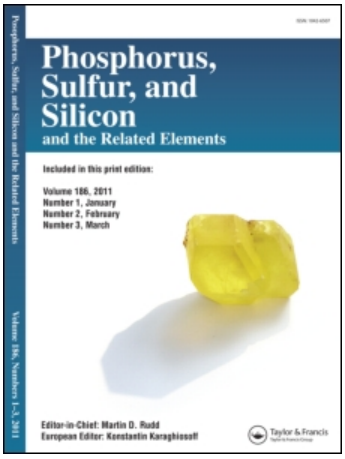

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The effect of purification of wet-process phosphoric acid (WPA), obtained from Kola apatite in one of the Polish plants, on sodium tripolyphosphate (STPP is a key constituent of detergents) formation and polymorphic transformation was investigated. Phase composition of the product, prepared by neutralisation of phosphoric acid with NaOH up to a molar ratio of Na/P = 5/3, water evaporation from the solution, and heating of the dry residue obtained, depends on the presence of SO_4^{2-}-ions in the acid and on the temperature of heating (250–550°C). When crude WPA, having 2 wt. % of SO_4^{2-}, was used, the formation of STPP was suppressed up to a temperature of 400°C, at which the low-temperature modification $Na_5P_3O_{10}$-II was observed. Transformation of $Na_5P_3O_{10}$-II (Form-II) → $Na_5P_3O_{10}$-I (Form-I), that was expected to occur in the range of 450–500°C, was also suppressed. To obtain Form-I heating at a temperature of 550°C was required. After WPA was purified down to 0.1 wt. % of SO_4^{2-} using $CaHPO_4{\cdot}2H_2O$ (with $Ca^{2+}/SO_4^{2-} = 1$) the low-temperature Form-II was not observed at any temperature of heating. The high-temperature modification (Form-I), that appeared at temperature as low as 300°C, remained stable while heated up to 550°C.

Keywords Phosphoric acid; purification; sodium tripolyphosphate; sulfate effect

INTRODUCTION

Sodium tripolyphosphate ($Na_5P_3O_{10}$)— STPP— is the key constituent of modern synthetic detergents.[1–5] It forms with Ca and Mg ions

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water-soluble complexes, buffers washing media, and protects the washing machine against corrosion. In contrast, the phosphate-free detergents, based on water-insoluble zeolites, absorb by ion-exchange Ca but not Mg. To increase the washing efficiency of the phosphate-free detergents several additional chemicals are required, such as non-biodegradable polycarboxylates, EDTA, citrate, enzymes, and other ingredients. Concerning the potential risk in surface water eutrophication related to the use of phosphates, CEEP (Centre European d'Etudes des Polyphosphates) estimates that the detergent phosphate contributes only about 10% to the total phosphate input to European surface waters. The remaining part is coming mostly from human wastes in sewage, and also from agriculture, industry and natural bed-rock erosion. The European Union Urban Waste Water Treatment Directive 91/271/EEC requires a removal of phosphates in sewage works even for small agglomerations in Europe. That means the necessity of phosphate removal from human wastes, independently whether phosphorus-containing or phosphorus-free detergents are used.

STPP exists in three crystalline monoclinic forms; the hexahydrate $Na_5P_3O_{10}{\cdot}6H_2O$ and two anhydrous modifications known as the low-temperature Form-II = $Na_5P_3O_{10}$-II (F2) and the high-temperature Form-I = $Na_5P_3O_{10}$-I (F1).[6–10] Depending on the temperature of heating, the STPP appears in one of the anhydrous forms. The polymorphic transformation, a complex and in the literature not entirely described process, has been observed in quite a wide (415–500°C°C) temperature range.[5] More frequently, the phase transformation has been reported in the temperature range of 450–500°C°C and, according to Van Wazer, is usually not complete even at higher temperature. It is commonly found that STPP heated above 500°C contains several % of the low-temperature form F2.[5,6,10]

The form F1 exhibits "lumping" properties resulting from extremely high solubility in water and the simultaneous formation of hexahydrate $Na_5P_3O_{10}{\cdot}6H_2O$ crystals from the supersaturated solution obtained. In the past, washing powders were made with high content of F2 because the lumping properties of F1 caused serious problems in the use of spray dryers. Modern technology makes the use of the STPP with high content of F1 possible. This involves shorter hydration time in the laundry detergent process. To meet the requirements of washing powder producers, the weight ratio of F1/F2 is either controlled by the temperature of heating or by mixing the final products of either form. Commercial STPP of diversified grades contains both crystalline phases, some small varying amounts of tetrasodium diphosphate ($Na_4P_2O_7$) and crystalline sodium metaphosphates $(NaPO_3)_n$.

A large number of starting materials can be employed in sodium tripolyphosphate preparation, providing that the molar ratio of Na/P is 5/3. Condensed sodium pyro- and polyphosphates are usually produced with the use of a two-stage dehydration method. The first of these stages consists in spray drying of the sodium orthophosphates solution obtained by the reaction of phosphoric acid with soda ash or NaOH. The second one is calcination of the dried orthophosphates in the directly heated rotary kiln.

