

Invited Review

Phosphoric Acid, Phosphates and Fertilizers for the Future

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(Received on 30 November 1990; after revision 25 February 1991; Accepted on 28 January 1992)

The last few decades have witnessed a tremendous agrarian development that has no parallel in the agricultural history of the world. This revolution which has resulted in a phenomenal increase in crop output per unit of land and has so remarkably scaled down the dimensions of the food crisis, has its roots in two main sources—the evolution of innumerable new varieties of crops with high yield potentials and the ready availability of fertilizers which form the life line for meeting their increased nutritional demands. Intensive cropping of high yielding varieties characterises the new world agriculture, with the consequence that fertilizers have become indispensable regardless of the nature of the soil. In fact, fertilizer requirement for the same unit of produce has been increasing steadily both in terms of quantity as well as nature of nutrients. With rapid nutritional depletion of soils, that is only to be anticipated as a consequence of the adoption of even more intensive agricultural practices, fertilizer application can be expected to further increase in the future.

Concomitant with frequent addition of high doses of fertilizers, is the magnification of the environmental hazards to the soil and water. Accumulation of anions like Cl^- and SO_4^{2-} , soil salinisation and acidification, leaching of NH_4^+ , NO_3^- , etc., and the subsequent contamination of ground water are some of the damages caused by long term fertilizer application. Although acute awareness of the problems, resulting from such

treatments, does exist, yet little can be done at present to avoid it. The main reason for this is the near total dependence on the use of water soluble salts as macro- and micro-nutrient fertilizers. The high solubility of fertilizers is not only the factor for leaching and contamination of ground water but is also, for the same reason, an economically wasteful proposition. Thus quite often, even upto 80% of urea added to a soil, may be lost by leaching and volatilisation and only a small fraction of micronutrients, that are used as foliar sprays, is available for plants. With the growing need for efficient utilisation of resources, such a waste of materials is most deplorable and calls for a radical change in the nature of the inorganic fertilizers.

The obvious solution to overcome the drawbacks of the traditional fertilizers is to replace them with compounds that are only sparingly soluble in water. Most insoluble salts, however, are not usable as fertilizers since the nutrient ions in them are not readily 'available' to plants. Only compounds from which plant roots can extract ions by exchange reactions, and compounds which undergo hydrolysis and solubilisation at optimum rates to fulfil the requirements of the plants, are suitable as fertilizers. The insoluble fertilizers must be, therefore, either 'slow-releasing' or must contain nutrients in exchange sites. Slow-releasing fertilizers are the latest concept in fertilizer technology. The so-called 'coated' fertilizers are not, *sensuo stricto*, slow-releasing be-

cause once the coating is lost or even broken, they become factually soluble fertilizers. A real slow-releasing fertilizer can only be formulated at the molecular level. A prime example of the application of this concept is the production of urea-formaldehydes (Sauchelli 1964, 1967) and other such N-fertilizers of low solubility (NDC 1968) including crotonylidene diurea (CDU) and isobutylidene diurea (IBDU). These fertilizers, in spite of their obvious advantages, have, however, found only very limited applicability. The main reason for it is the cost viability of the compounds which are produced from fairly expensive raw materials. Other such slow-releasing fertilizers of phosphorus and potash have fared no better for the same reasons. Albeit, in spite of the unfavourable economics of the existing slow-releasing fertilizers, there is no doubt that such materials are the only answer to the problems of inorganic fertilization and the sooner they replace the conventional water soluble fertilizers, the more beneficial it will be.

The problem may be largely resolved if newer compounds were to be synthesised which would be more cost effective. The first step in this direction is to use cheaper raw materials and if possible to adopt processes of lower energy requirements. Polymeric compounds produced from organic raw materials have generally proved to be relatively expensive as revealed by the simplest case of the urea-formaldehydes. On the other hand, inorganic polymers based on the phosphates are much more promising since here the organic materials are substituted by phosphoric acid or phosphates which are themselves much cheaper.

