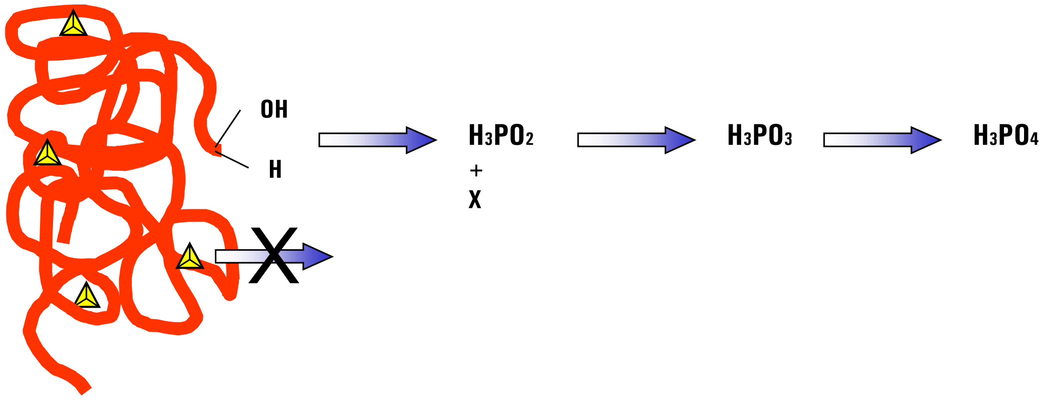
Chemical Behaviour of Red Phosphorus in Water



Prepared by:

Clariant GmbH
BU Additives – Flame Retardants
65840 Sulzbach
Germany

Contact:

Dr. Rüdiger Walz
Tel: +49 6196 757 8109
Fax: +49 6196 757 8977
e-mail: ruediger.walz@clariant.com

Dr. Adrian Beard
Tel: +49 2233 48-6114
Fax: +49 2233 41236
e-mail: adrian.beard@clariant.com

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List of Abbreviations

calc.	calculated
d.l.	detection limit
EC 50	median effect concentration value
NMR	Nuclear magnetic resonance spectroscopy

1 Summary

This report describes the chemical behaviour of red phosphorus in water and compares it to the reactions of white phosphorus. Whereas white phosphorus consists of P_4 molecules, spontaneously ignites near room temperature and is highly toxic, red phosphorus is an allotropic modification of elemental phosphorus which is mostly an amorphous polymer so that the physico-chemical properties of red phosphorus are very different from white phosphorus. Red phosphorus ignites only above 260 °C, is of very low toxicity and moderate reactivity.

Even white phosphorus has a very low solubility in water of about 3 mg/L. Due to its polymeric nature, red phosphorus is practically insoluble in water. However, since elemental phosphorus is thermodynamically unstable in the presence of water and oxygen, red phosphorus will very slowly react via intermediates such as hypophosphorous acid (H_3PO_2), phosphorous acid (H_3PO_3), and phosphine (PH_3) to phosphoric acid (H_3PO_4). These reaction products dissolve in water and contribute to a concentration of total phosphorus compounds (calculated as phosphorus) of 1 mg/L after 24 hours starting from 100 mg/L. Even after 4 months and starting from 10 000 mg/L the concentration of phosphorus compounds reaches only 270 mg/L corresponding to a conversion rate of the red phosphorus of only 2.7 % (see Table 3 and Table 4). Since these disproportionating and hyrolysis reactions proceed at a very slow rate, even critical products like phosphine (not readily soluble in water) will be finally converted to phosphoric acid in oxygen containing environments.

Experiments indicate that the traces of white phosphorus ($<$ 200 mg/kg) present as a contaminant in red phosphorus cannot be readily extracted by water. As a consequence, the new and so far unpublished experimental data in this report indicate that the content of white phosphorus in red phosphorus should not be used as a sole reference for extrapolating the toxic effects of red phosphorus to aquatic organisms.