In the industrial manufacturing procedure thermal or highly-purified wet-process phosphoric acid is mostly used. When the wet-process phosphoric acid (WPA) is used the effect of impurities, derived from the phosphate rock, on the quality of STPP should be taken into consideration. For example, pre-concentrated up to 77–80 wt. % H_3PO_4, industrial WPA, obtained from Kola apatite in one of the Polish plants, contains about 2% of SO_4^{2-}, 0.1% F, 0.5% Al, 0.3% Fe, 0.15% Ti, and some other elements at a lower level.[11] Considering the detergent (not food ingredient) industry production and the cost of purification of WPA, the question arises to what extent the phosphoric acid should be purified and how the impurities may affect the phase composition of the final STPP.

The aim of the investigations carried out in our laboratory is to determine how some impurities, present in phosphoric acid, may affect the phase composition of the STPP. It appears that such ions as Al^{3+} and Fe^{3+} stabilise the high-temperature modification (F1) and promote the transformation of F2 → F1 at a lower temperature compared to the impurity-free STPP temperature range.[12]

The present paper reports the effect of SO_4^{2-} on phase composition and polymorphic transformations of the STPP prepared from the following acids:

1. from reagent-grade phosphoric acid (*Reagent PA*) without impurities and with SO_4^{2-} ions introduced (the effect of SO_4^{2-} - ions); and
2. from commercial wet-process phosphoric acid produced in one of the Polish plants; (*crude WPA*, containing 2 wt. % of SO_4^{2-}), and purified from sulfate (*WPA-1*, containing 0.1 wt. % SO_4^{2-}).

RESULTS

Phase Composition of the STPP Obtained from (*Reagent PA*). Effect of SO_4^{2-} on the Polymorphic (F2 →F1) Transformation

The XRD patterns presented in Figures 1–3 demonstrate some differences in the STPP phase composition depending on SO_4^{2-} presence and

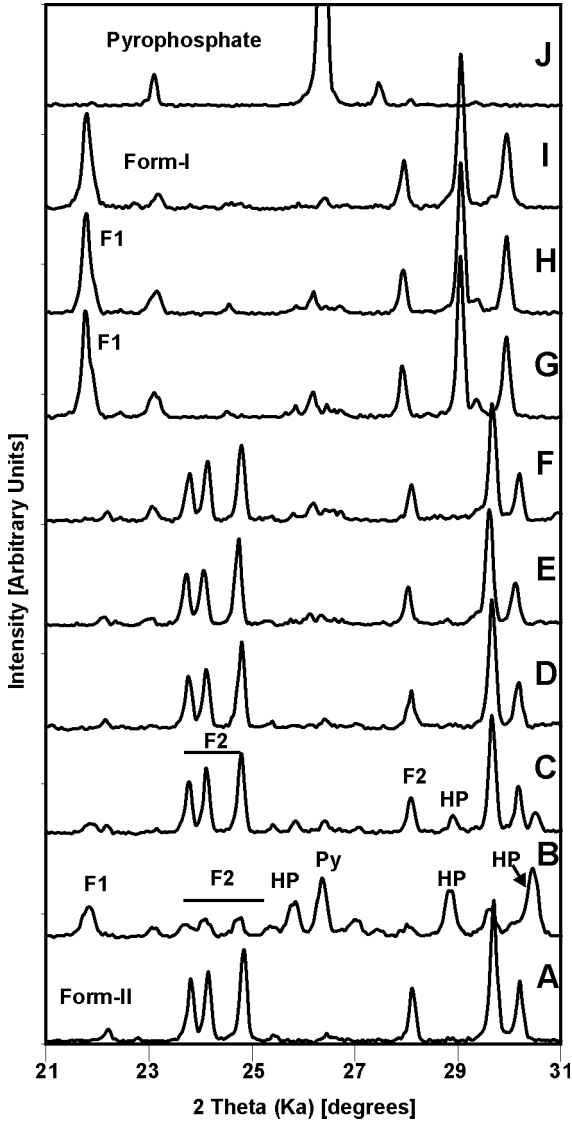

FIGURE 1 XRD patterns of impurity-free $Na_5P_3O_{10}$ heated with increasing temperature: (B) = 250°C; (C) = 300°C; (D) = 350°C; (E) = 400°C; (F) = 450°C; (G) = 500°C; (H) = 550°C in comparison to (A) $Na_5P_3O_{10}$-II (Form-II)—standard; (I) = $Na_5P_3O_{10}$—I (Form-I) – standard; and (J) = $Na_4P_2O_7$ (pyrophosphate)—standard. (Peaks: F1 = Form-1, F2 = Form-II, Py = $Na_4P_2O_7$, HP = $Na_2H_2P_2O_7$).