The interesting characteristic of the phosphates which makes them so suitable for the production of polymeric fertilizers is that the orthophosphate ion, i.e., PO_4^{3-} , polymerises on heating with the formation of linear chains of P-O-P bonds. In the final stages of condensation, branched chain polymers may also be formed (Van Wazer 1966). Thus, in a metaphosphate containing linear phosphate chains the negatively charged oxygen atoms may be neutralised by K^+ ,

Ca^{2+} or NH_4^+ ions. Since these ions are held in exchangeable positions on an anionic polymer chain, they possess the dual property of being almost insoluble in water but being readily solubilised by complexants and by cation exchange. Moreover, slow hydrolysis of the P-O-P groups occurs (Ohashi 1964) causing solubilisation of the cations. It is noteworthy that polyphosphates of all the macro- and micro-nutrient ions may be prepared; additionally, their solubility can be varied to desired levels by controlling the degree of polymerisation of the chain. In general, polyphosphates of the monovalent ions are readily solubilised by exchange even in high molecular weight materials (Thilo 1962). With the higher valent ions, however, exchange ability decreases rapidly with increasing molecular weight (Van Wazer 1966).

One of the best known of such polyphosphate based fertilizers is the potassium metaphosphate $(\text{KPO}_3)_n$ (Waggaman 1952, Van Wazer 1968, Vol'fkovich et al. 1975, NDC 1976, Hudson & Dolan 1982). Potassium metaphosphate is produced by dehydration of KH_2PO_4 at $300^\circ\text{-}800^\circ\text{C}$ (Van Wazer 1966, Beglov 1977), by heating a mixture of KCl and H_3PO_4 at 400°C or higher (Madorsky & Clark 1940; Jacob 1953; Harris 1963; NDC 1965; Namazov et al. 1975), and by combustion of KCl and elemental phosphorus (Sauchelli 1967). The main problem in $(\text{KPO}_3)_n$ manufacture is the starting material, viz., KH_2PO_4 . The compound KH_2PO_4 itself is too expensive as a source because it is produced by neutralisation of KOH. Alternatively, as mentioned earlier, KH_2PO_4 may be replaced by a mixture of KCl and H_3PO_4 which, when heated, evolves HCl leaving a residue of potassium phosphates. For this process, however, higher temperatures are required, which cause major problems of furnace corrosion as observed in pilot plant studies by the TVA (Jacob 1953). In fact, at elevated temperatures phosphoric acid is reactive towards most metals and their oxides and can even dissolve gold and platinum (Van Wazer 1966). The most suitable materials of construction for phosphoric acid at temperatures below 400°C , are carbon or graphite bricks; at higher

temperatures, these are susceptible to oxidation (Sauchelli 1967). Therefore, handling solutions containing phosphoric acid at temperatures above 400°C, is a difficult and expensive operation. However, studies have shown that it is possible to overcome this problem (up to temperatures below fusion point of the phosphates) by proper design of equipment. Thus, in processes described by a number of workers (Rastrick & Raitt 1962, Harris 1963, NDC 1965, Hudson & Dolan 1982), counter-current heated M.S. rotary kilns have been successfully used at reaction temperatures of 450°-500°C without significant corrosion of the equipment. Apparently, a coating of the metaphosphate, which adheres to the surface of the vessel, acts as a protective shield (Harris 1963).

