

The Variety of Phosphates for Refractory and Technical Applications by the Example of Aluminium Phosphates

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In 1669 the chemical element phosphorus was discovered by *H. Brandt*, an alchemist. In 1694 *Boyle* made the first phosphoric acid by dissolving phosphorus pentoxide (P_2O_5) in water. This was the start of the phosphorus chemistry. Since this time phosphoric acid and its salts have a firm place in chemistry and technical applications. Phosphates are part of our life and are used in a variety of ways also in industrial fields like refractories, glass, ceramics, construction industry and for a lot of other technical purposes.

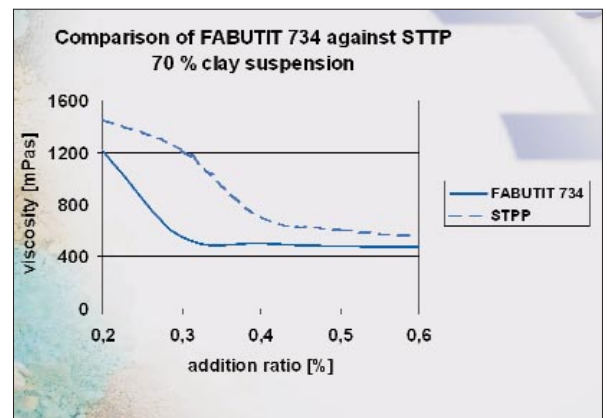
Phosphates in Refractory and Technical Industries

The most common and well known phosphates for technical applications are sodium tripolyphosphate ($Na_5P_3O_{10}$), sodium hexametaphosphate [$(NaPO_3)_n$] or monoaluminium phosphate ($Al(H_2PO_4)_3$). These phosphates are used as deflocculants, additives or binders. Sodium tripolyphosphate, abbreviated STPP (sodium **tripoly**phosphate), is a commonly used deflocculant for clay or materials containing clays in the ceramics industry, in refractories or in oil and gas prospect drilling. Already in these applications, phosphates show their variety. STPPs are not all the same. Modifications exist, which have a remarkable influence on the properties. FABUTIT 734 is an example for a chemical modified sodium tripolyphosphate. This product has an improved solubility, which effects the liquefaction in a positive way. Fig. 1 shows the result of a comparing test between a modified product like FABUTIT 734 against a commercial standard STPP.

In addition, STPP exists in two different crystal structures, a low and a high temperature phase. According to the production process the amount of the high temperature phase can be adjusted. This so called

Phase-I-content influences, for example, the dissolution property of STPP in water. The choice of the right phosphate can already be the crucial point even with such a "simple" phosphate like sodium tripolyphosphate.

The next step into the direction of complexity is a phosphate called sodium hexametaphosphate (SHMP) in colloquial language. In fact, the chemical name is a mistake. The name sodium hexametaphosphate would stand for a sodium phosphate with a ring structure ("meta"). But SHMP has a chaintype structure as can be proved. These melted glassy phosphates are polyphosphates with different chain lengths. The average chain length and thus the properties of the phosphate, like the pH-value for example, are controlled by the production process. Additionally the final product can be refined, for example by the process of instantising. This leads to sodium polyphosphates which have an improved solubility and dissolution speed. At the same time the hygroscopicity is reduced. The **Chemische Fabrik Budenheim** manufactures sodium



polyphosphates (SHMP) with pH-values between three and nine, most of the products also in an instantised quality (Fig. 2).