2 Technical red phosphorus

2.1 Economic background

About 7 000 tons per year of red phosphorus are produced world wide. The most important producers of red phosphorus are located in Europe, in Germany and Italy in particular. The overall estimated capacity in the world is shown in Figure 1. The main market is Europe followed by China and India.

Red Phosphorus is produced by thermal conversion of white phosphorus. The obtained red phosphorus still contains up to about 100 mg/kg of white phosphorus. The upper limit given in the product data sheets is 200 mg/kg white phosphorus. Red phosphorus is a red powder which can be handled easily compared to the safety precautions necessary when handling white phosphorus. Main applications are matches, aluminium phosphide and flame retardants (see Figure 2).

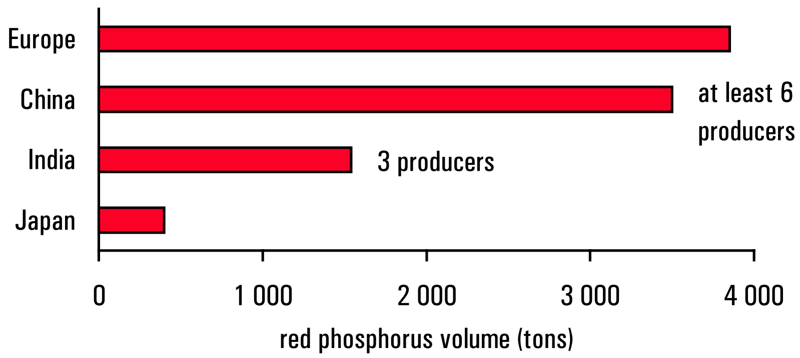

Figure 1: Global capacities for production of red phosphorus (total is 9 300 tons)

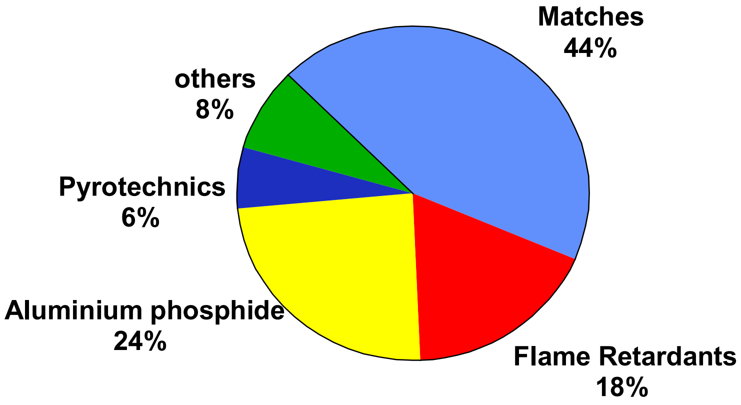

Figure 2: Application areas of red phosphorus. Total global demand is about 7 150 tons.

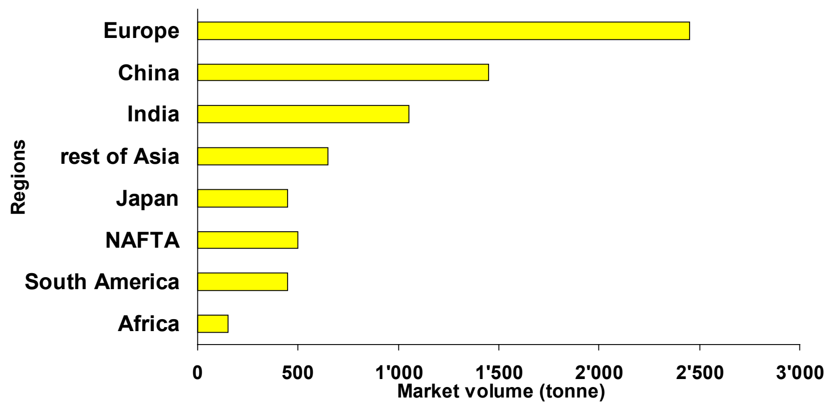

Figure 3: Red phosphorus market by key regions

The major distributor for red phosphorus for matches is located in Europe. Europe is also the principal market for red phosphorus due to the production of aluminium phosphide and the use as flame retardant in plastics. In Europe red phosphorus plays an important role as a flame retardant for plastics, especially for polyamides in electronics, polyurethanes and latex. Despite of its red colour it is used because in some cases it is the only material which meets the high safety requirements for the end products combined with the high technical requirements. In polyamides for electrical and electronic applications it is preferred because of its high stability which enables the use of such plastic materials up to high voltages.

