

Article

Non-Crystalline Aluminum Polyphosphates: Preparation and Properties

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Received: May 31, 1996; June 5, 1996

A mistura simultânea de nitrato de alumínio, polifosfato de sódio e hidróxido de amônio produz polifosfato de alumínio não-cristalino. Oito amostras diferentes foram obtidas e caracterizadas por análise elementar, difração de raios X, espectrofotometria de IV, microscopia eletrônica de varredura e análise termocundutimétrica. As propriedades dos pós são fortemente dependentes da sua composição química, principalmente da sua relação molar P:Al. Grande estabilidade térmica é observada quando $P/Al \leq 1$. Se $P/Al \geq 1$, as partículas sinterizam a aproximadamente 500 °C e amolecem e expandem a cerca de 700 °C, produzindo pós e monolitos com poros fechados. As temperaturas de amolecimento podem ser detectadas pelas análises termocundutimétricas.

Simultaneous admixture of aluminum nitrate, sodium polyphosphate and ammonium hydroxide yields aluminum polyphosphate powders. Preparations were performed following a two-level factorial plan in which the variables were the reagent concentrations. Eight different powders were obtained and characterized by elemental analysis, X-ray diffraction, infrared spectrophotometry, scanning electron microscopy, and thermalconductimetric analysis. The properties of the powders are strongly dependent on their chemical compositions, specially on the P/Al mol ratio. A higher thermal stability is observed when $P/Al \leq 1$. In the case of $P/Al \geq 1$ powder particles sinter at *ca.* 500 °C, and they soften and expand at *ca.* 700 °C yielding closed cell monoliths and powders. Softening temperatures are easily detected by thermalconductimetric analysis.

Keywords: *aluminum polyphosphate, non crystalline solids, thermalconductimetric analysis*

Introduction

Many non-crystalline inorganic solids appear under various circumstances in the nature, within laboratories and chemical plants. These solids have never received as much attention as related crystalline inorganic substances or as non-crystalline organic polymers.

Non-crystalline hydrous metal oxides and hydroxosalts (phosphate, sulfides, carbonates, etc.) are normally charac-

terized by a number of spectroscopic, scattering, morphological and other (electrical, optical, thermal) techniques. However, experimental results often point to a great complexity, which can be easily understood considering that these solids are highly cross-linked supramolecular networks, made of ions which have large connectivities, in variable stoichiometric ratios¹.

For instance, we may consider iron (III) and aluminum polyphosphates, prepared within an aqueous environment.

Aquo-iron (III) and aluminum ions have maximum connectivity equal to 3; they may be hydrolyzed forming hydroxocations, which are polyelectrolytes having a large connectivity for ionic contacts. On the other hand, the connectivity of oligomers such as triphosphate may be two or greater, up to five. Larger polyphosphate chains connectivity may reach many tens². For these reasons, non-crystalline iron and aluminum oxide phosphates are probably among the most complex chemical networks. In this respect, they are comparable to substances such as highly cross-linked rubbers, lignins and polyelectrolyte gels^{3,4}.

A number of substances may be prepared by simple admixture of sodium polyphosphate and iron or aluminum salt (chloride, nitrate, sulfate) aqueous solutions. In previous work we have shown that non-crystalline iron and aluminum polyphosphates present some interesting and unusual properties as precursors of new materials. Iron polyphosphate powder yields a rigid foam, when heated to ca. 700 °C. Further heating to 1100 °C produces a low viscosity glass⁵. Aluminum polyphosphate and orthophosphate powders are used to make particles containing closed cells, which are powerful light scatterers and can be used as white pigments, in coating films^{6,7}. Beyond that, thermoreversible gel^{8,9} and nanoparticles¹⁰ are formed from aluminum polyphosphate aqueous solutions. Notwithstanding the simple preparation technique, these solids present great complexity, because of their large range of chemical compositions.

In this work we describe the formation of non-crystalline aluminum polyphosphate solids under different reagent concentration ratios and their characterization.

