

PS6-8 – 6197

Phosphine – The natural cycle*S. Schmitt¹***Abstract**

The migration of phosphorus from the soil to the sea and vice versa is published in several natural cycles. In this context phosphine, a gaseous phosphorus compound, has not been considered although beside the non-natural phosphine source it also exists as natural compound.

The presentation focuses on phosphine as the most widely used fumigant and the relations between natural raw materials for the manufacturing of the elements (aluminium and phosphorus) and the production of phosphide containing fumigants. The degradation of phosphine in air to natural compounds completes this phosphorus cycle. It is also illustrated if energy is required or released during the chemical reactions.

The cycle emphasizes the special position of phosphine as ideal fumigant in view of the non-ecotoxic properties.

Key words: aluminium phosphide, phosphorous cycle, phosphine, fumigation.

The natural cycle

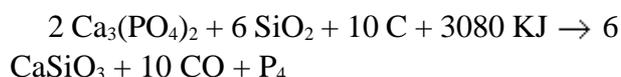
In view of the increasing environmental interest of humans and the prevention of additional man-made environmental problems the attention is focused on the ecotoxic properties of chemicals. These facts led to the Montreal Protocol and the phase-out of methyl bromide.

Phosphine is an alternative for methyl bromide. It is already widely used as fumigant against stored product pests. So, what about the ecotoxic properties of phosphine? Phosphine is released from metal phosphide formulations after having been exposed to the atmosphere. Aluminium phosphide is a popular compound and stands as an example in order to discuss the ecotoxic properties.

Due to their strong affinity to oxygen aluminium and phosphorus only exist in nature as oxides. Aluminium oxides respectively hydroxides as well as calcium phosphate are natural compounds. Aluminium oxides occur in clay and calcium phosphate is an integral part of teeth and bones. According to the following equation the fused-salt electrolysis of aluminium oxide yields aluminium.



The phosphorus is synthesized by an electrothermic reaction of calcium phosphate with carbon.



Due to the reducing properties of aluminium and the oxidizing properties of phosphorus the exothermic redox reaction between these elements yields the active ingredient aluminium phosphide.



¹Detia Degesch GmbH, Dr-Werner-Freyberg-Str. 11, 69514 Laudenbach, Phone +49 6201 708 300, Fax +49 6201 708 205, e-Mail Stefan_Schmitt@Detia-Degesch.de

It is well known that aluminium phosphide formulations like tablets, pellets or bags liberate phosphine after being exposed to the atmosphere. The formulations differ in their decomposition rate which depends on moisture, temperature and the formulation itself.

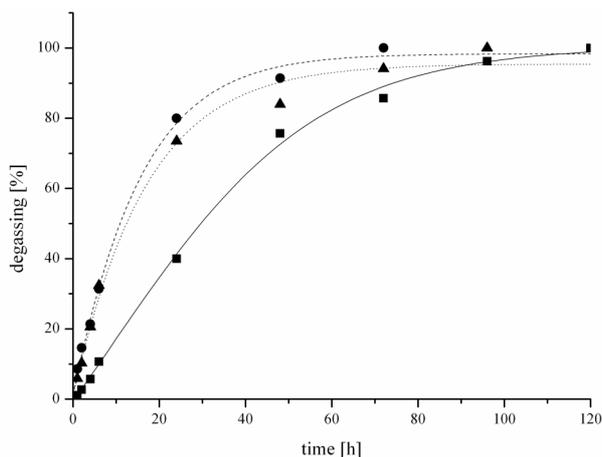
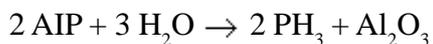
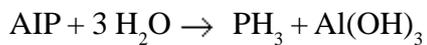


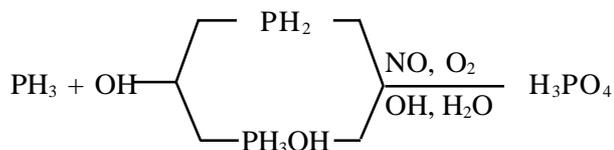
Figure 1. Comparison of the degassing properties of three fumigants at 20 °C and 60 % r.h. (pellets = circle; rounds = triangle; bags = rectangle).

According to the following equations the residues consist of a mixture of aluminium oxide and aluminium hydroxide. Both compounds are of natural origin and are the starting material for the production of aluminium.



After fumigations the treated structures are ventilated and the phosphine is diluted in the atmosphere. Phosphine reacts very fast with OH-radicals of the troposphere. Due to this short half-time phosphine will not reach the stratosphere and therefore will not damage the ozone layer. As shown in the following equation two initial reactions are possible which result via a chain reaction in the formation of phosphoric acid. Formal, the phosphoric acid is the corresponding acid of phosphate which is the raw material for

the production of phosphorus.



In comparison to other industrial emissions the pH shift of the rainfall or the eutrophication caused by the emission of phosphine is negligible.

As shown in Figure 2 the production of the elements aluminium and phosphorus and the production of the active ingredient aluminium phosphide as well as its application can be described by a cycle. The starting materials used for the production of the elements, i.g. aluminium oxide (respectively hydroxide) and a phosphate, are again being received after the fumigation. These facts underline the special position of phosphine as ideal fumigant in view of the non-ecotoxic properties (Van Walzer, 1958; Reichmuth et al., 1981; Reichmuth and Noack, 1983; Hollemann and Wiberg, 1985; Klapötke and Tornieporth, 1994).

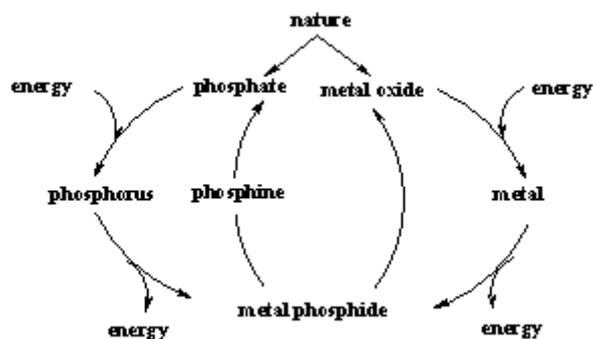


Figure 2. phosphorus cycle of phosphine as fumigant.

Reference

Hollemann, A.E., Wiberg, N., 1985. Lehrbuch der Anorganischen Chemie. Walter de Gruyter, Berlin.

Klapötke, T.M., Tornieporth, O., 1994.
Nichtmetallchemie. VCH, Weinheim.

Reichmuth, C., Noack, S., 1983. Zur Beurteilung
der Umweltverträglichkeit von
Begasungsverfahren im Vorratsschutz.
Getreide Mehl Brot 37, 139-144.

Reichmuth, C., Noack, S., Wrede, A., 1981. Zur
Emission von Phosphorwasserstoff im
Vorratsschutz. Nachrichtenblatt des
Deutschen Pflanzenschutzdienstes, 33, 132-
136.

Van Walzer, J.R., 1958. Phosphorus and its
compounds. Interscience Publishers, New
York.