2.2 Red phosphorus: short process description

Red phosphorus is one of the allotropic forms of elemental phosphorus. It is largely amorphous and is considered a polymeric version of white phosphorus. Commercial red phosphorus is normally produced by heating the white phosphorus at a temperature range of 250 – 350 °C for 40 – 50 hours in a closed furnace (exclusion of oxygen) and at ambient pressure.

After the polymerisation, the product is milled in presence of water then treated with an alkaline solution in order to remove traces of white phosphorus and finally filtered, washed and dried. Although this special treatment is applied for removing white phosphorus in the production process, some mg/kg of white phosphorus still remain in the final product. Specifications of commercial red phosphorus are presented in annex 1. The specifications state that the level of white phosphorus is $<$ 200 mg/kg, but the present technology is able to reduce the white phosphorus content to $<$ 100 mg/kg.

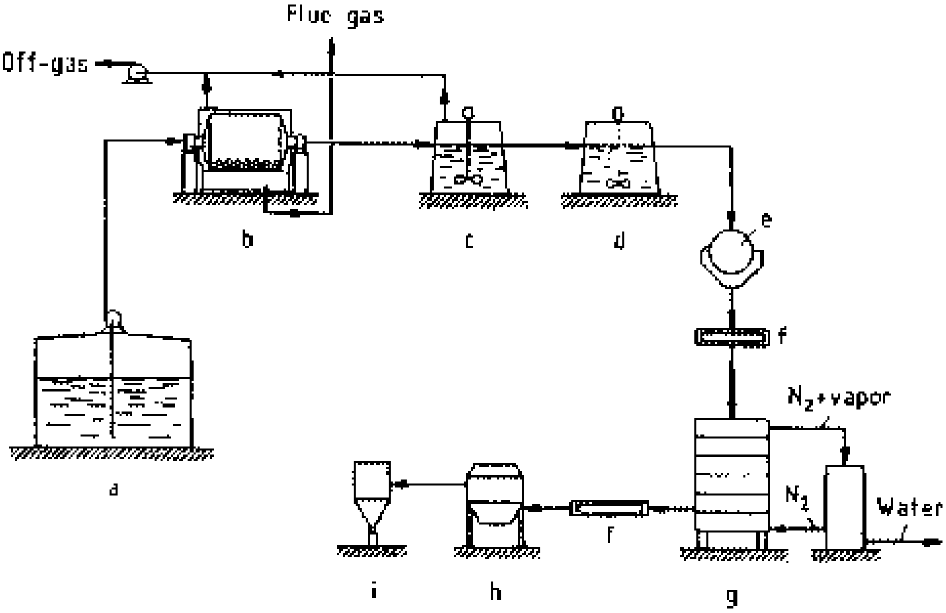

Figure 4: Manufacturing process of red phosphorus[1] with a) phosphorus storage, b) reactor, c) + d) treatment of phosphorus-water mixture, e) filtration, f) conveyor, g) dryer, h) air classification and sieving, i) predelivery storage

1 Ullmann's Encyclopedia of Industrial Chemistry, Sixth Ed., 1999 – PHOSPHORUS, Wiley-VCH, Weinheim, Germany

2.3 Characteristics of red phosphorus in comparison to white phosphorus

Table 1: Comparison of white and red phosphorus

	white phosphorus	**red phosphorus**
CAS-number	12185-10-3	7723-14-0
structure	contains discrete P_4 molecules	highly polymeric P_n
appearance	crystalline, waxy, translucent	amorphous or crystalline, opaque
melting point	44 °C	585 – 610 °C
vapour pressure	high	very low
density	1.83 g/cc	2.0 ... 2.4 g/cc
solubility:		
in organic solvents:	yes	no
in water:	only ~3 mg / L	no (very slow hydrolysis)
toxicity	highly toxic	very low toxicity
heat of sublimation	13.4 k cal/mol	30.0 k cal/mol
chemiluminescence	yes	no
ignitability	- spontaneous ignition in air at room temperature - spontaneously ignites in chlorine	- ignites only above 260 °C - heat necessary for ignition in chlorine
smell	characteristic	no smell
reaction with aqueous alkali	produces phosphine	none