It is obvious that most of the difficulties associated with the manufacture of $(\text{KPO}_3)_n$ could be resolved if KH_2PO_4 could be directly used as a starting material. Moreover, the use of KH_2PO_4 being cost prohibitive for the reasons stated earlier, an alternative and less expensive means of producing KH_2PO_4 may provide the solution to this problem. One such process consists of extracting a mixture of KCl and H_3PO_4 with organic solvents so that HCl is removed in the organic phase and $\text{KH}_2\text{PO}_4 \cdot \text{H}_3\text{PO}_4$ remains as a solid residue (NDC 1968); the latter is further converted to KH_2PO_4 by washing with water, methanol (NDC 1968) or KH_2PO_4 solution (Varadachari 1986a, b). In another process, KH_2PO_4 has been produced from waste muscovite mica by reacting with phosphoric acid at 250° to 350°C (Varadachari 1986a, b, Ghosh & Varadachari 1987a, b). Detailed investigations were carried out to understand the unique reaction between phosphoric acid and muscovite mica. It was concluded that the dissolving action of hot phosphoric acid is due to the production of OH^- ions which attack the $\text{Si}-\text{O}-\text{Si}$ and $\text{Si}-\text{O}-\text{Al}$ bonds in the mica and also other $\text{P}-\text{OH}$ groups, forming $\text{Si}-\text{OH}$, $\text{Si}-\text{O}-\text{P}$, $\text{Al}-\text{O}-\text{P}$ and $\text{P}-\text{O}-\text{P}$ bonds. The product consists of an amorphous cross-linked polyphosphate of Si^{4+} , Al^{3+} and K^+ which covers a core of unreacted mica. It is depolymerised by boiling in water and free

phosphoric acid is removed by solvent washing. Subsequently, KH_2PO_4 is recovered from the residue of $\text{KH}_2\text{PO}_4 \cdot \text{H}_3\text{PO}_4$. The KH_2PO_4 is then readily converted to $(\text{KPO}_3)_n$ by heating at 300°C. Considering that immense quantities of muscovite micas are to be found in several regions of the world in the form of low grade ores as well as high grade mine wastes (which constitute about 80% of the total quantity of high grade muscovite mined), the effective utilisation of such a cheap source for the production of a high value potassium metaphosphate may provide the necessary fillip for a more wide-spread use of this slow-releasing fertilizer. Moreover, in countries like India which have no deposits of soluble potash salts and are entirely dependent on imports, this process may provide an alternative means of meeting their potash fertilizer requirements. Thus, the versatile character of phosphoric acid reflected by its powerful solubilising action and by its polymer-forming capacity, serves a dual purpose of making available an alternative source of potassium in addition to producing a fertilizer of very superior quality.

The concept of polyphosphate-based slow-releasing compounds may also be utilised for nitrogen fertilizers and obviously for phosphate fertilizers too. The ammonium polyphosphates serve both these purposes. Ammonium polyphosphate liquids are readily prepared by ammoniation of polyphosphoric acids (Slack 1960, NDC 1968, Van Wazer 1968). However, because of their solubility they do not offer any significant advantage over conventional materials like urea, except that they are high analysis compounds. The solid ammonium polyphosphates are much more promising; there are, however, many difficulties associated with their manufacture. The ammoniation of superphosphoric acids to produce solid insoluble compounds requires conditions of high pressure as well as high temperature (Kubasova 1964, NDC 1968, Relo 1977). High pressure may be avoided by adopting a two-stage counter-current ammoniation process, in which the heat of ammoniation is utilised to polymerise the phosphoric acid (NDC 1968). The solubility of the product obtained by this process is, how-

ever, strongly influenced by the nature of the impurities in the feed acid. Alternatively, P_2O_5 , NH_3 and H_2O may be reacted at high temperature, with the polyphosphate chain-length being controlled by the amount of H_2O added to the system (Sauchelli 1967). Rigid control of reaction conditions is necessary to ensure uniformity of the products. The P_2O_5 used in this process may be replaced by elemental phosphorus which is burnt in air prior to reaction with NH_3 and H_2O (Driskell 1955). Christian (1958) suggested that a mixture of NH_3 , O_2 and an inert gas (N_2) may be directly reacted with molten phosphorus to produce ammonium metaphosphate of low solubility. Although numerous similar processes exist, most of which have been patented several decades ago, none of them seem to have made much headway on a commercial scale. The economic factor is probably mainly responsible for this, since both P_2O_5 and P are fairly expensive raw materials. The future outlook for ammonium metaphosphate can be considerably improved only if processes based on the less expensive phosphoric acid are utilised for its production. For this, better methods are necessary to ammoniate superphosphoric acid. On the other hand, many of the difficulties associated with the ammoniation step may be avoided, if ammonium metaphosphate could be produced by the exchange reaction between some other cation metaphosphate and an ammonium salt. Production of mixed metaphosphates containing the ammonium ion may also provide a technically more simple alternative to the pure ammonium compound.

