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GENERAL RESEARCH

An Investigation on the Reaction of Phosphoric Acid with Mica at Elevated Temperatures

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Various aspects of the reaction of phosphoric acid with muscovite mica at 250, 300, and 350 °C were studied with a view to understanding the nature of such reactions, particularly (i) the reaction kinetics, (ii) the relation between muscovite dissolution and polymerization of phosphoric acid, (iii) the probable mechanism of reaction, and (iv) the nature of the residue. Solubilization of the K^+ ion from muscovite was observed to be linearly dependent on the degree of dehydration of the system as well as the average chain length of the poly(phosphoric acid) formed. It is suggested that the breakdown of the complex muscovite structure is due to attack by OH^- ions, which are produced when phosphoric acid polymerizes; oxide bonds are cleaved forming M-OH and M-O-P bonds, and the elimination of water from other P-OH groups results in polyphosphates. The reaction product consists of soluble and insoluble amorphous polyphosphates that form a coating over the core of unreacted mineral.

1. Introduction

Phosphoric acid at elevated temperatures shows a remarkable reactivity that is unique among the inorganic acids. Thus, at high temperatures, phosphoric acids and phosphates have been observed to react with quartz (Mellor, 1925), with silicates and glasses (Kingery, 1950; Ray, 1970), and with a large number of metals and oxides (Bailar et al., 1973; Thilo, 1962), including gold and platinum (Van Wazer, 1966). Such reactions of phosphates find use in the manufacture of phosphate glasses (Ohashi, 1964), phosphate-bonded refractories (Kingery, 1950; Mamykin et al., 1973), and micronutrient fertilizer glasses (Roberts, 1975). In spite of the varied application of the phosphate-silicate/oxide reactions, however, the nature, mechanism, and products of such reactions have neither been investigated in detail nor been established with certainty. Thus, although the nature of polymerization of phosphoric acid and phosphate melts (Van Wazer, 1966) is now fairly well understood, its reactions with silicates and refractory oxides are subject to a great deal of speculation. There are indeed very few studies pertaining to the mechanism of such reactions. Reactions of glasses with phosphoric acid have been studied by Ray (1970) and Walters (1983). According to Ray (1970), the reactivity of the glass is a function of acid dehydration, whereas Walters (1983) attributed the solubilization to attack by polyphosphates produced during heating. Ohashi (1964) proposed that the reaction occurs due to the ability of PO_4

units to form copolymers with silicates and other elements having XO_4 tetrahedra. Workers who have extensively investigated the products of the reaction of phosphoric acid with phyllosilicates concluded that various crystalline phosphates of silicon and aluminium are produced by the replacement of SiO_4 tetrahedra of the silicate, by the corresponding tetrahedra of the acid; their nature depends on the temperature and the relative proportions of the constituents (Kingery, 1950; Lyon et al., 1966; Mamykin et al., 1973; Zamyatin et al., 1972). The existing knowledge is, however, quite inadequate for understanding exactly how and why stable polymeric structures, such as the silicates, are broken down so readily to their component units by hot phosphoric acid. Neither can it explain the unique reactivity of this acid and the cause of the unusual change in its properties on heating.

In this paper, the results of a comprehensive study on the high-temperature reaction of phosphoric acid with a silicate are presented. It is hoped that this investigation will provide a better understanding of the reactions of hot phosphoric acid with silicates and oxides in general and perhaps also provide a clue to the cause of its phenomenal solubilizing power. The study has accordingly been dealt with in four parts, which may be broadly classified as (1) the reaction kinetics of muscovite dissolution by phosphoric acid, (2) kinetics of polycondensation of phosphoric acid, (3) deduction of the reaction mechanism, and (4) identification of the products of reaction.

2. Methodology

2.1. Studies on the Dissolution of Muscovite by Phosphoric Acid. Large flakes of muscovite (from Gir-

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idih, Bihar, India) were dry-ground in an electric grinder and sieved to obtain the 80–150 mesh B.S. (British Sieve) fraction. The sample thus obtained was dialyzed and dried at 105 °C. X-ray diffraction (XRD) of the sample was recorded on a Philips PW 1140 X-ray diffractometer using Ni-filtered Cu K α radiation and a scanning speed of 1°/2 θ /min (precision in 2 θ , $\pm 0.1^\circ$); characteristic lines of well-crystallized muscovite were obtained. The major reflections correspond to d_{hkl} of standard muscovite crystals (JCPDS, 1971). Thermogravimetry (TG) was carried out on a Gebrüder-Netzsch Instrument (No. 404) at a heating rate of 10 °C/min; muscovite showed a single dehydration peak at 950 °C. Chemical analysis of the sample was done according to a combined scheme of Shapiro-Brannock and Riley (Jeffery, 1970; Maxwell, 1968). Determination of Si⁴⁺, Al³⁺, Fe^{3+/2+}, and Ti⁴⁺ (precisions of ± 0.02 , ± 0.01 , ± 0.02 , ± 0.1 ppm, respectively) were done colorimetrically as molybdenum blue, alizarin red S, o-phenanthroline, and H₂O₂ complexes, respectively; Ca²⁺ and Mg²⁺ (both ± 0.05 ppm) were determined by EDTA, Na⁺ (± 0.05 ppm), and K⁺ (± 0.025 ppm) by flame photometry and H₂O⁻ and H₂O⁺ (both ± 0.2 mg) by gravimetry (Black, 1965; Jeffery, 1970; Maxwell, 1968). The average percent compositions of the various elements obtained, from analysis carried out in triplicate, were 21.67% (± 0.1) Si, 17.75% (± 0.05) Al, 1.21% (± 0.02) Fe, 0.23% (± 0.005) Ti, 0.37% (± 0.01) Ca, 0.27% (± 0.01) Mg, 1.18% (± 0.05) Na, 8.20% (± 0.05) K, 0.21% (± 0.05) H₂O⁻, and 5.01% (± 0.1) H₂O⁺, where the figures in brackets are the standard deviations in the data. The corresponding composition of the mineral is K_{1.61}Na_{0.41}Ca_{0.08}Mg_{0.09}Si_{6.27}Al_{5.35}Fe_{0.17}Ti_{0.04}O₂₀(OH)₂.