The mentioned examples illustrate the multiplicity of the phosphates. Beside STPP and SHMP, ammonium phosphates, aluminium phosphates, boron phosphates, calcium phosphates, alkaline phosphates, magnesium phosphates or zinc phosphates are used in different technical areas. To explain the variety of possible uses for phosphates in the field of refractories, additives, glass or enamel, the

Fig. 1
FABUTIT 734, a modified STPP against a standard STPP

Grade	Product No.	Bulk Density (g/l)	Chain length approx.	pH-value approx.	P ₂ O ₅ approx. (%)	Na ₂ O approx. (%)
BUDIT 3	N 16-07	1000	> 30	3.0	71.0	28.0
BUDIT 3 H	N 16-63	750	> 30	3.0	70.5	27.5
BUDIT 4	N 16-10	1000	30	3.8	69.5	30.0
BUDIT 4 H	N 16-31	750	30	3.8	69.0	29.5
BUDIT 6	N 16-36	1000	28	5.7	69.5	30.5
BUDIT 6 H	N 16-32	750	28	5.7	68.0	29.5
BUDIT 6 HF	N 16-36	1000	28	5.7	68.0	29.5
BUDIT 7	N 16-13	1000	16	7.0	67.0	32.5
BUDIT 7 H	N 16-39	750	16	7.0	66.5	32.0
BUDIT 8	N 16-14	1000	7	7.7	65.0	35.0
BUDIT 8 H	N 16-33	750	7	7.6	63.5	34.0
BUDIT 9	N 16-16	1000	4	8.7	61.0	39.0

H = instantised product / HF = instantised and fine milled

Fig. 2
BUDIT 3 to 9 as possible variations of sodium polyphosphate

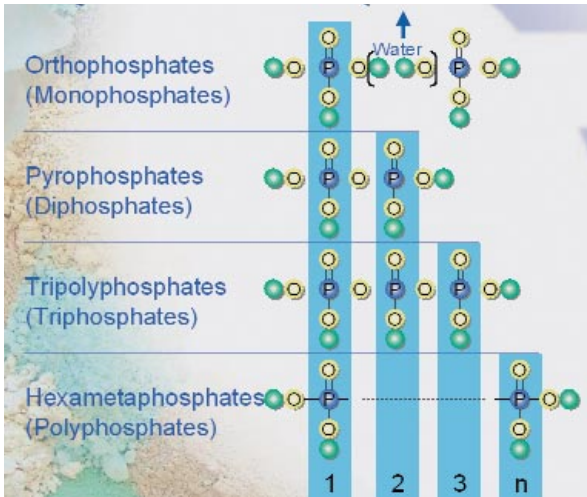


Fig. 3 Principle of polymerisation/types of phosphates

group of aluminium phosphates has been chosen and will be described in the following abstract.

The most well-known type of aluminium phosphate is of course the monoaluminium phosphate. But the family tree of aluminium phosphates is comprehensive and the possible uses of aluminium phosphate are extensive.

Aluminium Phosphates – Chemistry and Application

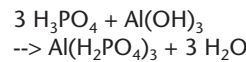
Aluminium phosphates exist in a variety of stages of polymerisation

and modifications. Starting point is always the reaction between phosphoric acid and a source of aluminium, like aluminium hydroxide, which leads to a monomer phosphate. The next step is the polymerisation process by temperature (Fig. 3). Polymerisation is the union of two or more molecules of given structure to form a new compound, usually accompanied by a thermal loss of water which results into the formation of di-, tri- or poly-phosphates.

In 1975 Tshako, Japan, summarized the formation of aluminium phosphates by thermal treatment (Fig. 4). The following illustrates the relevant aluminium phosphates in the areas of refractories, ceramics, glass and accompanying technical applications.

Monoaluminium Phosphate

The manufacturing process of monoaluminium phosphate from phosphoric acid and aluminium hydroxide can be described by the following equation of reaction:



This intense exothermic reaction must be controlled by the proper manufacturing process. The result is an aqueous solution marketed with a concentration between 40 and 60 %.

The raw materials for the production of monoaluminium phosphate are already important for the final quality. **Chemische Fabrik Budenheim** uses only a clear, white phosphoric acid of food quality. In the production process care is taken to ensure the correct basicity, the relation of Al_2O_3 to P_2O_5 , which has to be nearly exactly 1:3. This guarantees that no free phosphoric acid is present in the monoaluminium phosphate.