Purely phosphatic fertilizers are best synthesised as the calcium salt. The calcium metaphosphate is a product of dehydration of $Ca(H_2PO_4)_2$ (Van Wazer 1968). For commercial purposes, however, this has been produced by burning elemental P in air and then causing the hot products of combustion to react with phosphate rock (Sauchelli 1967). Problems of furnace corrosion, product composition control and the economics of the process are the major limitations to the manufacture of calcium metaphosphate by this method. A mixed calcium am-

monium metaphosphate has been prepared from phosphate rock and NH_4HSO_4 or NH_4Cl but the product was observed to be water soluble (Serazetdinov et al. 1969, Man et al. 1986). Other metaphosphates containing both Ca^{2+} and Mg^{2+} together with K^+ and NH_4^+ ions have been investigated by Bekturov et al. (1970) and Kinoshita et al. (1981); potassium calcium trimetaphosphates have been synthesised by Nurlybaev et al. (1973). Although it is not known whether the use of triple superphosphate as a raw material for calcium metaphosphate has ever been studied, this approach is worth investigating, as it appears to be the most promising one in terms of costs as well as conditions of polymerisation.

The concept of a polyphosphate base is also ideally suited for micronutrient fertilizers. Numerous such micronutrient polyphosphate formulations are available but these are usually in the form of liquids or soluble salts. Thus micronutrient salts are added to condensed phosphoric acids for use as liquid sprays (Slack 1968, NDC 1968, 1976); they are also mixed with ammonium polyphosphate solutions (NDC 1968). Potassium or calcium metaphosphates may be modified by traces of micronutrients which are added as oxides prior to reaction (Vol'fkovich et al. 1970, Bekturov et al. 1970, Vol'fkovich 1972). The properties of the transition metal metaphosphates, particularly their thermal changes and crystallinity, have been investigated in great detail (Durif 1969, Urikh et al. 1970, Nirsha et al. 1982, Narita 1983, Serazetdinov et al. 1983, Trojan et al. 1985, 1987, Trojan & Ludvik 1986). These studies are valuable aids in the synthesis of such polyphosphate compounds. Boron phosphates produced by the reaction of boric and phosphoric acids under various conditions have been described by Bekturov et al. (1970) and Vol'fkovich et al. (1972). It is, however, not very clear whether the boron, in the compounds prepared by them, is available to plants. The reaction of H_3BO_3 and H_3PO_4 results in the formation of a highly insoluble BPO_4 (Bailar et al. 1973) and this is the main reason why boron polyphosphates may be extremely difficult to prepare. Ray (1972) patented a product formed by a

similar reaction but its suitability as a boron fertilizer is not known.

Phosphate glasses containing various micronutrient ions have also been suggested as fertilizer material. These glasses are usually synthesised by fusing $\text{NH}_4\text{H}_2\text{PO}_4$ or NaH_2PO_4 with the oxides or hydroxides of the micronutrient ions at temperatures between 800° and 1400°C , and then rapidly cooling the liquid by pouring on to a cold plate (Roberts 1973, 1975, 1977, Davie 1974, Krems-Chemie 1975). Fertilizers containing a single micronutrient ion as well as those containing several such ions may be obtained by this means. The high temperatures employed for the syntheses of the phosphate glasses are, however, a serious limitation to large scale commercial production since the extreme corrosiveness of the molten phosphates at such temperatures (Van Wazer 1966) necessitates the use of the platinum containers which are prohibitively expensive, considering the value of the end product involved.