In all experiments, H₃PO₄ (GR, E. Merck) diluted to about 45% P₂O₅ was used. The P₂O₅ content of the acid (of which a sufficiently large stock was prepared) was determined by pH-metric titration (Van Wazer et al., 1954). Standardization of the acid was done on every alternate day of work. Reactions were carried out with 0.2 g of muscovite weighed in a Pt crucible into which a calculated amount of standardized H₃PO₄ (600, 700, or 800 mg P₂O₅, i.e., 300, 350, or 400 mg P₂O₅/(100 mg of muscovite)) was pipetted. The weights of the crucible before and after the addition of muscovite and acid were noted. The crucible was initially heated at 150 °C for 30 min to drive off excess water that causes spattering at higher temperatures. It was then placed in a furnace preheated to the required temperature (controlled to within ± 1 °C) and kept for the required length of time. After the crucible was cooled in a desiccator over P₂O₅, its weight was recorded. From these data, the percent weight loss of the reaction mixture was calculated (with a standard deviation of $\pm 0.1\%$). The contents were then filtered, washed and made to volume. The residue was dried and stored. Solutions were analyzed for Si⁴⁺, Al³⁺, and K⁺; Si⁴⁺ was analyzed (precision ± 0.02 ppm) according to Maxwell (1968) except that twice the recommended amount of molybdate and tartaric acid had to be added to compensate for excess phosphate; Al³⁺ was also analyzed (precision ± 0.01 ppm) according to Maxwell (1968)—phosphate was observed to cause no interference. The method for determination of K⁺ had to be modified because phosphate causes serious interference in both flame emission and absorption methods (Black, 1965; Pinta, 1975) due to the formation of insoluble KPO₃ in the flame (Black, 1965). Suppression of interference by the addition of Na⁺, which can act as a releasing element, was found to produce the desired results. Thus to eliminate interference from phosphate, NaCl concentration of the medium was maintained at

1.75%. Amounts of K⁺ were determined, with a precision of ± 0.025 ppm K⁺, on a flame photometer (AIMIL MK II) using standard curves (0–2.5 ppm) constructed from KCl solutions containing 1.75% NaCl; triplicate experiments on K⁺ solubilization showed maximum deviations of ± 0.05 mg of K⁺ for 100 mg of muscovite.

2.2. Studies on the Polymerization of Phosphoric Acid. The experimental setup was identical to the previous study on the reaction of muscovite and phosphoric acid, except that no muscovite was used here. As described in section 2.1, standardized H₃PO₄ of 45% P₂O₅ was pipetted into a Pt crucible to give a total of 600, 700, or 800 mg of P₂O₅. The crucible as usual was preheated at 150 °C for 30 min to drive off excess water and then heated at 250, 300, or 350 °C for the required length of time. Weights of the crucible and acid were recorded after cooling over P₂O₅ in a desiccator. From the initial weights of the acid taken, amounts of H₂O lost and hence, H₂O:P₂O₅ ratios, R , of the acids formed were calculated (observed deviations in this ratio are ± 0.01).

Utilizing the flexible-chain model, Van Wazer (1966) developed a method for calculating the number-average chain length as well as the distribution of various-sized chains in equilibrated condensed phosphoric acids from the H₂O:P₂O₅ mole ratio. In the following experiments, the H₂O:P₂O₅ mole ratio of the poly acids, produced after heating, were determined as described. From these values, the average chain length of the poly(phosphoric acids) and the contents of ortho- and pyrophosphates were deduced using the method suggested by Van Wazer (1966) [errors in these values, which are due to errors in the values of R , are respectively ± 0.04 , ± 0.002 and ± 0.007].

2.3. Identification of the Insoluble Products of the Reaction. A representative sample was obtained by heating muscovite with phosphoric acid (350 mg of P₂O₅/(100 mg of muscovite)) at 300 °C for 40 min as described earlier (section 2.1). The reaction product was washed with water to remove excess as well as soluble phosphates. This insoluble residue (designated M_i) was dried at 105 °C and used as such for further studies.

Chemical analysis of the sample, M_i, for Si⁴⁺ by the molybdenum blue method (precision ± 0.02 ppm) and for Al³⁺ as the alizarin red S complex (precision ± 0.01 ppm) was done according to the methods described in section 2.1. The total P was determined (Jackson, 1973) by fusing the sample in NaOH followed by analysis as the chlorostannous-reduced molybdophosphoric blue color in the sulfuric acid system (precision ± 0.02 ppm). It was observed, in trial experiments with this method, that Si⁴⁺, even if present in more than twice the maximum concentrations present in the solutions analyzed, did not interfere with the molybdenum blue color.

XRD of the samples was recorded as described in section 2.1. IR spectra (including the muscovite sample) were recorded on a Perkin-Elmer instrument (No. 1957) with a scanning range of 200–4000 cm⁻¹ using CsI as the matrix (resolution ± 5 cm⁻¹). Petrographic analysis was done on a Leitz polarizing microscope equipped with photographic arrangements.

3. Results and Discussion

3.1. Some Observations on the Rates of the Phosphoric Acid–Muscovite reaction. The reaction of phosphoric acid with muscovite results in the solubilization of its major cationic constituents, viz., K⁺, Al³⁺, and Si⁴⁺ from the crystal lattice. The solubilizations of K⁺ in the course of the reaction at various temperatures are shown graphically in Figure 1.