Monoaluminium Phosphate – All Liquids are not Alike

The use of the raw materials, the correct manufacturing process and chemical modifications leads to many chemical binders, which are all covered by the generic term of monoaluminium phosphate. Monoaluminium phosphate produced with technical phosphoric acid always lead to technical monoaluminium phosphates, which usually are unstable solutions of bad storability, where impurities tend to flocculate and sediment. A wrong basicity for example gives either a very unstable solution or very "reactive" solutions with a high amount of free phosphoric acid. Beside this, many technical monoaluminium phosphate liquids contain impurities like sulphur, heavy metals or fluorine (!), which are according to experience detrimental to any installations and facilities. This is the main reason why the **Chemische Fabrik Budenheim** only uses high-quality raw materials.

The torture of choosing applies also to monoaluminium phosphate.

The first monoaluminium phosphate liquid was produced in the roaring twenties and used as binder for chamotte. The outlier for the industrial use was the *Metallgesellschaft AG* (later the *Chemetall GmbH*) with the development of a binder called "Feuerfestbinder 32". This binder was based on a clever idea, covered by a publication with the headline "Mineralleim zur Bindung von Chamotten" (= engl. mineral glue to bind chamotte). This "mineral glue" had a similar composition as monoaluminium phosphate. The *Metallgesellschaft* turned this proposal to advantage and

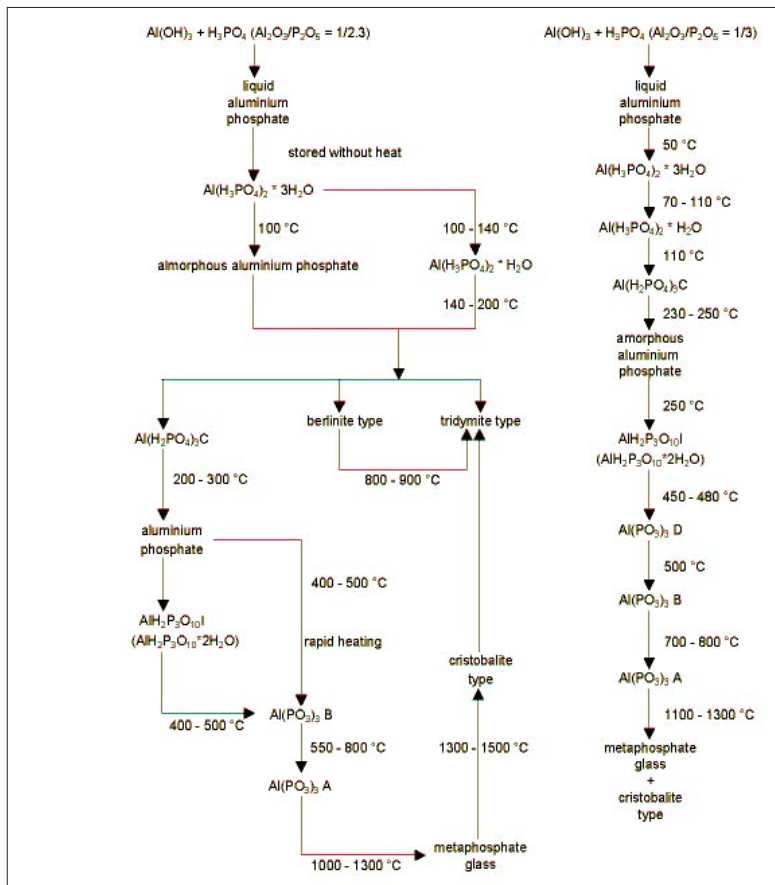


Fig. 4 The formation of aluminium phosphates by thermal treatment [Tshako]

developed the chemical binder FFB 32 using a sludge from amblygonite, a lithium-aluminium-phosphate, and phosphoric acid. This was the birth of phosphate-based bonding agents in Germany.