Experimental

Aluminum polyphosphates were prepared by admixture of aqueous solutions of aluminum nitrate, sodium polyphosphate and ammonium hydroxide, following a factorial plan¹¹. The variables used in this plan are the molar

concentrations of the reagents at two levels each, as shown in Table 1. As a result, a total eight substances of different compositions were obtained. The precipitations were performed in a semibatch 150 mL stirred reactor, initially filled with 20 mL of water, at room temperature (22-25 °C). 30 mL of each reagent were added simultaneously, using a peristaltic pump. Following this procedure, the molar ratios of the reagents and the pH were kept constant during each preparation. The white precipitates thus obtained were centrifuged and washed four times with 1:1 (v/v) aqueous ethanol solutions. Each solid was then spread in Petri dishes, dried in an oven for 5 h at 120 °C, passed in a two-roll mill, sieved in a 400 mesh screen, and finally stored in closed vials.

Aluminum was determined by atomic absorption spectrophotometry in a model 5000 Perkin-Elmer spectrophotometer using a nitrous oxide flame. Phosphorus was determined spectrophotometrically, by using the molybdenum blue method¹². Sodium was determined by flame photometry in a B262 Micronal photometer.

X-ray diffractograms were obtained at room temperature using an XD3A Shimadzu diffractometer; Cu K α radiation was generated at 30 kV and 20 mA. Infrared spectra of CsI pellets (1:200 mass ratio) were obtained in the 4000-200 cm⁻¹ range, by using a 1430 Perkin-Elmer IR spectrophotometer. Thermogravimetric analysis (TGA) was done using a model 9900 Du Pont balance and differential thermograms were obtained in a DTA-

Table 1. Levels of the variables used in the factorial design for aluminum polyphosphate synthesis.

Variable	Low level	High level
Al(NO ₃) ₃ concentration	1.0 mol/dm ³	2.0 mol/dm ³
(NaPO ₃) _n concentration	1.0 mol/dm ³	3.6 mol/dm ³
NH ₄ OH concentration	0.7 mol/dm ³	3.6 mol/dm ³

Table 2. Elemental composition of aluminum polyphosphates.

Sample Number	Supernatant pH	Aluminum % \pm 0.1 %	Phosphorus % \pm 0.2%	Sodium % \pm 0.2%	Stoichiometric ratios		
					Al	P	Na
1	3.5	14.5	21.8	0.0	1.00	1.20	0.00
2	3.0	15.2	18.9	0.0	1.00	1.00	0.00
3	5.4	8.0	24.0	6.7	1.00	2.60	1.00
4	2.5	10.4	16.7	0.5	1.00	2.10	0.05
5	9.8	19.2	16.5	3.5	1.00	0.70	0.20
6	8.5	19.8	11.3	1.6	1.00	0.50	0.10
7	10.0	11.7	23.3	10.7	1.00	1.70	1.00
8	9.0	12.9	20.8	7.3	1.00	1.40	0.70

7000 Perkin-Elmer instrument (from Instituto de Química de Araraquara).

Thermalconductimetric analysis was performed using an instrument assembled in this laboratory, fitted with a cell mounted within a furnace¹³. The cell can be heated up to 1000 °C, using heating rates in the 5-10 °C/min heating rate range. Powder pellet diameter was 13 mm, and the pellets were obtained using a constant powder weight. Prior to the measurements, the pellets were heated to 300 °C and cooled back to room temperature. The heating ramp was then started, and AC (1 kHz, 0.5 V peak voltage) electrical resistance was recorded.

Scanning electron micrographs (SEM) were obtained in a JEOL T300 instrument. Powder pellets were fractured, glued with a conductive paint over the sample holder and carbon/gold coated by sputtering.