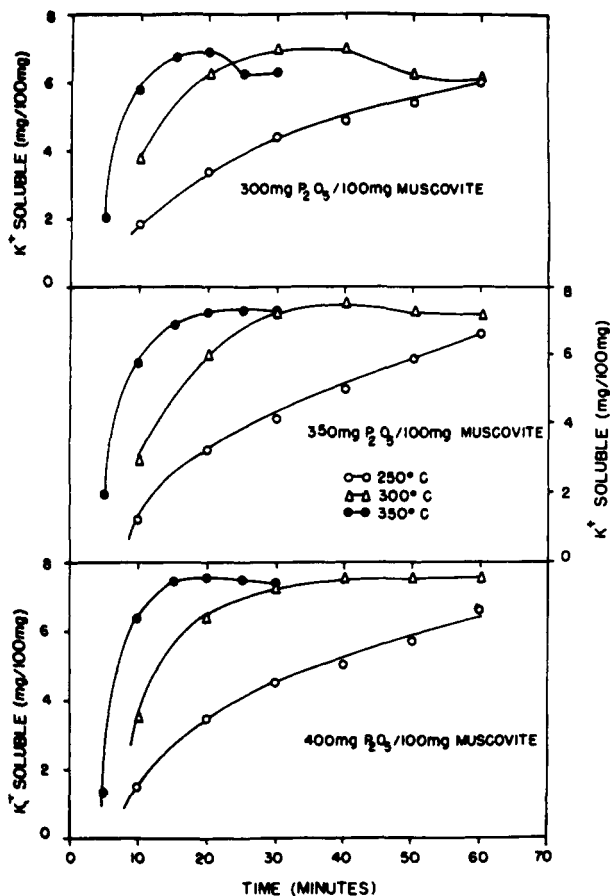


Figure 1. Solubilization of potassium from muscovite with time at various temperatures and P_2O_5 levels.

From Figure 1, it may be observed that K^+ solubilized increases with an increased time of reaction up to a certain point, after which it decreases again. This unusual behavior is probably due to the precipitation of K^+ ions by the formation of less soluble and higher molecular weight polyphosphates on prolonged heating.

On detailed examination of the curves, many other peculiarities may be noted which cannot be satisfactorily explained. The rate curves at different temperatures cannot be fitted into any single kinetic equation because the order of the reaction appears to change with temperature. Moreover, on increasing the amount of acid, the amount of K^+ released does not always increase. For example, after 10 min of heating at 300 °C, the release follows the order $300 > 400 > 350$ mg of P_2O_5 . At 350 °C, however, the order is $400 > 300 > 350$ mg of P_2O_5 . All these observations indicate that K^+ release is not due to a simple process of exchange between the H^+ of the acid and the K^+ in the muscovite because such processes would show normal kinetic behavior associated with first-order or second-order reactions.

On the other hand, it was observed that the dehydration curves (Figure 2) of these systems bear a close similarity to the K^+ solubilization curves (Figure 1). When K^+ solubilized was plotted against the percent weight loss (Figure 3), a remarkable linear correlation was obtained. This direct dependence of K^+ release on the extent of dehydration suggests that the reaction is probably a consequence of dehydration of the acid; in other words, polymerization of phosphoric acid is the rate-limiting step of the reaction.

Data for Al^{3+} and Si^{4+} in solution (not reproduced) show haphazard trends with longer periods of heating. Moreover on storage, even within a day, the solutions deposit a fine

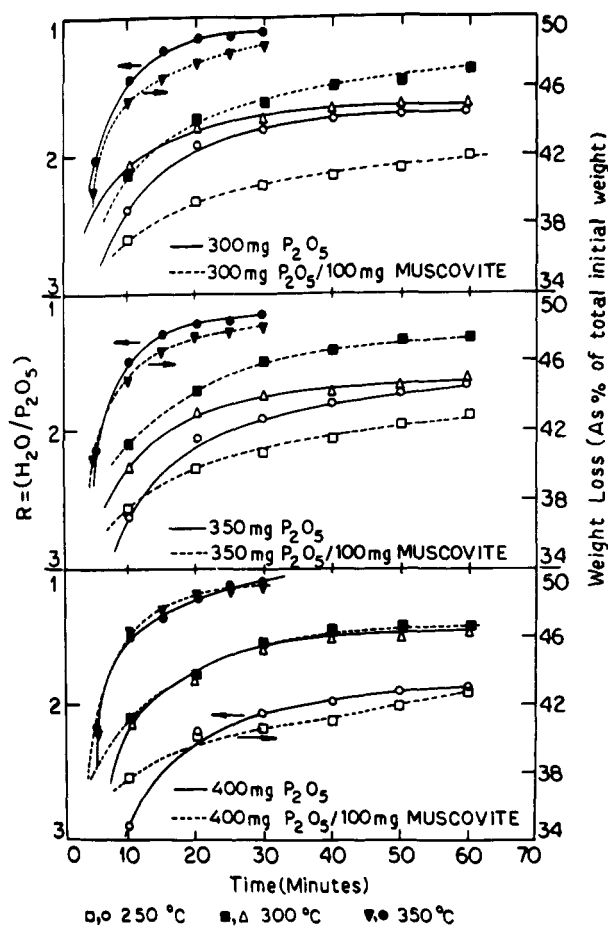


Figure 2. (a) Weight loss of the phosphoric acid-muscovite systems with time at various temperatures and P_2O_5 levels (dashed lines). (b) Polymerization of phosphoric acids with time at various temperatures and P_2O_5 levels (bold lines).

precipitate consisting of aluminium phosphate and silica. Therefore, not much can be inferred from the data. In general, solubilization of Si^{4+} is much less than that of Al^{3+} . The observation that fairly large amounts of Si^{4+} (up to about 30%) are solubilized under such highly acidic conditions is itself intriguing. The only possible explanation is that Si^{4+} is removed by complexation with phosphoric acid. In fact, silica has been known to dissolve in phosphoric acid with the formation of a six-coordinated silicon phosphate (Boullé and Jary, 1953; Iler, 1979), which is probably the form in which it is present in these solutions.