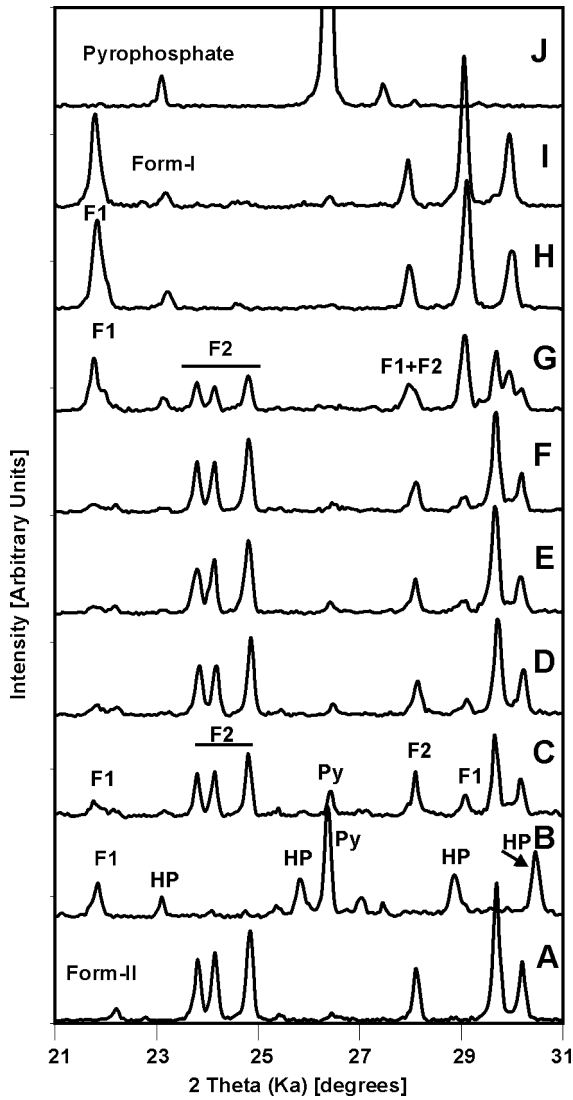

FIGURE 2 XRD patterns of $Na_5P_3O_{10}$ (with 0.5 wt. % of SO_4^{2-}) heated with increasing temperature: (B) = 250°C; (C) = 300°C; (D) = 350°C; (E) = 400°C; (F) = 450°C; (G) = 500°C; (H) = 550°C in comparison to (A) $Na_5P_3O_{10}$—II (Form-II)—standard; (I) = $Na_5P_3O_{10}$—I (Form-I)—standard; and (J) = $Na_4P_2O_7$ (pyrophosphate)—standard. (Peaks: F1 = Form-1, F2 = Form-II, Py = $Na_4P_2O_7$, HP = $Na_2H_2P_2O_7$).

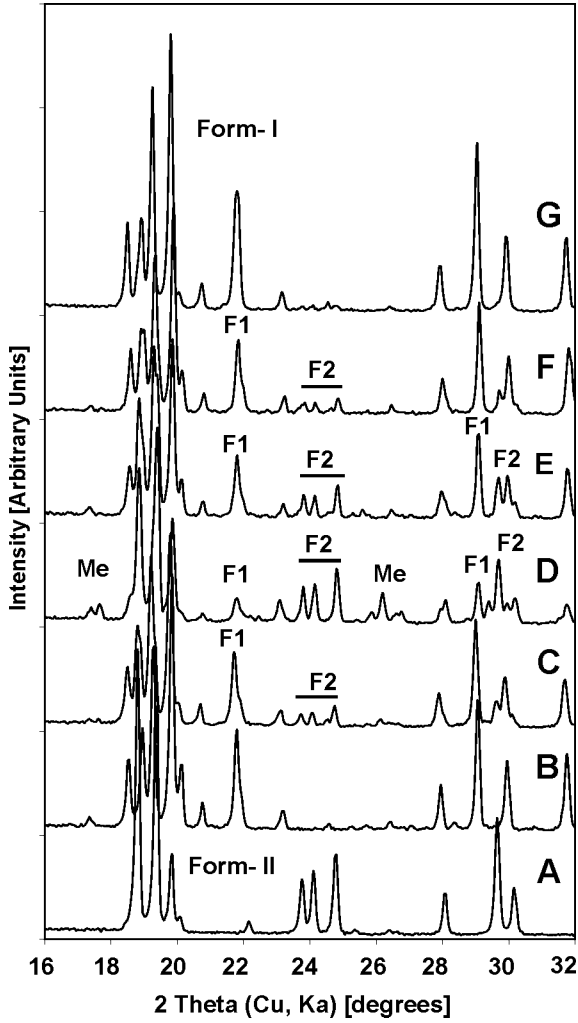

FIGURE 3 XRD patterns of $Na_5P_3O_{10}$ heated at a temperature of 500°C. (A) = $Na_5P_3O_{10}$—II (Form-II)—standard; (B) = impurity-free (reference sample); (C) = ($Na_5P_3O_{10}$ with 0.1 wt.% SO_4^{2-}); (D) = ($Na_5P_3O_{10}$ with 0.15 wt.% SO_4^{2-}); (E) = ($Na_5P_3O_{10}$ with 0.5 wt.% SO_4^{2}); (F) = ($Na_5P_3O_{10}$ with 1.0 wt.% SO_4^{2-}); and (G) = $Na_5P_3O_{10}$—I (Form-I)—standard. (Peaks: F1 = Form-1, F2 = Form-II, Me = $NaPO_3$).

on temperature of heating. For comparison, the XRD patterns of F1, F2, and also of tetrasodium pyrophosphate ($Na_4P_2O_7$) are included as standards in the figures. For identification of F1 in the mixture (F1 + F2) the unique non-overlapping diffraction peak of a reasonable intensity at

$2\Theta \approx 21.7$ and another one at $2\theta \approx 29.0$ degrees have been used.[13] The positions of the other peaks, located outside the range of $2\theta = 21–31^\circ$, are not helpful in phase analysis because of their superimposition.