Results

The elemental composition of the solids obtained by precipitation following admixture of aluminum nitrate, sodium polyphosphate and ammonium hydroxide aqueous solutions is given in Table 2. Al/P molar ratio ranges from 2 to 0.36, Na/Al ratio ranges from 0 to 1. There is not a predominant stoichiometry. Considering the charge balance, examination of Table 2 shows that every sample should have an excess of positive charges, assuming that the relevant species are Al^{3+} , Na^+ and PO_3^- . Consequently, either aluminum ions are present as hydroxocations or nitrate counterions are still retained in the gel particles. As shown in Table 2, final pH in these reactions ranges from 2 to 10. Samples having a large P/Al ratio have also a large Na content, and are thus better described as sodium-hydroxoaluminum polyphosphates. There is no simple correlation between the P/Al ratio

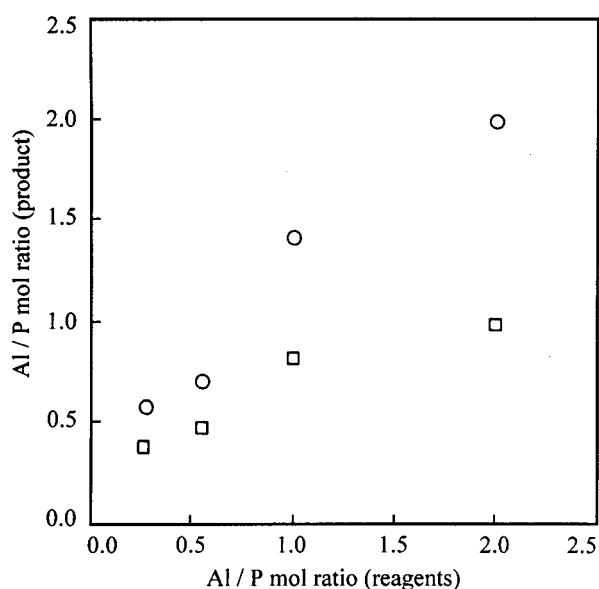


Figure 1. Al/P mol ratio in the solids as a function of Al/P mol ratio in the reaction admixtures.

used in a given admixture and the ratio in the solid obtained, as shown in Fig. 1.

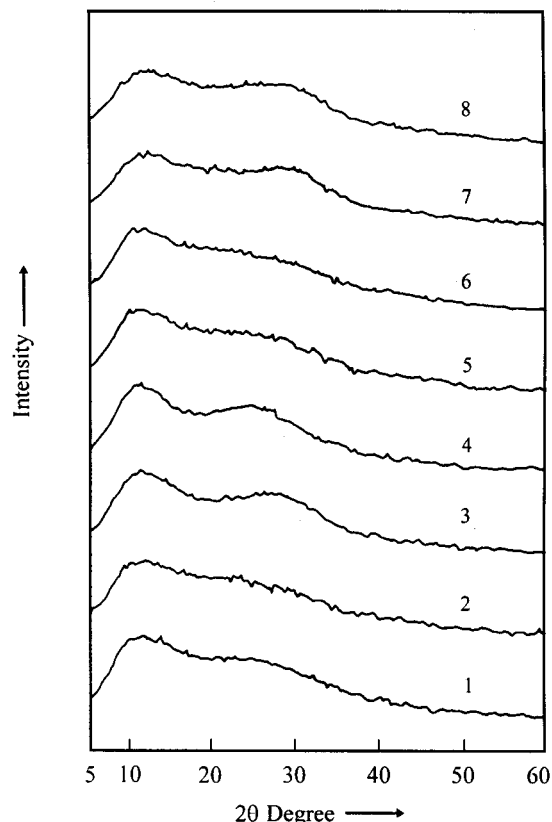


Figure 3. X-ray diffractograms of aluminum polyphosphate samples (sample numbers are the same as in Table 1).

