air is used to blow away the phostoxin waste. This approach causes air pollution and poses serious danger to human health and environment.

Ingestion of phosphides may cause nausea, vomiting, diarrhoea and abdominal pain, tightness in the chest and coughing, headache and dizziness. In more severe cases this may progress to cardiovascular collapse and respiratory failure. Occasional cases of accidental exposure of the general population to phosphine have occurred in the region of fumigation operations\[^6\].

Generally, insects, a group of principal target, are susceptible, though the susceptibility at different stages of the life-cycle varies. Wild birds and mammals are similarly vulnerable to both phosphine and phosphides\[^4\].

Traditional means of disposal of aluminium phosphide ash as approved by the FMEnv and as similarly prescribed by the manufacturers are the wet and dry method. The wet method involves using deactivating solution on the waste while the dry method requires extension of the fumigation period. This deactivated waste is disposed in approved sanitary land fills.

One of the key objectives of the FMEnv policy on waste regulation is research into possible reuse and recycle of hazardous wastes. Along this line, this paper focuses on a novel technique of reusing the phostoxin waste. The principle is based on the fact that phostoxin wastes consist of mainly the original inert alumina and hydrated alumina; which is the by-product of the reaction in Equation 1. This waste is reacted with sulphuric acid to produce hydrated aluminium sulphate-alum.

**MATERIALS AND METHODS**

Spent phostoxin was sourced in an industry in Zaria, Nigeria. The waste was treated in a similar way as prescribed in the wet method of deactivating phostoxin waste. Residual phostoxin was poured slowly in warm water and stirred intermittently so as to thoroughly wet all the particles. This was done in a fume cupboard for three days. The beneficiated waste was then dried to constant weight, in an oven, at 105°C.

Chemical analysis of the beneficiated phostoxin ash was undertaken, using x-ray fluorescence (XRF) machine (Phillips, PW 1660) for all the parameters, except phosphate, which was undertaken separately, using atomic absorption spectroscopy (AAS) (UNICAM 969). Beside, samples of the deactivated phostoxin were reacted with sulphuric acid, with the aim of generating concentration, temperature and reaction time related kinetic data using aluminium sulphate as product. The reacting medium was placed in a round bottom flask, which was heated with a thermostatically controlled electric heater.

<table>
<thead>
<tr>
<th>Table 1: Composition of Spent Phostoxin and the Deactivated Waste</th>
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<tr>
<td><strong>Composition</strong></td>
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<tr>
<td>Al(_2)O(_3)</td>
</tr>
<tr>
<td>Fe(_2)O(_3)</td>
</tr>
<tr>
<td>SiO(_2)</td>
</tr>
<tr>
<td>CaO</td>
</tr>
<tr>
<td>MgO</td>
</tr>
<tr>
<td>K(_2)O</td>
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<tr>
<td>Na(_2)O</td>
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<td>AlP</td>
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First, an optimum reaction temperature was established, by varying temperature from 30°C to 90°C at constant acid to water concentration and reaction time of 40 wt% and 20 minutes respectively. Thereafter, reaction time and acid strength ranges of 5 minutes to 60 minutes and 30 wt % to 50 wt%, respectively, at an established optimum temperature of 70°C were used.

Equation 2 represents the reactions.

\[ 2\text{Al}_2\text{O}_3 + 3\text{H}_2\text{SO}_4 \rightarrow \text{Al}_2(\text{SO}_4)_3 + 3\text{H}_2\text{O} \] (2)

In all cases, a factor of five, excess sulphuric acid, based on stoichiometry, was used, after the excess method described by Levenspiel [8]. This prevents mud formation of the solid alumina and aid in complete reaction.

Alum crystals were obtained from reaction products by cooling the saturated solution of aluminium sulphate to 2°C in a refrigerator. The quantity of alum, whose quality was not ascertained, was obtained gravimetrically, using spectrophotometric approach, after adequate calibration.

**RESULTS AND DISCUSSION**

Assays of spent and deactivated phostoxin are presented in Table 1, while Figure 1 shows the results of alum yields, with varying temperature, at constant reaction time of twenty minutes. The table shows a reduction of aluminium phosphide in the spent phostoxin, by deactivation, from 1.960 to 0.274 weight percent. The low level of 1.960 wt% of aluminium phosphide in the spent phostoxin as opposed to 55 wt% in the fresh phostoxin demonstrates the high level of resident experience of handling the dispensers of the phostoxin in industry. However, the very low level of 0.273 wt% aluminium phosphide in the deactivated spent phostoxin, notwithstanding, when disposed by land filling, is still potentially harmful to beneficial soil fungi, bacteria, nematodes, etc. Table 1 shows that alumina is the main constituent of the inert, being 68.3 wt% and 70.080 wt%, in the spent and deactivated phostoxin respectively, while the fresh phostoxin is rich in aluminium phosphide [9]. It is interesting to note that the alumina content of spent phostoxin is far in excess of the average alumina content in Kankara clay, which is about 40 wt%, as reported by Atta [9]. This robustly indicates that spent phostoxin, can serve as a rich source of alum, by leaching with sulphuric acid. Figure 1 shows a gradual increase in the yield of alum from reaction temperatures of 30°C to 70°C, with a stabilization between 70°C and 90°C. The reaction temperature of 70°C was chosen as optimum, even though yield was still increasing at the point, because flame was observed at a temperature of 90°C, during the experiment, perhaps because of build up of phoshine gas.

Figure 2 presents alum yield, with varying reaction time, at a constant temperature of 70°C, in all cases, and acid concentration of 30 wt%, 40 wt% and 50 wt%, one after the other, under the prescribed conditions of time and temperature. Between the reaction time of 5 minutes and 60 minutes, use of 30 wt% of sulphuric acid showed the lowest yield of alum, compared with the yields for the other two acid concentrations of 40 wt% and 50 wt%. However, the alum yield versus time plot of the experiment results for 40 wt% and 50 wt% were superimposed on each other between reaction time of 5 minutes and 30 minutes. Subsequently, the alum yield for 50 wt% acid decreases in contrast with that of 40 wt%. This phenomenon can be attributed to occlusion of acid within the crystal lattice of the alum for the prolonged reaction period. The results suggest the selection of 40 wt% acid and 30 minutes, as optimal acid concentration and reaction time, respectively, for leaching alum from deactivated spent phostoxin.

Equation 3 was suggested as a model for the rate of formation of alum, \( r_A \), based on the method of excess sulphuric acid, B, and the alum, A, adopted in the experiments.

\[ r_A = kA^A B^B \] (3)
Accordingly, the experimental results translated to Equation 4.

$$r = 2.9885 \ (Al_2O_3)^{1.435} \ (H_2SO_4)^{0.2846}$$

(4)

The optimum conditions for producing alum from spent phostoxin, using sulphuric acid are 40 wt%, 70°C and 30 minutes of sulphuric acid concentration, reaction temperature and time, respectively. Under these conditions, the kinetic model $$r = 2.9885 \ (Al_2O_3)^{1.435} \ (H_2SO_4)^{0.2846}$$, was developed for the reaction.

Further work is recommended to establish the following: determine and upgrade the quality of alum in tandem with end use, the efficient and effective recovery and recycling of acid, complete recovery and reuse of phosphide and establish hydrodynamic and mass transfer conditions, as prelude to the design of appropriate reactor

ACKNOWLEDGEMENT

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