Summary. The reaction of phosphoric acid with muscovite at elevated temperatures solubilizes the elements in the muscovite structure. Kinetics of K^+ solubilization indicate complex reaction mechanisms, other than simple proton exchange. An unusual correlation between K^+ release and percent weight loss of the system indicates a rate-controlling step involving polymerization of the acid.

3.2. Observations on the Polymerization of Phosphoric Acid. These studies were undertaken in order to understand the nature of phosphoric acid polymerization and subsequently to assess whether muscovite dissolution could indeed be a consequence of this phenomenon. It may be mentioned that when phosphoric acid is heated (at temperatures above 200 °C), it polymerizes by the successive abstraction of H_2O between molecules forming, initially, linear chains connected by P-O-P bonds. Since polymerization proceeds in a regular and sequential manner, it is possible to calculate the average chain lengths and the chain sizes from a knowledge of the extent of

Table I. Characteristics of Phosphoric Acids after Heating to 300 °C

	for 300 mg of P ₂ O ₅ at given time (min)						for 350 mg of P ₂ O ₅ at given time (min)						for 400 mg of P ₂ O ₅ at given time (min)					
	10	20	30	40	50	60	10	20	30	40	50	60	10	20	30	40	50	60
(H ₂ O/P ₂ O ₅) mole ratio (<i>R</i>)	2.056	1.786	1.726	1.690	1.635	1.627	2.252	1.879	1.745	1.700	1.652	1.608	2.103	1.701	1.565	1.437	1.490	1.411
no.-av chain length (\bar{n})	1.894	2.544	2.755	2.899	3.149	3.190	1.597	2.275	2.685	2.857	3.068	3.289	1.813	2.853	3.540	4.107	4.082	4.867
wt fraction of total P in ortho- phosphate	0.198	0.084	0.070	0.063	0.055	0.054	0.329	0.114	0.074	0.065	0.058	0.052	0.227	0.065	0.049	0.045	0.044	0.041
wt fraction of total P in pyro- phosphate	0.460	0.315	0.270	0.243	0.201	0.196	0.476	0.379	0.284	0.250	0.214	0.182	0.471	0.251	0.152	0.105	0.106	0.068

dehydration (Van Wazer, 1966). Table I shows such parameters for phosphoric acid heated at 300 °C. Rates of polymerization are shown graphically in Figure 2 as H₂O:P₂O₅ (*R*) versus *t* (time of heating). The ratio (*R*), which is an index of the degree of polymerization of the acid, decreases for more polymerized acids; it equals 3.0 for the monomeric orthophosphate and has a limiting value of 1.0 for the very long chain metaphosphates. Figure 2 reveals that there is a tendency for plateau formation at each temperature. Such plateau formation indicates that an equilibrium has been reached and further polymerization will not occur at that temperature. However, this equilibrium may be shifted toward higher chain lengths by increasing the temperature (Figure 2). At 300 °C, the orthophosphate content is negligible (Table I) and the pyrophosphate content is much less than that at 250 °C. At 350 °C, long-chain polyphosphates are predominant; metaphosphates are also formed (data not presented).

Summary. Polymerization of phosphoric acid tends to definite equilibrium values at each temperature. Higher temperatures favor longer chain lengths with the nature of the species ranging from predominantly pyro forms at 250 °C to long-chain meta forms at 350 °C.

3.3. Deducing the Reaction Mechanism. The reaction of phosphoric acid with muscovite may be hypothesized to be caused by one of the following, viz., (a) acid attack on the silicate structure, (b) anion attack by ortho-, pyro-, or other polyphosphates, or (c) attack by some other ions/radicals.

(a) Acid Attack. Acid attack as the sole operative factor of K⁺ release appears improbable for two reasons. First, as pointed out earlier, the kinetic data do not evidence a simple proton-exchange process as the rate-limiting step of reaction. Secondly, no other acid (including concentrated H₂SO₄) shows comparable dissolving action; thus at 300 °C after 60 min, H₂SO₄ solubilizes only 25% of the K⁺ solubilized by phosphoric acid under the same conditions.

(b) Anion Attack. As proposed by Ray (1970) and Walters (1983), dissolution may be due to the formation of certain reactive polyphosphates produced in phosphoric acid on heating. If this hypothesis is true, then there should be a definite correlation between the amount of K⁺ solubilized and the amount of ortho- or polyphosphate formed. The concentration of the orthophosphate and individual polyphosphates in the acids formed at 300, 350, and 400 °C (one representative example in Table I) shows no such relation with the K⁺ solubilized. This indicates that the polyphosphates are not directly involved in the rate-limiting step of muscovite dissolution.

(c) Attack by Other Ions. The highly corrosive nature of hot phosphoric acid as compared to its relative sluggishness at room temperature suggests that phosphoric

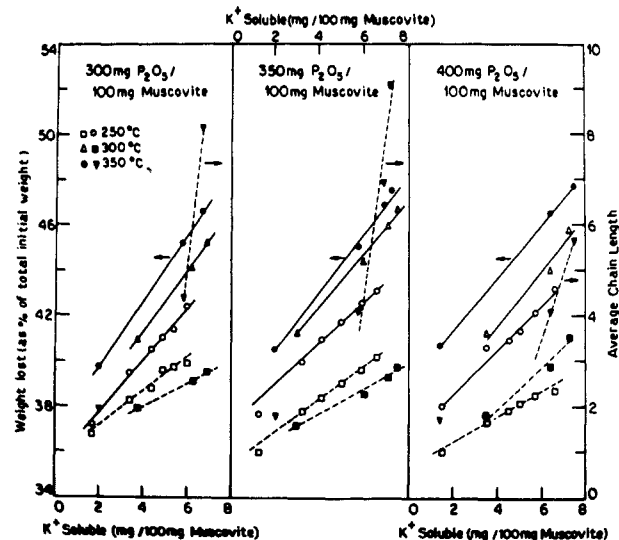


Figure 3. (a) Solubilization of potassium versus percent weight loss of the phosphoric acid-muscovite systems (bold lines). (b) Solubilization of potassium versus average chain length of phosphoric acids (dashed lines).