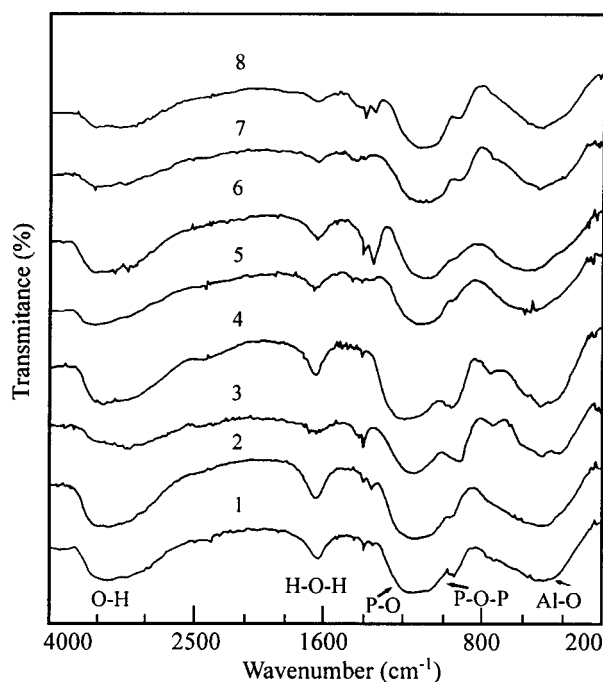


Figure 2. Infrared spectra of aluminum polyphosphate samples (sample numbers are the same as in Table 1).

Infrared spectra obtained for these samples are in Fig. 2. They show that these are hydrous solids; other characteristics of these spectra are the bands which can be assigned to P-O ($1200 - 1100 \text{ cm}^{-1}$), P-O-P ($970 - 930$ and 750 cm^{-1}) groups, as well as to Al-O ($600 - 530 \text{ cm}^{-1}$). The intensities of the bands assigned to P-O-P group are higher in the samples richer in phosphorus.

X-rays diffractograms show that these are non-crystalline solids (Fig. 3). Under heating, they can crystallize into different phases, according to their compositions. For instance, AlPO_4 and $\text{Al}(\text{PO}_3)_3$ are formed upon heating samples 4 and 6, respectively (Fig. 4).

Thermal behavior

All of these solids loose weight upon heating, what is assigned to water loss (Fig. 5). This is essentially complete at $400 \text{ }^\circ\text{C}$. Differential thermograms (Fig. 6) present broad endothermic bands up to $400 \text{ }^\circ\text{C}$ and small exothermic peaks. The later occur at temperatures dissociated from any singularities in the thermogravimetric curves, for which reason they are assigned to the onset of crystallization.

Thermalconductimetric analysis results are presented in Fig. 7 and show that all samples are dielectric at room temperature but the resistance of sample 6 is

markedly lower than that of the other samples. Upon heating, there is a pronounced decrease in electrical resistance of all samples with the exception of samples 2 and 6. Since the decrease in electrical resistance of these solids can only be assigned to ionic conduction, we conclude that the P-rich samples (resp. 3, 4, 7 and 8), are those in which large ionic mobility takes place at lowest temperatures. The behavior of samples 3, 7 and 8 is very similar to each other and these are the samples with the highest sodium content. Sample 2, which is exempt of sodium and has one of the largest Al/P ratios is the most refractory of all samples.

Morphological changes

The polyphosphate samples were pressed into pellets and heated. In some cases, the pellets underwent expansion and were transformed into rigid foams. In other cases, the pellets shrunk and became dense. Again, sample 6 behavior is quite different from all others: first, under cold-pressing it gives dense and translucent pellets as was described previously in Refs. 10 and 14. Fracture micrographs of the heated pellets (Fig. 8) show two different patterns: i) the pellets of P and Na-rich samples produce rigid foams; ii) the pellets of Al-rich samples are dense and have a low porosity, after heating.