The most important characteristics of red phosphorus in comparison to white phosphorus are summarized in Table 1. These data show that the two products do have only little in common, as a matter of fact they are far different in chemical structure, physico-chemical properties, reactivity and toxicity.

The term red phosphorus is used for describing a variety of different amorphous forms of the elemental phosphorus showing a range of colours from the orange to dark-violet. Such differences in colour can be explained by differences in:

- particle size of the powder,
- molecular weight,
- impurities normally present on the red phosphorus surface[2].

Although the red phosphorus is largely amorphous, X-ray diffraction, optical microscopy, and differential thermal analysis (DTA) have established the existence of several crystalline red varieties of pure elemental P in addition to the amorphous form. Normally the commercial red phosphorus is amorphous and the crystalline form is present only to a limited extent (< 10 % w) which is due to the ordered framework of different degrees of polymerisation[2].

Red phosphorus has been described as a complex three-dimensional polymer in which each P atom has a pyramidal arrangement of three bonds linking it to neighbouring P atoms as shown in Figure 5.

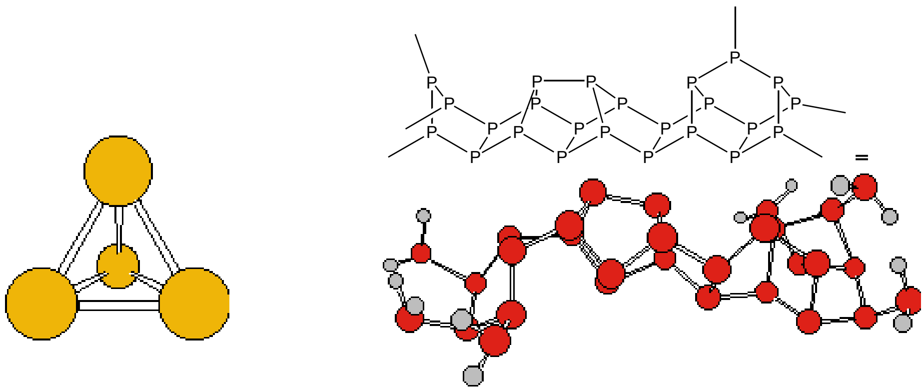

Figure 5: Structures of white and red phosphorus: tetrahedral structure of white phosphorus on the left and a possible substructure of red phosphorus on the right with three dimensional view (bottom); the grey circles symbolize free valences where the chain could continue or where terminal groups like –H or –OH or other heteroatoms (from impurities) could be attached.

2 Corbridge, D.E.C.: Studies in inorganic Chemistry 10 – Phosphorus: an outline of its chemistry, biochemistry and technology (Fourth edition). Elsevier 1990 pp. 56-65

It seems likely that all forms of red phosphorus are built from the pyramidal white phosphorus structure (Figure 5), and that the polymer growth is terminated by the occluded impurities such as halogen, oxygen or hydroxyl groups.

In conclusion, the amorphous red phosphorus probably consists of entirely random networks of P atoms terminated by oxygen or hydroxyl groups as depicted in Figure 5. This assumption is confirmed by NMR spectra of the solid red phosphorus material. Due to the fact that red phosphorus is a polymer, it is not a surprise that physico-chemical characteristics, the reactivity and the stability are far different from white phosphorus: the white phosphorus is crystalline, contains discrete P_4 molecules, has a melting point of about 44 °C, is very soluble in organic solvents like CS_2 and benzene, is very unstable and spontaneously ignites in presence of air. Whereas white phosphorus is a very toxic product, the red phosphorus is not toxic (LD 50 oral rat is $>$ 2000 mg/kg) as expected on the basis of the polymeric structure.