At a temperature of 250°C at the beginning of STPP formation the metastable high-temperature modification F1 was observed in the impurity-free (Figure 1B), as well in the SO_4^{2-}-containing sample (Figure 2B). F2 that appeared within the temperature range of 250–300°C, was stable up to 450°C (Figure 1C–F, 2C–F). In the impurity-free STPP, the polymorphic transformation of F2 → F1 occurred within the temperature range of 450–500°C (Figure 1F–G), which is in agreement with the literature,[5,6] while in the presence of sulfate ions the transformation into F1 was not completing in that temperature range. STPP with sulfate ions (0.5 wt. % SO_4^{2-}) obtained at 500°C (Figure 2G) was still a mixture of F1/F2 and to complete the polymorphic transformation temperature higher than 500°C was required. A selection of XRD patterns presented in Figure 3 indicates, that the inhibiting effect of SO_4^{2-} on the F2 → F1 transformation observed at 500°C does not depend on the investigated concentration (0.1–1.0 wt. %) of SO_4^{2-}. In some cases, when metaphosphate $NaPO_3$ (denoted as Me in Figure 3D) appeared, the suppressive effect (less F1 at 500°C) on the polymorphic transformation was stronger. That can be referred to van Wazer's opinion, that converted products, in which there is a large proportion of crystalline metaphosphate, cannot be further converted to sodium tripolyphosphate by heat treatment even for a long time.[5]

The results with sulfates reported in the present work correspond, to some extent, to those described by Dombrovski et al., indicating an inhibitory effect of Na_2SO_4 (5–15 wt. %) on thermal dehydration and subsequent condensation of Na_2HPO_4 (but not of NaH_2PO_4, or of the double salt $Na_3H_3(PO_4)_2$.[14] However, those amounts of sulfate were too large to be compared with the present work.

Phase Composition of the STPP Obtained from Industrial Wet-Process Phosphoric Acid

Figures 4 and 5 demonstrate that the phase composition of the STPP obtained from wet-process phosphoric acid neutralized with NaOH up to a ratio Na/P = 5/3, depends not only on the temperature of heating but also on the purification of the acid from SO_4^{2-}. An exception is the XRD pattern of the solid obtained at 250°C, which shows the presence of pyrophosphate ($Na_4P_2O_7$) and which does not depend on the purification of WPA from SO_4^{2-} (compare Figure 4A with Figure 5A).

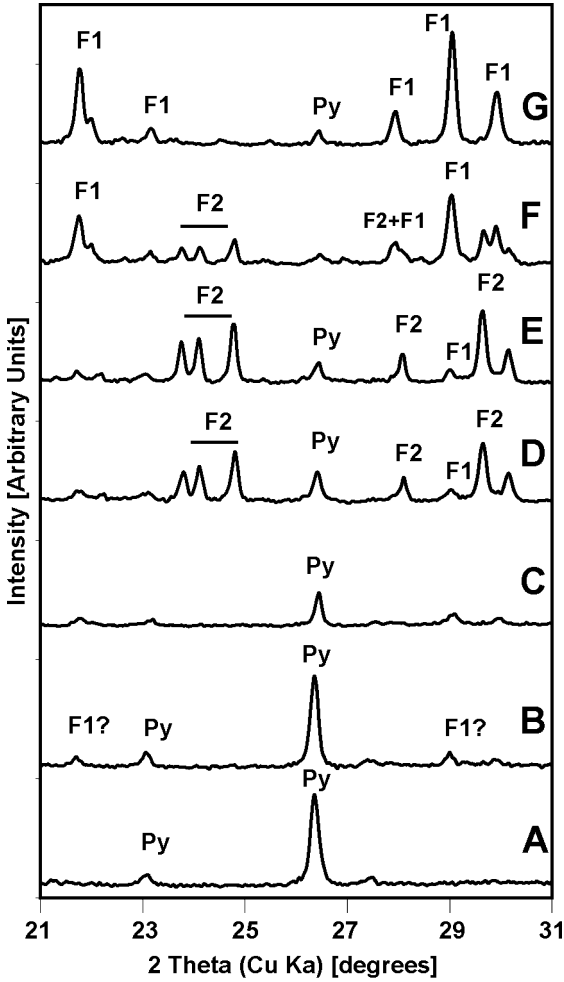

FIGURE 4 XRD patterns of $Na_5P_3O_{10}$ obtained from *crude WAP* and heated with increasing temperature: (A) = 250°C; (B) = 300°C; (C) = 350°C; (D) = 400°C; (E) = 450°C; (F) = 500°C; and (G) = 550°C. (Peaks: F1 = Form-1, F2 = Form-II, Py = $Na_4P_2O_7$).