An alternative concept of slow-releasing micronutrient fertilizers is now being developed with synthesis routes involving much lower temperatures, technically simple operations and cheaper materials of construction (Varadachari 1990). Here, low molecular weight linear polyphosphates are used as metal ion carriers, rather than the three dimensional branched-chain phosphate glasses. The reasons why such compounds have not yet been utilised as fertilizer materials are: (i) there is a wide distribution of chain lengths of the linear polyphosphates formed, because of which a product may contain a high percentage of soluble compounds. The amounts of these compounds may be decreased by further heating and polymerisation but this also increases the formation of higher molecular weight and highly insoluble fractions from which the micronutrient ions may become non-available to plants. It is not possible to obtain compounds in which the soluble polyphosphate fractions are not present, and at the same time to limit the size of the high chain length fractions so that the micronutrients remain in an available form; and (ii) low molecular

weight polyphosphates are hygroscopic and also acidic.

It has been possible to overcome these major hurdles and synthesize micronutrient fertilizers which have excellent chemical as well as physical characteristics (Varadachari 1990). Controlling polymerisation to an optimum level and producing mixed polyphosphates containing Ca^{2+} , Mg^{2+} or NH_4^+ , in addition to micronutrient ions, are the key factors for achieving the desired result. Temperatures used are between 250° and 350°C and the reaction is carried out in ceramic vessels. So far micronutrient fertilizers containing zinc, copper and boron have been prepared (Ray et al. 1990, Varadachari 1990). This concept can be readily extended to all other micronutrients such as Fe^{3+} , Fe^{2+} , Mn^{2+} , Co^{2+} , Mo^{6+} , etc., with some modifications of the process. The notable characteristics of the polyphosphate fertilizers prepared in this way are their non-hygroscopic powdery nature, very low solubility in water ($< 1\%$), and ready solubility in citric acid and similar complexants, indicating 100% available plant nutrients. Fertilizer trials show that the polyphosphates are either as good as or better than the conventional micronutrient fertilizers (Varadachari 1990). The advantages of the polyphosphates as micronutrients carrier are: (i) leaching losses are minimum, hence lower doses are required and the residual effect is significant; (ii) in highly alkaline and acidic soils, the nutrients remain available and, unlike traditional fertilizers, are not converted to non-available forms; and (iii) addition of overdoses does not result in toxicity.

In fact, an overall view of the properties of low molecular weight polyphosphates indicates that they are ideally suited for the formulation of slow-releasing fertilizer compounds of micro- as well as macro-nutrients. Controlling the degree of solubility and availability of the nutrient ions is very simple and, if necessary, multinutrient fertilizers with a wide range of composition ratios can be prepared. Most important of all, water and soil pollution hazards are minimised and the economics of fertilizer use is significantly improved. All this can be achieved with just cheap and readily available raw materials and using

processes that are both technical simple and fairly low energy-consuming. It would appear that in the long run polyphosphates are indeed the answer to the problem of choosing the right fertilizers for the needs of the future.

Acknowledgements

The author acknowledges with gratitude financial assistance rendered by the Council of Scientific and Industrial Research, Government of India, New Delhi, Indian National Science Acade-

my, New Delhi and the Department of Science and Technology, Government of India, New Delhi for their respective research projects on "Utilisation of mica dust wastes as a source of potassium for fertilizers", "Novel slow-releasing micronutrient fertilizers: Formulation, synthesis and applicability" and "Production of potash fertilizers from mica wastes on a pilot scale", which have been instrumental in the development and furtherance of many of the new concepts advanced here.