2.4 Content of white phosphorus in red phosphorus

Even with state of the art technology it cannot be prevented that red phosphorus contains traces of white phosphorus. This amount of white phosphorus is determined by extraction with carbondisulfide and subsequent measuring by phosphorus-NMR spectroscopy in comparison with a standard sample of white phosphorus in toluene. The average content of white phosphorus in commercial red phosphorus is normally about 50 – 100 mg/kg, even if the upper limit given in the specifications is 200 mg/kg.

3 Solubility of white phosphorus in water and related reactions

White phosphorus is hardly soluble in water (about 3 mg/L) so that it can be stored and transported under a protective aqueous layer. A comprehensive study on the literature of the chemical behaviour of phosphorus in the environment has been carried out[3]. If white phosphorus is exposed to both water and air under conditions in which it will not ignite, a complex mixture of oxyacids of phosphorus and phosphine is slowly formed at room temperature. The following chemical reactions occur in water (only qualitative description):

$$P_4 + H_2O + O_2 \rightarrow H_3PO_2 + H_3PO_3 + H_3PO_4 + PH_3$$

Measurements carried out by Clariant by P-NMR could not detect any phosphine in aqueous extracts of white phosphorus (detection limit of 1 mg/L). As far as the white phosphorus itself is concerned it is not clear whether the solubility of 3 mg/L is due to completely dissolved phosphorus or partly suspended colloidal particles. Anyway, this may be the reason for the extraordinary toxicity of white phosphorus to aquatic animals, because it might be incorporated in elemental form. Maddock and Taylor4 claimed to have detected elemental P4 in the organs of cod fish.

This is a fundamental difference to red phosphorus were no elemental phosphorus in water can be observed (see chapter 4.2). Even the amount of white phosphorus detected in the red phosphorus can not be extracted or dissolved in water.

[3] SRI International Project LSU-4937-I "Environmental fate of white phosphorus/felt and red phosphorus/butyl rubber military screening smokes: Phase I – Literature Review"

[4] Maddock B.G. and D. Taylor, *Water Research*, Vol. 10, pp 289-294 Pergamon Press 1976

4 Solubility of red phosphorus in water and related reactions

4.1 Theoretical approach

Red phosphorus shows a totally different chemical behaviour than white phosphorus. Red phosphorus is a polymeric allotropic modification of phosphorus. White phosphorus consists of reactive P_4 – tetrahedra (molecular weight: 124 g/mol) whereas red phosphorus has a polymeric structure of P_n . Consequently, the reactivity of red phosphorus is much lower than of white phosphorus. Yellow phosphorus has to be handled under water otherwise it will start to burn spontaneously. White phosphorus has a wax like appearance whereas red phosphorus is a red to violet coloured powder which can be handled in air. The vapour pressure of white phosphorus at 25 °C is 0.05 mbar whereas red phosphorus has no detectable vapour pressure at this temperature.

Due to these differences the reaction velocity of red phosphorus with water is much slower compared to white phosphorus, but the main reaction products are also phosphorus-containing acids (see Figure 6). If the total amount of white phosphorus contained in commercial red phosphorus (upper limit 200 mg/kg) were to dissolve in water, the following concentrations given in Table 2 would be achieved. One has to bear in mind that white phosphorus also reacts with water so that these calculated amounts of white phosphorus can only be achieved theoretically. Laboratory experiments revealed that the yellow phosphorus contained in red phosphorus is not readily extractable with water.