When *crude WPA*, having 2% of SO_4^{2-}, was used the STPP formation was suppressed at low temperatures (Figure 4A–C) up to 400°C, when the low-temperature form F2 was observed (Figure 4D). Within the range of 400–450°C the crystalline low-temperature form F2 was dominant, while F1 was a negligible component. The polymorphic transformation of F2 into F1, expected within 450–500°C, was suppressed;

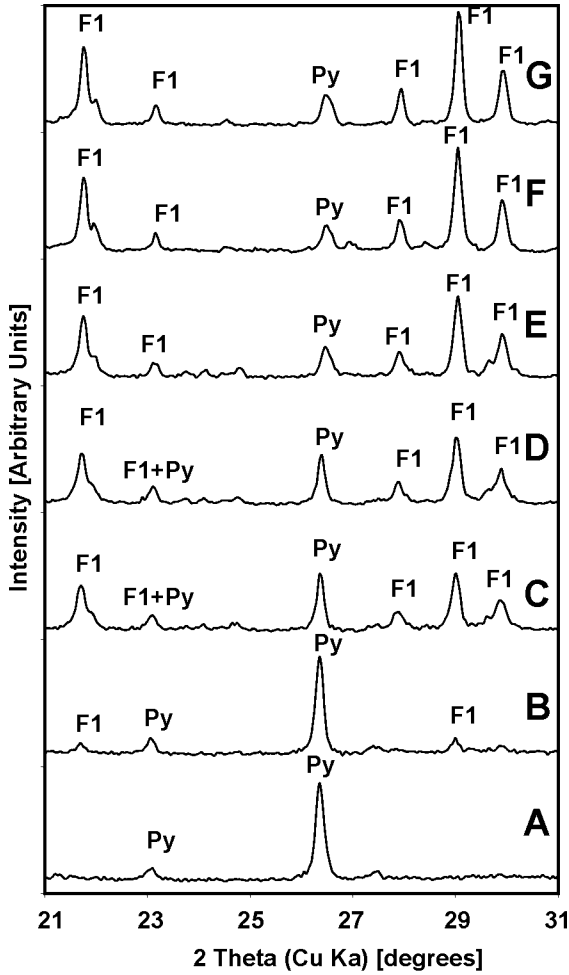

FIGURE 5 XRD patterns of $Na_5P_3O_{10}$ obtained from purified from sulfate*WAP-1* and heated with increasing temperature: (A) = 250°C, (B) = 300°C; (C) = 350°C, (D) = 400°C; (E) = 450°C°C; (F) = 500°C; and (G) = 550°C. (Peaks: F1 = Form-1, F2 = Form-II, Py = $Na_4P_2O_7$).

heating at 500°C (Figure 4F) yielded still a mixture of F1 and F2 similar to that obtained from (*Reagent PA*) containing SO_4^{2-}, (Figures 2G and 3C–F). For completion of the polymorphic transformation a temperature higher than 500°C was required.

Purification of *crude WPA* down to 0.1 wt. % SO_4^{2-}, yielding *(WPA-1)* by sulfate precipitation using $CaHPO_4{\cdot}2H_2O$ with a stoichiometric molar ratio $Ca^{2+}/SO_4^{2-} = 1.0$, significantly affects the phase composition

of STPP (Figure 5). The low-temperature form F2 was not observed at any temperature of heating. The high-temperature modification (F1) started to form directly from pyrophosphate at temperatures as low as 300°C (Figure 5B) and remained stable while subsequently heated at higher temperatures up to 550°C (Figure 5C–G). The observed increase in the intensity of the F1 peaks indicates that the amount of F1 in the STPP increased at the expense of pyrophosphate while temperature was rising.

DISCUSSION

The data published in the literature refer mostly to the dehydration of mono- and/or disodium orthophosphates.[10,16–21] In the phosphate industry, condensed sodium pyro- and polyphosphates are usually produced not by direct thermal decomposition of solid Na_2HPO_4 and NaH_2PO_4 but with using a two-stage dehydration method. The first of these processes consists in water evaporation from the sodium orthophosphate solution. The second stage is heating of the dry residue obtained. In some reports an emphasis has been put on the role of an amorphous phase in the STPP formation and its polymorphic transformation. Drying of an orthophosphate solution with a Na/P = 5/3 molar ratio yields a mixture of the anhydrous double salt $Na_3H_3(PO_4)_2$, $Na_2HPO_4{\cdot}2H_2O$, anhydrous Na_2HPO_4, and sometimes a small amount of $Na_4P_2O_7$. Subsequent heating of the above mixture at higher temperatures results in further dehydration and subsequent condensation to give crystalline $Na_4P_2O_7$ and an amorphous phosphate phase, which according to Edwards and Herzog, on prolonged heating at 200°C transforms into crystalline $Na_2H_2P_2O_7$.[15] The appearance of the amorphous phase was deduced from the difference between the amount determined by chromatographic and XRD methods. The chromatographic indicated ortho-, pyro-, tripoly-, and tetrametaphosphates, while the XRD method showed crystalline $Na_4P_2O_7$ and $Na_5P_3O_{10}$.[10,15] Further heating, at temperatures higher than 250°C, results in evolution of more water and, at a temperature around 300°C, in the formation of $Na_5P_3O_{10}$ according to the reaction: $2\ Na_4P_2O_7 + Na_2H_2P_2O_7 \rightarrow 2\ Na_5P_3O_{10} + H_2O$. The mechanism postulated by J. Edwards and A. H. Herzog at a lower temperature of heating, involves dissolution of $Na_4P_2O_7$ in the amorphous phase, countercurrent migration of Na^+ and H^+ and, without the need of diffusion of the bulky phosphate ions at any degree of condensation, the formation of possibly amorphous $Na_5P_3O_{10}$ at the crystal-amorphous phase interface.[15] Most of the orthophosphate mixture heated to 350–400°C is converted into the low-temperature modification $Na_5P_3O_{10}$–II.[6,10]