FFB 32 still exists. It is a clear, pure 50 % monoaluminium phosphate liquid for ceramics and refractories, produced by **Chemische Fabrik Budenheim**, which took possession of the binders activities of Chemetall at the end of 1999. Today monoaluminium phosphate, like FFB 32, is widely used as bonding agent or coating. Monoaluminium phosphate reacts with oxidic and non oxidic raw materials by the formation of phosphate salts, even at low temperatures. This is one of the main advantages of this sticky chemical binder. Starting at about 100 °C, bonded materials already have a high strength, which constantly increases until the ceramic bond comes into effect. From 300 to 350 °C the phosphate changes to an insoluble form. This is the reason why this temperature is often recommended when using monoaluminium phosphate. As a matter of principle the usage of monoaluminium phosphate is followed by lower firing temperatures as well as by a cost reduction in energy. But chemistry of course found ways to modify monoaluminium phosphate

Example: Inhibited Solutions

FFB 705 is an example for such a solution containing an inhibitor. In the manufacturing process an inhibitor is added and integrated into the chemical structure. Despite the very low content of the inhibitor included in the structure, the effect of the inhibitor is remarkable. The inhibitor is added to prevent or reduce undesired reactions with metallic iron, which are often included in minerals and raw materials, caused by the processing or by the deposit. The reaction of the metallic iron and the acid binder causes an undesired gas development. Additionally the inhibitor protects the facility and aggregates, because it reduces the attack on steel and iron. The effect of an inhibitor is shown by a test with steel plates, which were stored over night in phosphoric acid. Fig. 5 illustrates the attack of phosphoric acid and the protection of an appropriate inhibitor.

Additional modifications are possible. Today many different concentrations of liquid monoaluminium phosphates are found, or the amount of free phosphoric acid is adjusted. The production of a monoaluminium phosphate in powder type form is also possible. The varied use of such orthophosphate is remarkable.

The most common and well known application for monoaluminium phosphate is the bonding of refractories. Besides raw materials based on Al₂O₃, also basic raw materials can be used, which form quick setting refractories. Among other things the strong exothermal and very fast reaction between MgO and monoaluminium phosphate is used to produce cold setting systems. Examples for such self setting materials are repair mixes or modern materials like self setting inorganic foams, which isolate and which are fire proof (Fig. 6).

Monoaluminium phosphate is also needed for the oxidation protection. In this case the phosphate is used as coating to form a protective layer on graphite materials to reduce the deflagration of carbon. Another application for monoaluminium phosphate is so called electro insulating plates. In this case the property of monoaluminium phosphate to have a strong affinity to metal is advantageous. Also the use as binder for fibre materials is known. The bond with monoaluminium phosphate is brittle and hence not flexible, but the binder can withstand very high temperatures. This is a remarkable advantage compared with organic binders, like phenolic resins.

Other applications and uses are not only possible, but are found in practice. Monoaluminium phosphate penetrates applications which are far away from the classic ceramics or refractories industry. The **Chemische Fabrik Budenheim** always tries to find new fields of application, according to the slogan "Off the beaten track".

Aluminium Tripolyphosphate

Monoaluminium phosphate is the base for the production of aluminium tripolyphosphate (AlH₂P₃O₁₀) and additional polymeric aluminium phosphates. Aluminium tripolyphosphate is the next step of stable aluminium phosphates. Other intermediate stages like dialuminium phosphate for example, are sometimes

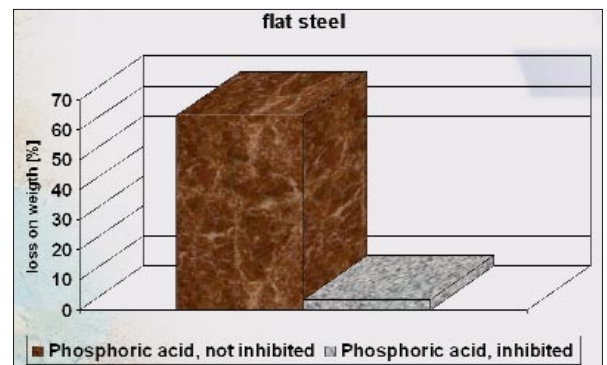


Fig. 5
The effect of an inhibited phosphoric acid coating on steel plates after storing over night

mentioned in the literature, but their existence has not yet been proved. It is to be accepted that such a dialuminium phosphate is an unstable intermediate stage of the polymerisation process.