Table 2: Theoretical concentrations of white phosphorus in water from a dispersion of solid red phosphorus containing 200 mg/kg of white phosphorus

red phosphorus loading	white phosphorus
10 mg / L	2 μg / L
100 mg / L	20 μg / L

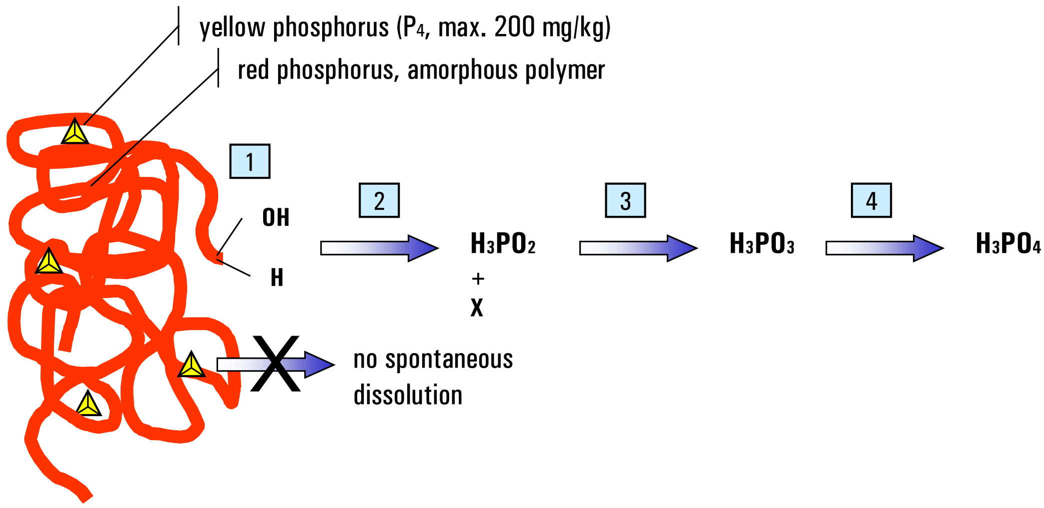

Figure 6: Schematic overview of reactions of red phosphorus in water. Annotations to the individual reactions:

1	initial reaction is disproportionating or oxidation of phosphorus in the polymer chain; this is the overall rate limiting step
2	the first products in aqueous solution are hypophosphorous acid and at least one unknown compound X; phosphine (PH_3) is also formed as an intermediate in trace amounts
3 + 4	further oxidation via phosphorous acid to phosphoric acid

4.2 Experimental data

4.2.1 Phosphorus-containing acids

Red phosphorus reacts very slowly with water according to the reaction scheme presented in Figure 6. The reaction products can be detected by NMR or ion chromatography. Clariant carried out a short term (24 hours) and a long term (4 months) experiment with red phosphorus stirred in water (see Table 3 and Table 4). The amount of these phosphorus compounds has been calculated as mg/L phosphorus for a straightforward comparison of values. From these experimental results the following conclusions can be derived:

- The reactions rates of red phosphorus with water are very slow. The overall conversion rate has been found to be always in linear correlation with the amount of the starting material as well as the stirring time of red phosphorus in water.
- By taking in account the reasonable stirring time of 24 h only 0.2 % of the starting material reacts with water.
- The reaction speed of red phosphorus in water is very slow and probably will never reach a steady state because the resulting oxo-acids are very well soluble in water.
- We were not able to detect any elemental phosphorus in water

Table 3: Reaction products after stirring 3 000 mg red phosphorus for 24 h in 1 liter of water

	concentration calc. as P [mg/L]	fraction
hypophosphite	1.0	18 %
phosphite	2.1	39 %
phosphate	1.4	26 %
unknown compounds	0.9	17 %
total phosphorus compounds	5.4	100 %
= fraction of nominal concentration	0.18 % (of 3 000 mg/L)	

Table 4: Reaction products of 10 000 mg red phosphorus in 1 liter of water after 1 and 4 months

	after 1 month		**after 4 months**	
	concentration calc. as P [mg/L]	fraction	concentration calc. as P [mg/L]	fraction
hypophosphite	19	19 %	50	19 %
phosphite	38	39 %	105	39 %
phosphate	34	35 %	98	36 %
unknown compounds	7	7 %	17	6 %
total phosphorus compounds	98	100 %	270	100 %
= fraction of nominal concentration (10 000 mg/L)	0.98 %		2.7 %	