Another reported observation suggests that the transition of F2 → F1 is a unidirectional process.[5] Tempering of $Na_5P_3O_{10}$-II above the transition temperature converts it into $Na_5P_3O_{10}$-I, but it does not reconvert the product to $Na_5P_3O_{10}$-II when tempered below the transition temperature, even for a very long time. However, when $Na_5P_3O_{10}$-I is formed from not crystalline (glassy) material, and then tempered below the transition point it reconverts to F2. That observation prompted van Wazer to the conclusion, that the appearance of the high-temperature form F1 observed during the low-temperature condensation of ortho-phosphates and its subsequent reconversion to F2 is catalyzed by the presence of the amorphous material.

In the present work, the appearance of the high-temperature modification (F1) shown in the Figures 1B and 2B can be justified by the Gay-Lussac-Ostwald step rule, which states, that in the case of substances exhibiting several forms the less stable form is usually produced before the stable form appears.[5] In such cases, the amount of the unstable form, if it appears below the transition point, becomes gradually larger, goes through a maximum and then declines as the stable modification starts to form. The peak at $2\Theta = 21.7^\circ$ (denoted as F1) corresponding to Form-1, which appeared at a metastable stage below the transition temperature, was declining and disappeared when the temperature was rising (Figures 1B–F). The observed phenomenon is consistent with that published by Edwards and Herzog.[15] Their XRD data on heating the orthophosphates at 250°C indicated variation in composition with time in the following sequence: $Na_4P_2O_7$ (after 15 minutes) → $Na_5P_3O_{10}$-I (after 30 minutes) → $Na_5P_3O_{10}$-II (after 60 minutes). The appearance of $Na_2H_2P_2O_7$ shown in Figures 1B and 2 B as HP-peaks is also in agreement with Edwards and Herzog.

Analyzing the effect of purification of WPA from sulfate ions, two different phenomena have been revealed by the present work. They are 1) the inhibitory effects of SO_4^{2-} ions; and 2) the total disappearance of the low-temperature modification (F2) after purification of WPA from sulfate.

Inhibitory Effects of SO_4^{2-} Ions

The SO_4^{2-} ions displayed inhibitory effects in 1) the polycondensation of phosphates obtained from *crude WPA* in the low temperature range of 250–400°C (Figure 4A-C); and 2) the polymorphic transformation of F2 → F1 in the temperature range of 450–500°C (Figure 4F, supported by Figures 2G, and 3C–F).

1. The inhibitory effect of Na_2SO_4 on dehydration and subsequent condensation of Na_2HPO_4 and of the mixture containing (NaH_2PO_4+ 2 Na_2HPO_4) was mentioned twice in the literature.[14,20] According to Dombrovski, the rate of phosphate condensation consisting of P—O—P formation and simultaneous water evolution is determined by a concentration of mobile protons (delocalized H^+) in the bulk and on the surface of the crystal, the presence of hydrogen bonds and point defects.[14,18] The additives that increase the H^+ concentration and its mobility in the crystal act in favor of phosphate condensation, while those that decrease the H^+ concentration counteract it. The existence of mobile protons treated as "proton gas" and their migration in crystalline acidic salts was proved by Murphy by ionic conduction measurement in $NH_4H_2PO_4$.[22] The H^+ ion migration by thermal diffusion through interstitial positions or crystal defects (cationic vacancies) increases the probability of a chemical reaction between the proton and an OH group, leading to phosphate condensation. The transfer of H^+ ions in crystalline Na_2HPO_4 is possible along a linear complex of HPO_4 tetrahedra linked by hydrogen bonds. According to Dombrovski it is possible, that substitution of HPO_4^{2-} by SO_4^{2-} decreases the concentration of protons and generates discontinuity in the line of HPO_4 tetrahedra linked by hydrogen bonds. The interference of SO_4^{2-} with phosphate ions may cause some hindrance to the mobility of the protons in the crystal thus hampering the process of condensation.[14,20] This can also be referred to the results obtained in the present work, when *crude WPA*, with high (2%) concentration of SO_4^{2-}, was used for the STPP preparation; the formation of STPP was suppressed up to temperatures high enough (400°C) to increase mobility of the lattice elements enabling their regrouping into $Na_5P_3O_{10}$ (Figure 4D).
2. It is commonly accepted that F2 transforms into F1 within a temperature range of 450–500°C. Such a transformation in that temperature range was observed also in the present work (Figure 1F–G) in the impurity-free sample. However, the examples in Figures 2G, 3C–F, and 4F indicate that to complete the polymorphic F2 → F1 transformation in the presence of SO_4^{2-} ions, temperatures higher than 500°C are required. That effect is also visible in the IR-spectra of STPP obtained from *crude WPA* as compared to *WPA-1*purified from sulfate. As an example the IR spectra of a sample obtained at 500°C is shown in Figure 6. An identification of the phases in the mixture of F1/F2 is based on the appearance of nonoverlapping IR bands at wavenumbers of 715 cm^{-1} and 756 cm^{-1}, corresponding to Form-I (marked as *) and of 667 cm^{-1} corresponding