Aluminium tripolyphosphate however exists in two different forms, an anhydrous product and a dihydrate. During the manufacturing process intermolecular water from the used monoaluminium phosphate is driven off. The resulting form is decided by the production temperature and the after-treatment.

The following equation of reaction describes the principle of polymerisation:



By firing at about 250 °C an aluminium tripolyphosphate anhydrous is produced, a material very rarely used in technical applications. But this material is the basis for aluminium tripolyphosphate dihydrate. The lost intermolecular water can be restored using thermal energy and water, which is done in a subsequent second manufacturing step. This leads to a phosphate, which is hardly soluble in water and acids. The main application for this phosphate is the use in corrosion protection, when aluminium tripolyphosphate is used to manufacture corrosion protective pigments.

Fig. 6
Inorganic foam bonded with monoaluminium phosphate



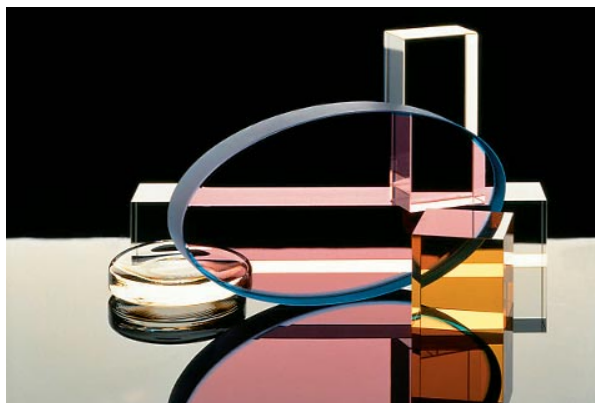


Fig. 7
Phosphate glass
products

But also aluminium triphosphosphate is a worthwhile candidate for application in new uses and to encounter new properties. At the moment the use of aluminium triphosphosphate is insignificant in refractories or the construction industry, but **Chemische Fabrik Budenheim** is looking for possible applications and possible modifications, either of chemical or of thermal kind to modify this phosphate in a useful way. An interesting field for example might be the incorporation into waterglass bonded systems to adjust the set time and to guarantee hardening of such mixes.

Trialuminium Phosphate

Trialuminium phosphate $AlPO_4$ exists in many different variants with different crystal structures. On the basis only of the manufacturing process two forms exist. The first is a thermally treated variant (trialuminium phosphate, heavy, anhydrous), the second one is prepared by precipitation and forms a lightweight, hydrated product. The variants prepared by a thermal process are insoluble in water and acids. The precipitated variant on the other hand tends to dissolve in distinct acids. In both cases the trialuminium phosphates dissolve in an alkaline environment and form aluminates and/or alkali phosphates. $AlPO_4$ has a very high melting point of approx. 1 850 °C and its crystal structure is isomorphous to quartz (SiO_2). This signifies that trialuminium phosphate also exists in the crystal structure of tridymite and cristobalite. The conversion temperatures of quartz in comparison to $AlPO_4$ clarify the relationship between these mineralogical phases.

SiO_2 : quartz
 \Leftrightarrow (867 °C) tridymite
 \Leftrightarrow (1 470 °C) cristobalite
 \Leftrightarrow (1 713 °C) melt

$AlPO_4$: berlinite
 \Leftrightarrow (705 °C) tridymite
 \Leftrightarrow (1 025 °C) cristobalite
 \Leftrightarrow (~ 1650 °C) melt

The inversion temperature at 575 °C between the low temperature quartz and high temperature quartz is also well known. Also in this case the behaviour is similar to trialuminium phosphate. But the inversion temperature of berlinite with 586 °C is a little higher. Meanwhile at least six types of $AlPO_4$ do exist, in accordance to the main variants of quartz.