acid undergoes some unique chemical change on heating, which no other common acids do. The most noticeable change, on heating, is that it polymerizes; this itself implies that the polymerization of phosphoric acid might have some bearing on its reactivity. A further confirmation of this line of thinking is the fact that a linear relation is observed between K⁺ solubilized and percent weight loss during the muscovite-phosphoric acid reaction (Figure 3). Since weight loss on heating is due to the polymerization of phosphoric acid, some relation between the extent of polymerization (i.e., chain length of the phosphate) and the amount of K⁺ solubilized is expected. In fact, when soluble K⁺ is plotted versus the average chain length of the phosphoric acid produced, under identical heating conditions, a good linear correlation is observed (Figure 3). This is particularly marked at 250 and 300 °C. Results at 350 °C are not very reliable because (i) in the first 5 min of heating excess H₂O is driven off and hence correlation with K⁺ release is not possible and (ii) at later stages of heating K⁺ concentration is lowered by insolubilization. The linear correlation (Figure 3) confirms the hypothesis that K⁺ solubilization is a direct function and a consequence of the polymerization of phosphoric acid.

Thus with this conclusion, the next step is to understand exactly how polymerization of phosphoric acid can cause dissolution or breakdown of the stable macromolecular muscovite structure. One may hypothesize that a copolymerization can take place between the OH units of phosphoric acid and the OH groups of muscovite with the

elimination of a water molecule. Such a scheme, however, does not explain how oxides or even the oxide sheets of silicates react with phosphoric acid, since they do not possess any OH groups. This scheme also suggests that the reaction can occur only at the edges and cannot proceed once all exposed OH groups have reacted with phosphates. Since this is certainly not true—an excess of phosphoric acid is capable of completely solubilizing muscovite—this hypothesis is untenable.

The answer to the problem may be deduced by analysis of the literature on reactions in molten alkali-metal oxides and silicates. Such reactions involving depolymerization of complex oxides were treated by Lux and later Flood and Förland as acid-base reactions (Audrieth and Kleinberg, 1953; Moellar, 1973). According to the "Lux-Flood concept", as it is known, a basic oxide furnishes O^{2-} ions to an acidic oxide which reacts with O^{2-} . Thus, the formation of the salt necessarily involves the breaking up of O^{2-} bridges of three-dimensional structures like quartz (SiO_2) by the O^{2-} ion of an oxygen donor material like Na_2O , to form smaller monomeric units.

The above concept of high-temperature acid-base reactions has been utilized to explain reactions in silicate melts. Because of the close structural analogy between phosphates and silicates, results of studies on silicate melts can be utilized in understanding properties of molten phosphates. According to Masson (1965), the building up of polymeric silicate species in melts, occurs by a series of condensation reactions in which O^{2-} is produced at each step, e.g., $2SiO_4^{4-} \rightleftharpoons Si_2O_7^{6-} + O^{2-}$. Toop and Samis (1962) considered anions in silicate melts to consist of three different quasi-chemical species, viz., O^0 = bridging oxygen atoms, O^- = singly bound O, and O^{2-} = free oxide ion. The polymerization reaction of a basic oxide with a silicate melt can thus be represented by the equation $O^{2-} + O^0 \rightleftharpoons 2O^-$.

In both of the above models (Masson, 1965; Toop and Samis, 1962), the reacting species is the O^{2-} ion, as suggested in the earlier Lux-Flood concept (Audrieth and Kleinberg, 1953; Moellar, 1973). These O^{2-} ions are also known to be produced in phosphate melts (Charlot and Tremillon, 1969). Moreover, polymerization in phosphate melts is known to be closely analogous to that in silicate melts (Fraser, 1977). Therefore, it may be envisaged that when phosphates (or phosphoric acid) are heated to polymerization temperatures, O^{2-} (or OH^-) ions are produced which are responsible for silicate dissolution just as, for example, the O^{2-} ions in a Na_2O melt are responsible for the dissolution of silicate.

Here, a mechanism has been proposed (Figure 4) for the dissolution of silicate by phosphoric acid at polymerization temperatures. First, the heating of phosphoric acid produces OH^- ions. Some of the P-O groups then condense to form polyphosphates (first and second lines, Figure 4). The OH^- ions may then attack the Si-O-Si and Al-O-Si bonds forming hydroxides and also phosphates (last three lines, Figure 4). Experimental data on muscovite dissolution also support the proposed mechanism. Thus, according to this mechanism, the production of OH^- ions in phosphoric acid is the rate-limiting step of the reaction. If this is true, then the concentration of polymerizing phosphate species and hence OH^- ions would be greatest at the initial stage of the reaction, and the rates of dissolution should, therefore, be greatest at this stage. As polymerization proceeds, fewer molecules would be available for reaction; consequently, the concentration of OH^- would decrease causing a slowing down of the reaction rate. The nature of the rate curves of K^+ solubilization at various temperatures is in agreement with this. Moreover, since

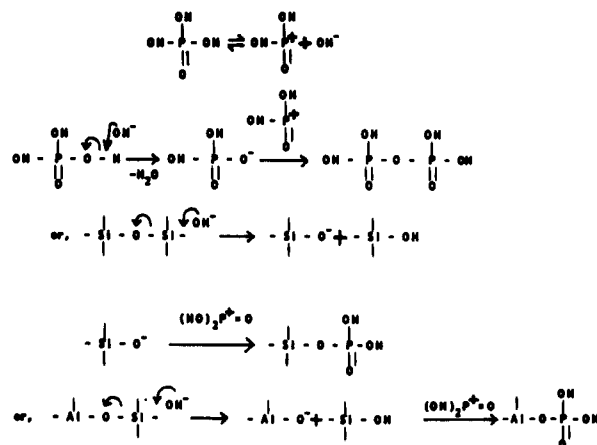


Figure 4. Mechanism of the reaction of phosphoric acid at elevated temperatures.