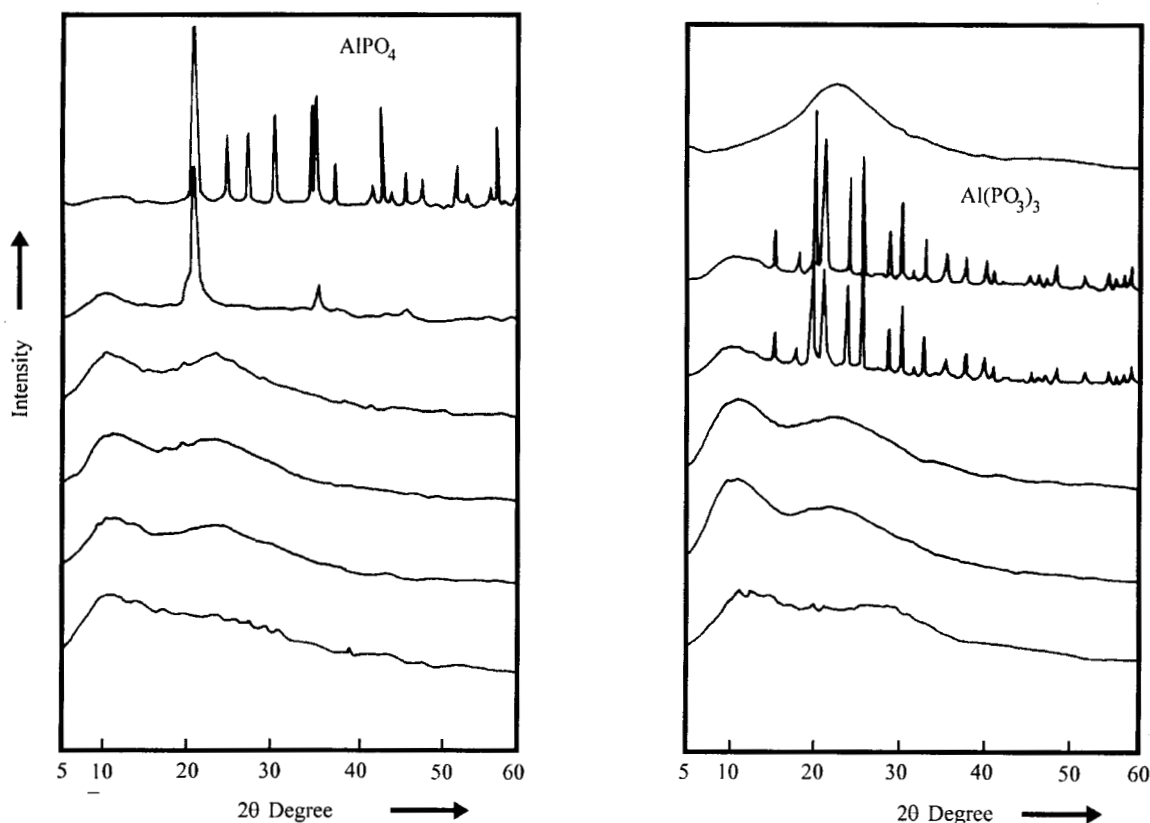


Figure 4. X-ray diffractograms of aluminum polyphosphate samples after heating for 30 min.: sample 4 (right), sample 6 (left). From bottom to top, the heating temperature is: 120, 400, 600, 800, 1000 and $1200 \text{ }^\circ\text{C}$.