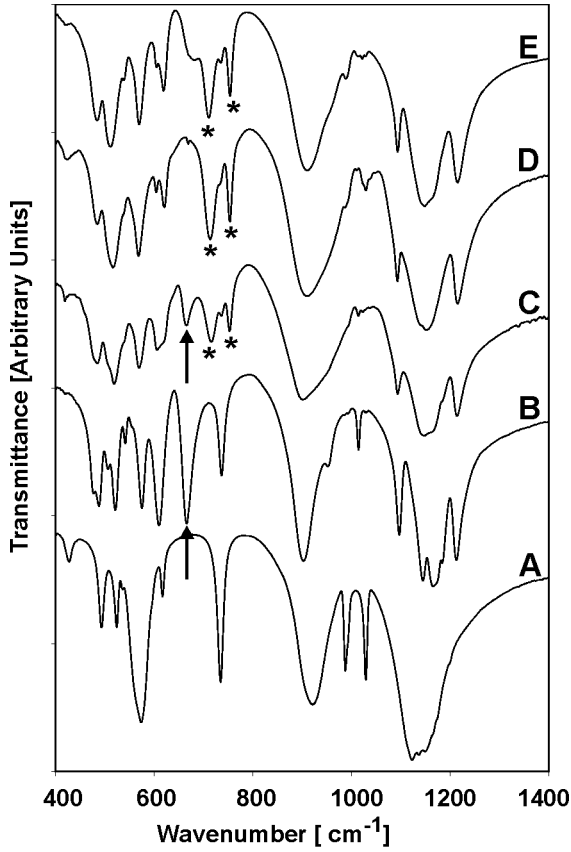

FIGURE 6 IR-spectra of $Na_5P_3O_{10}$ obtained from industrial wet-process phosphoric acid and heated at 500°C in comparison to (A) = ($Na_4P_2O_7$)—standard; (B) = $Na_5P_3O_{10}$—II (Form-II)—standard; (C) = STPP obtained from *crude WPA*; (D) = obtained from *WAP-1* (purified from sulfate); and (E) = $Na_5P_3O_{10}$—I (Form-I)—standard, IR bands: (*) = (715 cm^{-1}) and (756 cm^{-1}) = Form-I, (↑) = (667 cm^{-1}) = Form-II).

to Form-II (arrow). At the present stage of our investigations the suppressive mechanism by SO_4^{2-} on the polymorphic F2 → F1 transformation in the temperature range of 450–500°C cannot be described.

Total Disappearance of the Low-Temperature Modification $Na_5P_3O_{10}$- II (F2) After Purification of WPA from Sulfate

Purification of WPA from sulfate affects significantly the phase composition at the beginning of the STPP formation. The stable

low-temperature F2, that, according to the Gay-Lussac-Ostwald step rule, was supposed to follow the metastable F1, was not formed at any temperature of heating, while the high-temperature form F1 started to form at temperatures as low as 300°C (Figure 5B). The possible explanation can be found in our previously reported results, indicating the effects of Fe and/or Al on the STPP formation.[23] It appeared that Al^{3+} and Fe^{3+} stabilized the high-temperature modification (F1) in the temperature range of 300–450°C. The stabilizing effect was concluded to be a result of Al^{3+} and Fe^{3+} adsorption. The impurities adsorbed on the surface of the metastable Form-I are supposed to inhibit its conversion into the stable Form–II . The question arises why the stabilising effect of Al^{3+} and Fe^{3+} does not appear when the *crude WPA* is used. In *crude WPA* the amount of SO_4^{2+} (2 wt. %) dominates over the amount of other impurities, such as Al^{3+} and Fe^{3+} (0.3–0.5 wt. %). It is possible, that the effect of SO_4^{2-} on STPP formation is stronger than the opposite effects caused by Al^{3+} and Fe^{3+}, being at a lower concentration. After purification from sulfate, the concentration of cationic impurities in *WPA-1,* and their effects become dominant.

It seems that also in the present work the amorphous phase discussed earlier cannot be neglected in STPP formation and in the polymorphic transformation. When more than one crystalline phase is observed by XRD (example in Figures 1B and 2B) and quantitative assessment of the phase proportions is not possible, there is no direct evidence indicating the existence of the amorphous phase. However, when the XRD of the phosphates with a molar ratio of Na/P = 5/3 exhibits only crystalline $Na_4P_2O_7$ with the molar ratio of Na/P = 4/2, (Figure 4A–C), the rest of the sodium phosphates should be in the amorphous phase. That reasoning does not exclude the existence of the amorphous phase also in the samples presented in Figures 1B and 2B. When impurities such as Fe^{3+} and Al^{3+} are present, as it is the case in WPA, and they do not form a separate phase observed by XRD in the heated products, they may be in amorphous phase, adsorbed on the surface, and/or incorporated into another crystalline phase. If Fe^{3+} and Al^{3+} are in the amorphous phase, this may enhance the mediatory effect described by Edwards and Herzog between the $Na_4P_2O_7$ and $Na_5P_3O_{10}$, while STPP is formed.