OH^- ions are produced only during the polymerization of phosphoric acid, the extent of reaction is expected to show some dependence on the extent of polymerization. Such a linear proportionality between the two, viz., $[K^+] \propto \bar{n}$ (Figure 3) has also been observed, as pointed out earlier. The mechanism outlined in Figure 4 is, briefly, a purely theoretical deduction arrived at by (i) a process of elimination of several other hypotheses, based on the experimental data, (ii) the evidence of the involvement of phosphoric acid polymerization in the solubilization of muscovite, and (iii) extrapolation of the existing information on oxide, silicate, and phosphate melts to explain the reactivity of polymerizing phosphoric acids. Although in this investigation, direct experimental verification of the reaction mechanism has not been possible, such studies in the future are worth investigating.

Summary. Experimental data suggest that the muscovite-phosphoric acid reaction is neither due to acid attack nor due to dissolution by polyphosphate anions but is definitely caused by the polymerization of phosphoric acid. By analogy with alkali-metal oxide and silicate and phosphate melts, it has been suggested that OH^- ions are produced in polymerizing phosphoric acid solutions which can cleave the oxide bonds in the muscovite crystal causing structural breakdown.

3.4. Identification of the Insoluble Products of Reaction. Chemical analysis of the major constituents of the sample (M_s) gave: 15.89% (± 0.1) Si, 5.75% (± 0.05) Al, and 13.50% (± 0.1) P. The high percentage of P suggests that both Si and Al are probably present as phosphates.

XRD of the sample (Table II) does not reveal any crystalline phase other than residual muscovite (which is in a degraded form with broader basal spacings). Therefore, all phosphates are present as amorphous forms. IR absorption bands (Table III) in the 1080–1200- cm^{-1} region, indicate the presence of long-chain P-O-P bonds (Corbridge and Lowe, 1954).

In order to confirm the presence of aluminium phosphates and detect the formation of silicon phosphates, if any, the samples were heated progressively at 700, 800, 900, and 1100 °C with a soaking time of 3 h at each temperature, promoting crystallization. After the required heating, the samples were cooled and ground and their XRD and IR spectra recorded (Tables II and III).

The diffraction lines, of the muscovite phase, decrease in intensity on heating from 700 to 900 °C and disappear altogether on further heating at 1100 °C due to dehydroxylation of the lattice. The presence of silicon phosphates (as SiP_2O_7), which show (JCPDS, 1971) intense

Table II. X-ray Diffraction Data of Muscovite and Its Reaction Residue (M_r) before and after Heating

muscovite		reacted residue (M_r)		M_r heated to 700 °C		M_r heated to 800 °C		M_r heated to 900 °C		M_r heated to 1100 °C	
$d/\text{\AA}$	I	$d/\text{\AA}$	I	$d/\text{\AA}$	I	$d/\text{\AA}$	I	$d/\text{\AA}$	I	$d/\text{\AA}$	I
10.04	100	10.66	100	9.925	47.5	9.93	46	9.925	43	4.33	20
5.04	100	9.72	25	5.04	41	6.865	17	6.815	21	4.08	100
4.48	4	4.98	40	4.50	5	4.995	29	4.99	21	3.28	10
3.88	3	4.42	5	4.13	8	4.585	17	4.31	50	2.511	20
3.75	5	3.752	6	3.65	3	4.435	17	4.09	100	2.344	10
3.51	8	3.71	6	3.35	100	4.38	17	3.85	36	2.027	10
3.44	6	3.34	100	3.04	5	4.11	29	3.65	26		
3.35	100	3.20	7	2.885	3	3.65	43	3.495	6		
3.21	10	2.90	7	2.523	25	3.515	9	3.335	50		
3.00	14	2.866	7	2.349	5	3.35	100	3.00	29		
2.866	10	2.797	7	2.253	3	3.21	9	2.862	21		
2.796	11	2.725	3	2.014	25	3.02	11	2.512	50		
2.571	7	2.634	3	1.756	15	2.875	11				
2.501	40	2.564	6	1.684	4	2.512	29				
2.137	3	2.495	13			2.248	11				
2.002	100	2.382	3			2.006	20				
1.734	3	2.151	3								
1.666	6	1.997	47								
1.653	7	1.668	3								
1.566	3	1.647	4								
1.528	5										

Table III. IR Spectra of Muscovite and Its Reaction Residue (M_r) before and after heating

muscovite		reacted residue (M_r)		M_r heated at 900 °C		M_r heated at 1100 °C	
wavenumber/ cm^{-1}	absorbance	wavenumber/ cm^{-1}	absorbance	wavenumber/ cm^{-1}	absorbance	wavenumber/ cm^{-1}	absorbance
340	17	310	8	360	22	380	20
353	15	365	25	390–400	30	460	32
373	23	395	22	460–470	46	610–620	10
400	31	460	32	540–550	29	650	4
467	36	500	26	670	2	710	7
527	35	530	22	685	4	725	9
680 (b)	13	590	13	700	8	790	9
720	13	670 (b)	2	710	11	830	4
753	17	750	2	730	11	1080	34
800	18	800	6	740	10	1115	37
820	14	810	5	750	8	2330 and 2350	8 and 10
927	28	930 (b)	30	790	14		
980–1027	42	970	37	810	10		
2320 and 2347	7 and 7	1070–1100	54	830	8		
2387	3	1150	50	840	7		
3600 and 3613	17 and 16	1200 (b)	45	1000 (b)	33		
		1300	22	1100 (b)	44		
		1610	9	1200 (b)	34		
		1660	6	2300 and 2350	8 and 7		
		2320 and 2350	14 and 15	2400	3		
		3100–3600	20				