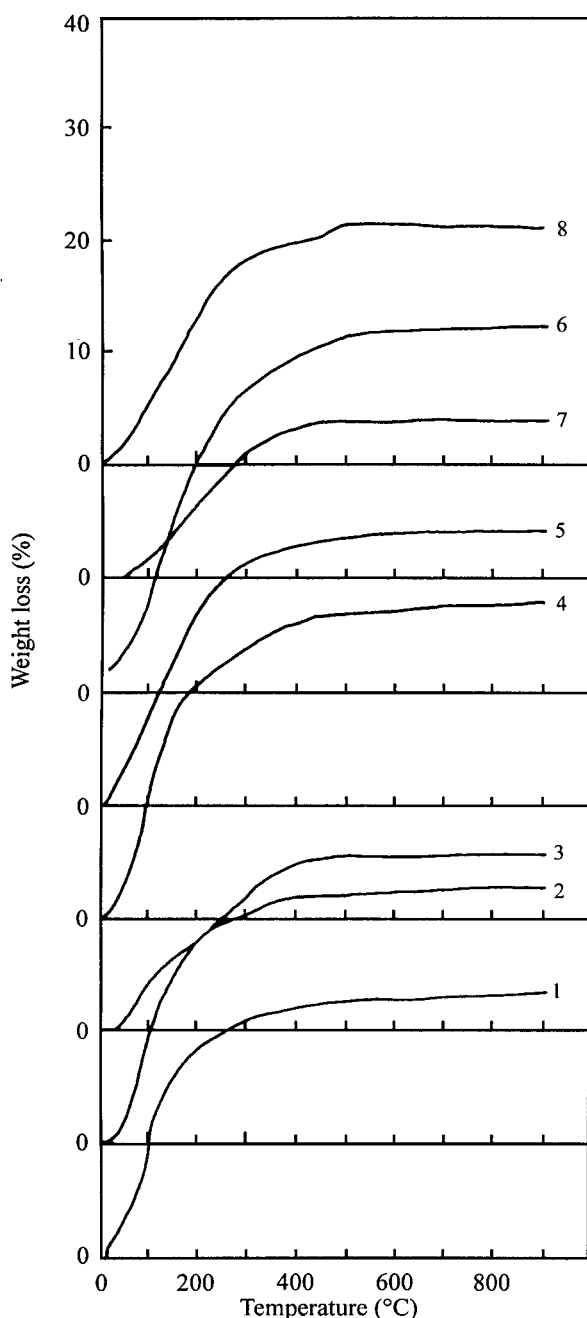


Figure 5. TGA curves of aluminum polyphosphate samples (sample numbers are the same as in Table 1).

Analogous observations can be made on the powders themselves: high-P solids undergo expansion changing into hollow particles, while the others show only a rounding-off of their corners and other sharp features, and a tendency to sinter^{6, 13}

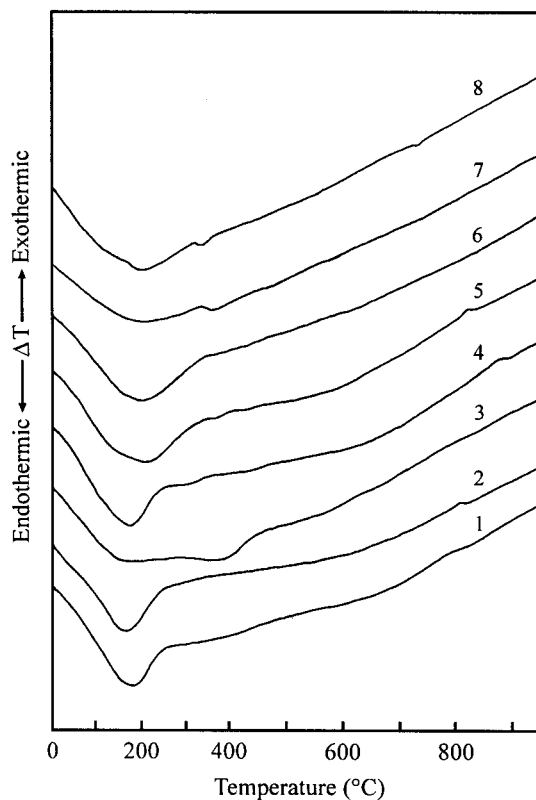


Figure 6. DMA curves of aluminum polyphosphate samples (sample numbers are the same as in Table 1).

Discussion

Previous reports in the literature have pointed towards a large diversity of formulas for aluminum polyphosphates¹⁴. This is verified in this work but using only minor changes in the preparative conditions.

The large range of properties displayed by these solids can be understood by analogy with the effect of cation substitution in silicate glasses: large concentrations of monovalent cations are found in softer, more soluble glasses; large contents of aluminum increase the water and alkali resistance of glasses as well as their softening points¹⁵.

However, we should attempt to understand why so many solids of different compositions are obtained.