4.2.2 No release of white phosphorus from red phosphorus in water

Elemental phosphorus could not be detected in any of the aqueous red phosphorus suspensions of the experiments in Table 3 and Table 4. The detection limit was 1 mg/L. To demonstrate that the white phosphorus contained in the solid red phosphorus does not dissolve in water (in contrast to pure white phosphorus which has a solubility of about 3 mg/L), the following experiments were performed with a type red phosphorus containing the relatively high concentration of 129 mg/kg white phosphorus:

a) 50 g of red phosphorus were extracted 3 times with 2.5 L of water for one hour. After extraction the concentration of white phosphorus in the solid red phosphorus had only slightly decreased to 122 mg/kg. This apparent reduction from the starting concentration is not significant, because it is within the range of the analytical error which amounts to ± 5 mg/kg. Furthermore, no elemental phosphorus could be detected in the water (limit of detection 1 mg/L).
b) 93 g of red phosphorus were extracted with 300 mL of water for three hours. The water was subsequently extracted with carbon disulfide (CS_2) and analysed for white phosphorus – no phosphorus could be detected at a limit of detection of 0.1 mg/L.

In summary, no elemental white phosphorus could be extracted from red phosphorus with water. Therefore, for instance an ecotoxicologic assessment of red phosphorus in the aquatic environment cannot be based on its content of white phosphorus but should be based on seperate studies with red phosphorus.

If traces of white phosphorus are released from the red phosphorus, they probably quickly react to phosphorus containing acids – the same products that the red phosphorus itself liberates. The source of these phosphorus containing acids be it white or red phosphorus cannot be distinguished by chemical analysis, because the products themselves are identical and red phosphorus as a starting material is present in immense excess.

4.3 Reaction rate of red phosphorus with water

Figure 7 indicates that the concentration of obtained hydrolysis products from red phosphorus steadily increases with the amount of dispersed red phosphorus in water. However, the reaction of red phosphorus with water is extremely slow. The average amount of reaction products from 100 mg/L after 24 h calculated as phosphorus is about 0.7 %. This fraction rises very slowly up to a maximum of 3.7 % of the nominal concentration of solid red phosphorus in water after 700 hours. In another experiment the soluble reaction compounds increased only up to 2.7 % after 2 880 hours (4 months). These data show that red phosphorus does not dissolve as such in water which renders the concept of a maximum solubility unapplicable. Instead, a continuous but slow series of reaction occurs leading to phosphorus containing acids. The amount of products formed increases with the available amount of red phosphorus and time.

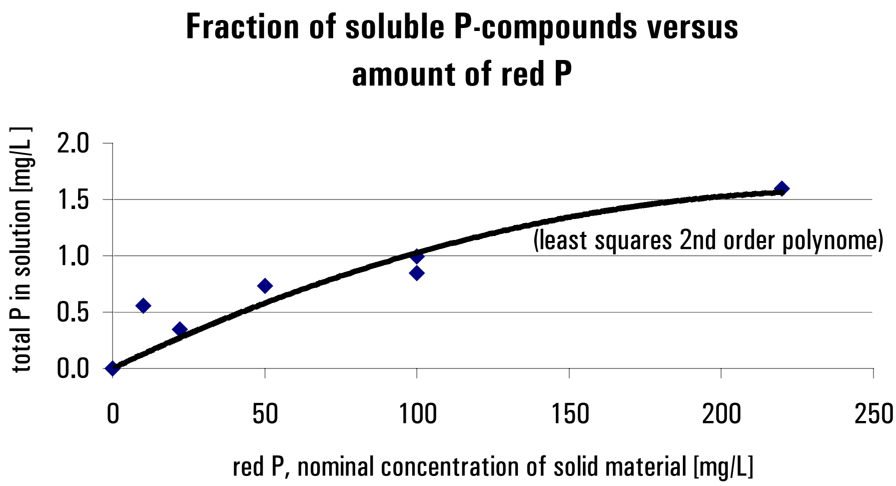

Figure 7: Concentration of phosphorus compounds (calculated as total phosphorus) in aqueous solution versus the amount of added solid red phosphorus