peaks at 3.70, 3.34, and 3.03 Å, is evident from the 3.65-Å line with the samples heated at 700, 800, and 900 °C; their intensities may be observed to increase with temperature due to increased crystallization. However, SiP_2O_7 is known to decompose at 1000 °C (Robinson and McCartney, 1964). The absence of the relevant peaks in the samples heated at 1100 °C, in fact, confirms the formation of SiP_2O_7 at the lower temperatures. It may be mentioned here that the diffraction around 3.3 Å does not follow the same pattern because it overlaps with the muscovite diffraction in the same region. The weak lines at 4.58, 2.87, and 2.52 Å of the diffraction pattern of the 800 °C sample are probably (JCPDS, 1971) those of $\text{Al}(\text{PO}_3)_3$; here too there is some overlapping with the diffraction lines of muscovite. The presence of $\text{Al}(\text{PO}_3)_3$ can nevertheless be confirmed by one of its strongest lines, viz., the 4.58 Å line, which disappears on heating at 900 °C, whereas those due to muscovite can still be observed. The decomposition product, AlPO_4 , however, cannot be confirmed by XRD alone because of the closeness of its lines with those of SiO_2 [4.08 and 4.33 Å for cristobalite and tridymite forms of AlPO_4 ; 4.04 and 4.33 Å for the same forms of SiO_2]

(JCPDS, 1971). The formation of both AlPO_4 and SiO_2 , in samples heated at 900 and 1100 °C, however, can be confirmed from their IR spectra. The AlPO_4 absorptions (von Rey, 1966) at 730 and 710 cm^{-1} distinguishes this mineral from SiO_2 and muscovite (which, in any case, is absent at 1100 °C, as observed from XRD data). Since these absorptions are shown by the sample (Table III), the presence of AlPO_4 is confirmed. Also, an absorption of moderate intensity in the 795- cm^{-1} region is shown (Corbridge and Lowe, 1954) by both tridymite and cristobalite forms of SiO_2 but is absent with AlPO_4 and muscovite. The absorption at 790 cm^{-1} (Table III) may thus be attributed to SiO_2 .

Results obtained thus far may be interpreted as follows: Crystalline SiO_2 , SiP_2O_7 , and AlPO_4 are formed in samples heated at 900 °C. These crystalline materials are not present in the original sample (M_r) and, therefore, M_r must contain silica, silicon phosphates, and aluminium phosphates in amorphous forms. The high phosphorus content of M_r , as well as its IR spectra (Table III) suggests that the amorphous materials are polyphosphates. Such polyphosphates may lose excess phosphates, on heating, to

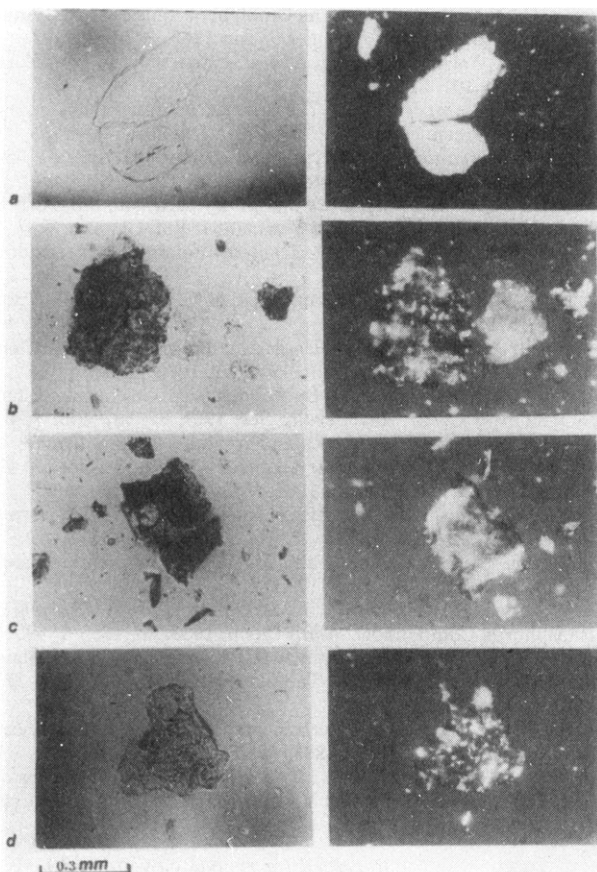


Figure 5. Petrographic microscope photographs (left-hand photos were taken in normal light and the right-hand ones in cross-polarized light): (a) muscovite; (b) reacted residue, M_r ; (c) M_r heated at 1100 °C; (d) M_r after boiling with water.

form crystalline compounds such as $AlPO_4$ or SiP_2O_7 (Robinson and McCartney, 1964).

According to the reaction mechanism suggested earlier (section 3.3), an exposed $Al-O^-$ or $Si-O^-$ group (produced by the attack on muscovite by a polymerizing phosphate) can react with one $>P^+=O$ group which may either belong to an acid or may be part of a silicon or aluminium polyphosphate chain. Thus, both Al^{3+} and Si^{4+} may exist in the same polyphosphate chain. Moreover, each Al^{3+} and Si^{4+} may bond with four P-O groups. The resultant residue must, therefore, be a three-dimensional polyphosphate network interlinked with Si^{4+} and Al^{3+} . In the initial stages of the reaction when the chains are small and there are fewer Si^{4+} and Al^{3+} in solution, interlinking would also be negligible and the polyphosphates more soluble. As the reaction progresses, cross-linking and condensation would cause insolubilization and would impart hardness to the residue. In fact, a visual observation of the reaction shows that initially a translucent, jellylike product is formed (soluble silicon and aluminium phosphates) which later changes to a white, hard, bloated mass with numerous holes on its surface. The bloating is due to the fact that as the surface begins to harden (due to cross-linking) sooner than the interior, the water lost in condensation, from within, pushes up and perforates the surface, giving it the characteristic appearance.