The variety of P/Al ratio in the products obtained in this work agrees with Cheung *et al.*¹⁶, who indicate two possibilities for the structure of amorphous aluminum phosphate obtained from precipitation. The first possibility is that constituent ions could be randomly arranged at a molecular level. The second is that these products are simply intimately mixed domains of alumina and aluminum phosphate. Vogel and Marcelin¹⁷, observed that approximately 6% of the phosphate from a 1:1 reagent mixture was not precipitated, at pH 8.5. Therefore, the corresponding por-

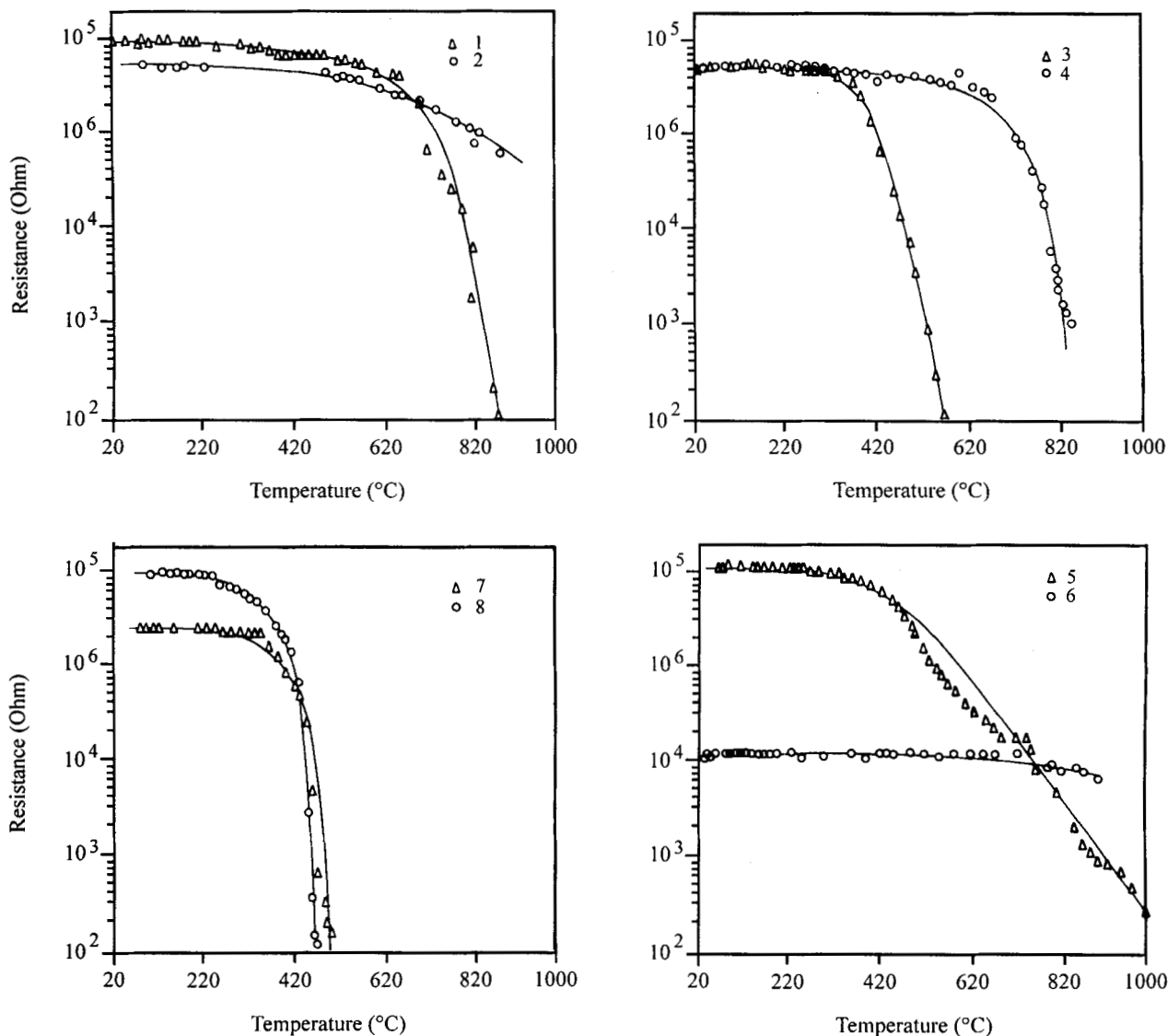


Figure 7. Thermalconductimetric analyses of aluminum polyphosphate samples (sample numbers are the same as in Table 1).

tion of aluminum must be present as the oxide. Other similar studies follow the same arguments^{18,19}.