After all this theoretical description the question arises for what purposes the industry uses such phosphates. The berlinite type material does have so called piezoelectric properties and is used for electronic devices.

$AlPO_4$ has a three dimensional structure. Its hardness and insolubility renders possible other applications. The structure and the apparent porosity, especially of the hydrated materials (Zeolite structure) make it possible to use such phosphates for the chemical catalysis, the desiccation of gas or additional chemical processes, like adsorption or ion exchange.

All these areas have nothing in common with ceramics and adjacent applications. But also here the trialuminium phosphate is suitable. The use for example in glass is known. The structural relationship of $AlPO_4$ to SiO_2 is already pointing into this direction. Both materials are known as materials having the capability of forming a glassy network by melting or in a glass melt.

According to this property trialuminium phosphate is used for example in glassy ceramic for dental application as well as in glassy coatings in ceramics or enamel. Glasses based on aluminium phosphates are characterised by a very good resistance against hydrofluoric acid (HF). Therefore this types of glasses are used for so called ionomeric glasses. Such glasses are employed in dental care, for example in ionomer glass cements below tooth-bridges or as filling for dental applications. Such organic/inorganic cements often contain fluorine, which are needed for healthy teeth. The fluorine is slowly released from the cement, but without destroying the cement itself. The trialuminium phosphate in the glass prevents the destruction of the ionomer cement.

Aluminium Metaphosphate/ Aluminium Polyphosphate

Aluminium metaphosphate and aluminium polyphosphate are manufactured from monoaluminium phosphate by a polymerisation process. The boundary conditions during the polymerisation determine the characteristic of the final aluminium phosphate, whether it will become a ring-type aluminium metaphosphate or an aluminium polyphosphate with a chain structure. Both products are nearly completely dehydrated, but due to the distinctive structures, the properties of the final phosphate are quite different. Both phosphates are insoluble in water and acids, but soluble in a strong alkaline environment. Due to its more stable ring structure aluminium metaphosphate dissolves much slower than the chain structured aluminium polyphosphate. The use and applications of the phosphates are closely assigned to these properties.

Aluminium metaphosphate is mainly used in glass and enamel. The very high amount of P_2O_5 of about 80 % makes this phosphate an ideal phosphorus source for glassy materials. The variety of aluminium phosphate glasses (Fig. 7) combined with the high demand in quality regarding colouring elements and impurities stretches from laserglass, optical glasses, filtering glasses to a glassy ceramic with a very low coefficient of expansion used as carrier for telescope mirrors as well as in the production for heat resistant glasses.

In the enamel industry the high P_2O_5 content is used mainly as a fluxing agent because of the glass network building property similar to SiO_2 . Contrary to SiO_2 the phosphate increases the coefficient of expansion of an enamel and also reduces the melting point. The alumina content of the aluminium metaphosphate improves the resistance of the glassy coating and also has a network building functionality.

Aluminium metaphosphate is already widely used in the industry, in contrast to aluminium polyphosphate with the chain structure, which, for the moment, has just a minor use. The manufacturing process of aluminium polyphosphate is much more difficult and requires very accurate production steps. Nevertheless, aluminium polyphosphate has very interesting properties which make it suitable for specific technical applica-

tions. Mainly the fact, that aluminium polyphosphate is more easily dissolved in an alkaline environment allows this phosphate to be used in some areas of the construction industry.

On the other hand it is noticeable that polymer aluminium phosphates arise in monoaluminium phosphate bonded refractories. This brings us back to the beginning and we have come to full circle.

Summary

This paper is an overview about phosphates and aluminium phos-

phates in particular. It is intended to give an impression about the chemistry and the use of phosphates and should give an idea for what kind of applications this products might be useful. It is always worthwhile to look into the complex inorganic phosphate chemistry when it comes to questions regarding chemical binders, additives or raw materials based on P_2O_5 .

The development and even the knowledge of aluminium phosphates and other phosphates are far from being complete. New manufacturing processes, new modifications and new ideas how to use

phosphates is the driven force of **Chemische Fabrik Budenheim**.

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