Another perplexing point regarding M_r is why residual muscovite persists and all K^+ cannot be solubilized in spite of heating with excess acid for prolonged periods (Figure 1). The photographs in Figure 5 provide the answer. At first glance, no muscovite flakes are visible in the residue M_r ; dark amorphous regions appear, interspersed with patches of crystallinity (Figure 5b). When the sample is

heated from 700 to 1100 °C, the lighter regions progressively lose their crystallinity whereas the darker regions become crystalline (Figure 5c). Thus in samples heated at 1100 °C, the dark patches (Figure 5c) show, under cross-polarizers, strong interference colors whereas interference is no longer visible in the lighter regions. Since muscovite loses its crystallinity at 1100 °C whereas silicon and aluminium phosphates crystallize (Table III), the lighter regions on the flake which become amorphous on heating must be the surface of muscovite. Over this, an opaque coating of the amorphous phosphate is formed which crystallizes at 1100 °C.

The observations may be interpreted as follows: On heating with phosphoric acid, the muscovite flake gradually becomes covered with an amorphous coating of the polyphosphates. This is proved by the fact that after boiling M_r with water, residual flakes of muscovite become visible (Figure 5d). Apparently, the coating is impenetrable to phosphoric acid, and this protects the muscovite from further attack. It was observed that when a large excess of phosphoric acid was used—such, that the phosphates remained in solution and could not form an insoluble coating—the muscovite reacted completely. The same was also observed when muscovite grains of smaller size (<200 mesh B.S.) were used for reaction. This proves that an amorphous coating is in fact formed, as revealed by the microscope studies.

Summary. The insoluble product obtained on reaction of phosphoric acid with muscovite is an amorphous, cross-linked silicon-aluminium polyphosphate covering a core of residual muscovite. The residual muscovite resists further decomposition because of the formation of an insoluble and impenetrable surface coating that prevents complete reaction of muscovite with phosphoric acid.

4. Conclusion

The reaction of phosphoric acid with muscovite causes the dissolution of K^+ , Al^{3+} , and Si^{4+} ions from the crystal lattice. Reaction kinetics suggests a complex reaction mechanism. Rates of release of K^+ at 250, 300, and 350 °C cannot be fitted into any single conventional kinetics equation. Rates of solubilization have, however, been observed to depend on weight loss during reaction. Kinetics of phosphoric acid polymerization was studied. The chain length of the polyphosphoric acid has been found to be linearly related to the K^+ release. On the basis of these experimental observations as well as on information available from the literature about reactions in phosphate and silicate melts, a mechanism for the reaction of hot phosphoric acid has been outlined. It has been proposed that phosphoric acid, when heated to polymerization temperatures, liberates OH^- ions which attack other P-OH or Si-O-Si/Al-O-Si bonds of muscovite forming P-O-P, Al/Si-OH, and Al/Si-O-P bonds and eliminating H_2O . Experimental findings support the proposed mechanism. Identification of the insoluble product of reaction was attempted utilizing XRD, IR, and petrographic methods. It has been concluded that the reaction of phosphoric acid with muscovite produces insoluble, together with soluble, cross-linked silicon-aluminium polyphosphates that surround a core of unreacted muscovite. The amorphous polyphosphate coating prevents complete attack by the acid on the grains of residual muscovite.

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Registry No. $\text{H}_3\text{O}_4\text{P}$, 7664-38-2; muscovite, 1318-94-1.

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Wet Milling of Alumina and Preparation of Slurries for Monolithic Structures Impregnation

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The wet grinding of alumina with HCl for forming stable dispersions was investigated in a laboratory ball mill. Acid concentrations in the range 1-10 wt % of dry alumina do not influence the wet-milling product. The viscosity of the alumina slurries produced from the wet-milling process is strongly dependent on pH while minimum viscosity was achieved at pH 3.5-3.8. Impregnation of ceramic monolithic substrates with alumina dispersions of varying particle size distributions affects the pore volume distribution of the alumina coating in the intermediate pore radius region.

Introduction

Thin-walled honeycombed substrates find extensive use as catalyst supports in catalytic exhaust converters. To be useful in catalytic reactions, the catalyst supports require that a high surface area coating must be deposited upon its surface. The coating should provide adequate porosity so that the catalytic materials present can be more effective. A coating comprising these requirements is that of γ -alumina.

The alumina coating is applied usually by the immersion of the substrate in an alumina slurry. The support coated with the wet slurry is blown with air to remove excess slurry and subsequently dried and calcined (Stiles, 1983).

To deposit the suitable amount of alumina in a single application, the solid content of the slurry has to be high. It is important to control the viscosity during the wash-coating process, in order to achieve high-slurry alumina loadings, to aid the adhesion of the alumina to the substrate and to prevent the plugging of monolithic structure channels.

Keith et al. (1967) prepared an alumina slurry by wet milling 970 g of alumina which had a composition of 86% γ -alumina and 16% boehmite with the addition of 910 mL of deionized water and 20 mL of concentrated HCl. The mixture was milled for 18 h at about 80-112 rpm to obtain a thixotropic slip, which was used to impregnate an α -alumina corrugated type block. This slurry has been found to be sufficient in providing a uniform coating to the α -alumina block with dimensions 6 in. by 4 in. by 3 in.

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