EXPERIMENTAL

Materials and Methods

STPP was prepared on a laboratory scale from the following starting materials.

1. Reagent-grade phosphoric (*Reagent-PA*) acid (86.3 wt. % H_3PO_4) (POCH-Poland) was used to make the reference sample of STPP without impurities. To prepare STPP with SO_4^{2-}ions an appropriate amount of $Na_2SO_4 \cdot 10H_2O$ was dissolved in *Reagent-PA*. The amount of SO_4^{2-} was such as to result in 0.1–1.0 wt. % of the ion in the final dry product. The investigated level of impurities covers the level of SO_4^{2-} in desulfated WPA to some extent.
2. Industrial, wet-process phosphoric acid, preconcentrated up to 80 wt. % of H_3PO_4, was obtained from Kola apatite in one of the Polish plants (*crude WPA*). It contained about 2 wt. % of SO_4^{2-}. The (*crude WPA*) was purified by sulfate precipitation using $CaHPO_4 \cdot 2H_2O$ as precipitant. The temperature of precipitation was 80°C, the time of precipitation was 60 min. The amount of $CaHPO_4.2H_2O$ was equivalent to a molar ratio of $Ca^{2+}/SO_4^{2-} = 1.0$. This resulted in (*WPA-1)* with 0.1 wt. % of SO_4^{2-}.

For the preparation of STPP phosphoric acid was neutralized with sodium hydroxide-containing 20 wt. % of NaOH until the molar ratio of Na/P became 5/3. From the solution of the orthophosphates obtained the water was evaporated. The dry residue was heated at temperatures of 250°C, 300°C, 350°C, 400°C, 450°C, 500°C, and 550°C for two hours. The heated materials were identified using powder X-ray diffraction (XRD) and IR spectroscopy. For the XRD, a Philips X'pert equipment with graphite monochromator PW 1752/00, radiation Cu K_α, Ni filter, and 2Θ from 10–60° at 30 kV, 30 mA was used. A Fourier Transform IR Spectrometer FTIR-FTS 175 (Bio-Rad) was used to record the IR spectra of the samples in KBr pressed pellets covering the wavenumbers 400–4000 cm^{-1}.

CONCLUSIONS

The phase composition of STPP, prepared by neutralization of phosphoric acid with NaOH until a ratio of Na/P = 5/3 is reached, water evaporation from the solution, and heating of the dry residue obtained, depends on the presence of SO_4^{2-} ions in the acid and on the temperature of heating.

For the STPP preparation, wet-process phosphoric acid obtained from Kola apatite in one of the Polish plants (*crude WPA*—without purification) and phosphoric acid purified from sulfate (*WPA-1*) were applied. For comparison, STPP was also prepared from reagent-grade phosphoric acid without impurities (reference sample) and in the presence of 0.1–1.0 wt. % of SO_4^{2-}.

In the low temperature range (250–300°C) at the beginning of STPP formation, a small amount of the high-temperature modification F1 was observed in all samples independently of the phosphoric acid used (reagent-grade or *crude WPA* or *WPA-1*).

In the STPP obtained from reagent-grade phosphoric acid the phase F1 transformed readily into the low-temperature phase F2, while the temperature was increasing up to 350°C. The appearance of the metastable form F1 in the low temperature range and its transformation into the stable form F2 is in agreement with the Gay-Lussac-Ostwald step rule.

When *crude WPA*, having 2 wt. % of SO_4^{2-}, was used for the STPP preparation, the formation of STPP was suppressed up to a temperature of 400°C, at which the low-temperature modification F2 was observed. Also, the transformation F2 → F1, which was expected to occur within the temperature range of 450–500°C was suppressed. To obtain F1 heating at temperature of 550°C was required.

When *WPA-1* purified down to 0.1 wt. % of SO_4^{2-} was used, the low-temperature form F2 was not observed at any temperature of heating, while the high-temperature modification (F1), which appeared at temperatures as low as 300°C remained stable up to 550°C. The observed anomaly results from the effect of Al^{3+} and Fe^{3+} described earlier.[12,23] These impurities, present in WPA on the level of 0.3–0.5%, exhibit an effect opposite to that of SO_4^{2-}. Al^{3+}, and Fe^{3+} promote the formation of F1 and stabilize it in the low temperature range. In *crude WPA the* effect of SO_4^{2+} dominates over the effect of Al^{3+} and Fe^{3+}. After purification from sulfate, the concentration of cationic impurities in *WPA-1* and their effects become dominant.

Practical Conclusion

The WPA could be applied for STPP preparation under the condition that (i) crude (not purified from sulfate) WPA is used to make the low-temperature modification (Form-II) of STPP by heating at a temperature of 400°C; and (ii) To obtain the high-temperature Form-I the WPA should be purified from sulfate down to 0.1 wt. % of SO_4^{2-}. For heating of Form-I, a temperature of 400–450°C, instead of 550°C, can be applied. The final product with the required ratio of Form-I/Form-II can be made by mechanical mixing of the single products: (i) + (ii).

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