In the present work, polyphosphate is used instead of orthophosphate. This certainly increases the degree of complexity of the system, due to the larger connectivities that are involved. However, the finding of significant amounts of sodium and the indirect evidence for hydroxo or nitrate anions (based on charge balance) was confirmed in a related paper from this laboratory⁸. This shows that amorphous aluminum phosphates are more diverse and complex entities than what has been reported in the literature.

Other work from this laboratory (to be published) shows that different patterns of behavior are also observed in the precipitation of aluminum, iron (III) and chromium polyphosphates. Only in the case of iron, the solids obtained by precipitation approach a definite, uniform

stoichiometry. This means that among these systems iron polyphosphates are the only ones which approach the equilibrium state. It is well-known that hexaquoiron (III) cations exchange ligands much faster than aluminum or chromium (III) aquoions²⁰. Characteristic exchange rates for the reaction are respectively 2 and 4 orders of magnitude faster for iron than for aluminum or chromium.

Thus, aluminum polyphosphate precipitation under conditions preventing approach to equilibrium (Ostwald ripening, etc.) "freezes-in" chemical structures which are formed just due to random ion association and are determined by kinetic as well as by minimum free-energy constraints.

We believe that the facts described in this work, besides revealing a chemical system with a large potential of gen-

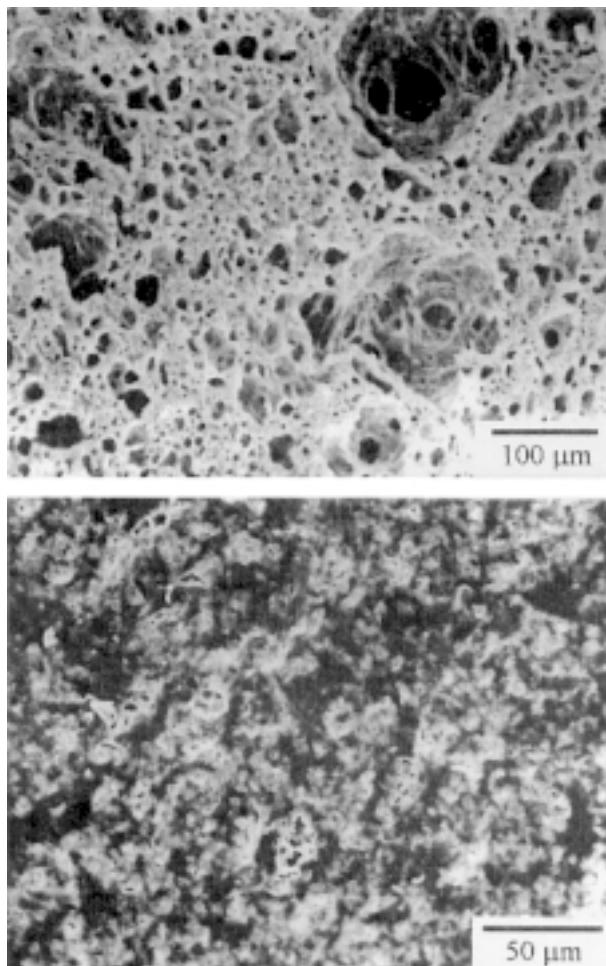


Figure 8. Scanning electron micrographs of fracture surfaces of: top) a rigid foam obtained by heating a pellet of sample 8 at 700 °C for 15 min; bottom) pellet of sample 5 after heating at 900 °C for 15 min.

erating new materials, have given us some clues about the general behavior of non-crystalline inorganic salts.

Acknowledgments

FG acknowledges support from CNPq, Fapesp and PADCT/Finep; during this work, ECOL received fellowships from CNPq and FAPESP.

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FAPESP helped in meeting the publication costs of this article