References

- Bailar (Jr) J C, Emeleus H J, Nyholm R and Trotman-Dickenson A F 1973 *Comprehensive Inorganic Chemistry* **2** pp 483, 505 (New York: Pergamon)
- Beglov B M 1977 Thermodynamic analysis of reactions forming condensed potassium phosphates; *Uzb. Khim. Zh.* **2** 35-39
- Bekturov A B, Tikhonov V V, Esik V K and Shaidarbekova Zh K 1970 Properties of condensed phosphate fertilizers; *Vestn. Sel'skokhoz. Nauki (Alma-Ata)* **13** 47-49
- Christian C G 1958 *US Patent* 2839375-6; in Sauchelli V 1967
- Davie W R 1974 Phosphate-borate glass frits as plant micronutrient *US Patent* 3762909; *Natl. Glass Budget* **89** 22
- Driskell J C 1955 *US Patent* 2713536; in Sauchelli V 1967
- Durif A 1969 Structural chemistry of mixed poly- and metaphosphates of monovalent and divalent cations; *Rev. Chem. Miner.* **6** 109-34
- Ghosh K and Varadachari C 1987a Process for the manufacture of pure potassium phosphate from white mica; *Indian Patent* 1167695
- — and — — 1987b Process for the manufacture of pure potassium chloride and simultaneous production of pure silica from black mica; *Indian Patent* 164859
- Harris F J 1963 Potassium metaphosphate: A novel method of manufacture and a summary of its behaviour as a fertilizer; *Fert. Soc. Proc. (London)* 28th Feb.
- Hudson R B and Dolan M J 1982 Phosphoric acid and phosphates; in *Encyclopedia of Chemical Technology Vol 17* (3rd edn) pp 426-472 eds H F Mark, D F Othmer, C G Overberger and G T Seaborg (New York: Interscience)
- Jacob K D 1953 *Fertilizer technology and resources* (New York: Academic Press)
- Kinoshita M, Kiyoshi I M and Kishioka A 1981 Dehydration of magnesium dihydrogen phosphate and calcium dihydrogen phosphate in the presence of phosphoric acid, and some properties of the products; *Gypsum Lime* **172** 92-100
- Krems Chemie—G.m.b.H. 1975 Complete fertilizers containing trace elements; *Austrian Patent* **32** 6160
- Kubasova L V 1964 Ammonium polyphosphates; *Zh. Pnikl. Khim.* **37** 955-959
- Madorsky S L and Clark K G 1940 Potassium metaphosphate—A potential high analysis fertilizer material; *Ind. Eng. Chem.* **32** 244-248
- Man M, Terdor L N F B L and Soare C F 1986 Ammonium calcium trimetaphosphate fertilizers *ROM RO* 89057
- Namazov Sh. S, Alsanov Kh A and Irgashev I K 1975 Interaction of potassium chloride with a mixture of wet process phosphoric and sulfuric acids; *Uzb. Khim. Zh.* **19** 10-12
- Narita E O T 1983 The thermal decomposition of manganese (III) phosphate monohydrate; *Bull. Chem. Soc. Jpn.* **56** 2841-2842
- NDC 1965 *Potash and Potassium Fertilizers*; Chemical Process Monograph No. 15 (New Jersey; Noyes Development Corporation)
- — 1968 *New Fertilizer Materials* (New Jersey; Noyes Development Corporation)
- — 1976 *Granulated fertilizers* (New Jersey: Noyes Development Corporation)
- Nirsha B M, Khomutova T V, Fakeev A A, Zhadanov B V, Agre V M, Kozlova N P and Olikova V A 1982 Study of thermal transformations of monosubstituted zinc orthophosphate dihydrate $[Zn(H_2PO_4)_2 \cdot 2H_2O]$; *Z. Neorg. Khim.* **27** 1121-1125
- Nurlybaev I N, Il'yasova A K and Bekturov A B 1973 Preparation of potassium calcium trimetaphosphate $[Ca(K_2P_3O_9)_2]$; *Izv. Akad. Nauk. Kaz SSR. Ser. Khim.* **23** 11-14
- Ohashi S 1964 Condensed phosphates containing other oxo acid anions; in *Topics in Phosphorous Chemistry Vol 1*, pp 189-240 eds M Grayson and E J Griffith (New York: John Wiley)
- Rastrick B and Raitt J S 1962 Low temperature metaphosphate processes; *US Patent* 304941
- Ray L F 1972 Boron phosphate; *US Patent* 3655357
- Ray S K, Varadachari C and Ghosh K 1990 Process for producing a slow-releasing zinc fertilizer; *Indian Patent App* No. 703/Cal/90
- Relo R P 1977 Preparation of ammonium polyphosphates

- and liquid fertilizers by the ammoniation of wet process phosphoric acids; *Zh. Prikl. Khim.* **50** 1676-1682
- Roberts G J 1973 Preparation and properties of glasses in the system $\text{FeO}-\text{K}_2\text{O}-\text{P}_2\text{O}_5$; *Am. Ceram. Soc. Bull.* **52** 383
- — 1975 $\text{FeO}-\text{K}_2\text{O}-\text{P}_2\text{O}_5$ glasses as a source of micronutrient iron in soil; *Am. Ceram. Soc. Bull.* **54** 1069
- — 1977 Micronutrient containing phosphate glasses; *Natl. Glass Budget.* **92** 21st July
- Sauchelli V 1964 *Fertilizer nitrogen* (New York: Reinhold)
- — 1967 *Chemistry and Technology of Fertilizers*. ACS Monograph Series pp 322-345, 634-648 (New York: Reinhold)
- Serazetdinov D Z, Kim M Kh, Bekturov A B 1969 Composition of water soluble polymeric ammonium-calcium phosphates; *Vesta. Akad. Nauk. Kaz. SSR* **25** 56-57
- Serazetdinov D Z, Evtushenko G K, Kim M Kh and Polyanskaya T S 1983 Physicochemical features of directed polymerisation of phosphates and their use in polyphosphate fertilizer; *Tr. Inst. Khim. Nauk. Akad. Nauk. Kaz. SSR* **59** 32-49
- Slack A V 1968 *Phosphoric acid Part II* (New York: Marcel Dekker)
- Thilo E 1962 Condensed phosphates and arsenates; in *Advances in inorganic chemistry and radiochemistry Vol 4* pp 1-66 eds H J Emeleus and A G Sharpe (New York: Academic Press)
- Trojan M and Ludvik B 1986 X-ray diffraction analysis of cyclophosphates of bivalent metals; *Vys. Sk. Chemicko-technol Pardubice* **49a** 225-231
- —, Sloc Z and Kuchler M 1985 A study of condensation reactions during formation of copper metaphosphate ($\text{C}-\text{Cu}_2\text{O}_4\text{O}_{12}$) by means of quasi-isothermal-isobaric thermal analysis; *Thermal Anal. Proc. ICTA*, 8th 463-466
- —, Brandova D and Sloc Z 1987 Study of the thermal preparation and stability of the tetrametaphosphates of bivalent metals; *Thermochim. Acta* **110** 343-348
- Urikh V A, Tikhonov V V, Serazetidinov D Z and Bektunov A B 1970 Kinetics of the thermal dissociation of some condensed phosphates; *Izv. Akad. Nauk. SSR Neorg Mater* **6** 2076-2077
- Van Wazer J R 1966 *Phosphorous and its Compounds Vol I* (New York: Interscience)
- — 1968 *Phosphorous and its Compounds Vol II* (New York: Interscience)
- Varadachari C 1986a Production of fertilizer-grade potassium values and simultaneous recovery of aluminosilica from muscovite mica; *Indian Patent* 168022
- — 1986b Production of fertilizer grade potassium values and production of pure silica from biotite mica; *Indian Patent* App No. 167663
- — 1990 *Final technical report* of the Research Project "Novel slow-releasing micronutrient fertilizers: Formulation, synthesis and applicability", (New Delhi: Indian National Science Academy)
- Vol'fkovich S I 1972 Polymeric fertilizers; *J. Appl. Chem. USSR* **45** 2479-2487
- — Al Shenavi H M, Kubasova L V and Zhuravleva M P 1972 Boron-phosphates and their properties; *J. Appl. Chem. USSR* **45** 2245-2247
- — Alexandrova G G, Kubasova L V and Cherepanova A S 1975 Potassium metaphosphate—a highly concentrated fertilizer; *Probl. S-Kh Nauki Mosk. Univ.* 236-244
- Waggaman W H 1952 *Phosphoric acid, phosphates and phosphatic fertilizers* (New York: Reinhold)