PROPERTIES OF SYNTHESIZED INORGANIC POLYMERIC PHOSPHATE MATERIALS AND POSSIBILITIES FOR PRODUCTION OF NEW ENVIRONMENTALLY FRIENDLY AND ECONOMICALLY VIABLE SUPPLIES FROM LOCAL INDUSTRIAL WASTE

M. Avaliani^{1,*}, V. Chagelishvili¹, E. Shapakidze², M. Gvelesiani¹, N. Barnovi¹, M. Vibliani¹, K. Chikovani¹

¹ R. Agladze Institute of Inorganic Chemistry & Electrochemistry I. Javakhishvili Tbilisi State University Tbilisi, Georgia *avaliani21@hotmail.com ² A. Tvalchrelidze Caucasian Institute of Mineral Resources I. Javakhishvili Tbilisi State University Tbilisi, Georgia

Accepted 2020 November 17

Abstract

In the paper, the data on obtaining and general properties of polymeric phosphates first time synthesized by the authors are considered. There are analyzed the possibilities of production of new geopolymeric binder materials by inclusion of small amounts of these condensed materials into industrial waste and using phosphoric acid.

Deteriorating of the environmental situation in the world has opened up new opportunities for scientists to seek ways to develop new technologies that will ensure suitable sustainable development. In the construction sector, new materials have emerged as an alternative, whose production is characterized by a lower degree of negative impact on the environment. One of these construction materials are geopolymers, which are considered as alternative for portland cement because they are characterized by properties similar to those of the mentioned cement, in particular, such as high physical-mechanical properties and durability. At the same time, the production of geopolymers is not associated with high carbon dioxide emissions. As is well-known that geopolymers are inorganic polymers consisting of repeating chains, such as silicon oxide (-Si-O-Si-O-), silicoaluminate (-Fe-O-Si-O-Al-O-), ferrosilicoaluminate (-Fe-O-Si-O-Al-O-) or alumophosphate (-Al-OPO-) chains formed through the polymerization process.

Primarily the influence of inherent characteristics of volcanic rocks on the creation of geopolymeric binders' structure was studied. Also, we are conscious: it would be very interesting to study in details some researches with participation of double condensed phosphates containing vitreous phase in curing of geopolymeric binders, these experiments will be conducted soon in the shortest possible time. At the first time the opportunity of activation of crystallized slag, with double condensed phosphates of mono- and polyvalent metals joint thermo-processing was examined, as well as influence of different modes of mechanical-

activation and curing on the reaction-ability of components of geopolymeric binders. Of course first of all we needed to we had to synthesize the phosphates we needed. We will try to make a more detailed point on this subject.

Generally condensed phosphates of polyvalent metals possess a number of rather interesting and appreciable properties, which explains various areas of their application. Actually anions are known for n = 3, 4, 5, 6, 8, 9, 10, and 12 [1 - 7].

Fairly high thermal stability of mentioned condensed phosphates, elevated content of phosphorus – these properties have caused their application as raw components for manufacture of phosphate glasses; The crystalline and non-crystalline ultraphosphates are used in quantum electronics, which are predetermined by their specific properties.

In fact it is necessary to underline, that some compounds of cyclophosphates vas primarily synthesized, firstly examined and determined by us, sometimes in collaboration with Dr. N. Chudinova and academician I. Tananaev [1, 3 - 5, 7 - 9]. In fact the achievements obtained by methods and direction of researches, named "Scientific School of Tananaev" in the vast and extensive domain of condensed phosphates is very remarkable.

Sufficient stability of polymeric phosphates in this respect makes it possible to identify and categorize them by the method of paper chromatography. This fact permitted scientists to examine the process of formation and the composition of many normal, basic and/or acid of both simple and double di-, tri-, tetra-, octa- and dodecaphosphates of polyvalent metals. This method together with the chemical analysis, IR-spectroscopy, thermogravimetry, X-Ray diffraction, and structural analysis was used by us.

The present data is the result of our studies – synthesis, analysis, examination of the experimental records and their comparison and / or correlation which achievements in the domain of inorganic polymer's chemistry [1 - 5, 7]. Condensed phosphates of polyvalent metals, notably double phosphates containing alkali metals enjoy a number of relatively remarkable and significant properties, which explains their appreciation and variable scenarios of their applications.

Beforehand we already knew that high thermal stability, elevated content of phosphorus – these preconditions have caused the various applications as raw components for manufacture of phosphates glasses, the use of crystalline and non crystalline ultraphosphates in quantum electronics are predetermined by specific properties.

Just for these reasons we synthesized many new double condensed oligo- and cyclophosphates, whose general properties we have examined [3 - 5, 7]: systematic investigation of M¹₂O-M¹¹¹₂O₃-P₂O₅-H₂O at 120 - 650 °C, where M¹ = alkali metals and M¹¹¹ - Ga, In, Sc, Al was executed. In addition investigation of systems Ag₂O-M¹¹¹₂O₃-P₂O₅-H₂O at 150 - 600 °C was examined. Many compounds were wholly studied and the structures are determined by X-ray structural techniques [1, 3 - 5].

Thus, presented work is the result of synthesis, analysis, investigation of the experimental records, their examination, determination and evaluation of their properties and correspondence with accomplishments and advances in the area of inorganic polymers' chemistry [2-6].

During last years' more of 85 new formerly unknown double condensed phosphates have been obtained, including the first representatives of double cyclooctaphosphate classs – $K_2Ga_2P_8O_{24}$ and $Rb_2Ga_2P_8O_{24}$ were obtained by M. Avaliani & N. Chudinova [4, 7], crystal structure was examined and described [1, 4, 5]. The structure of K₂Ga₂P₈O₂₄ (reminds crownether).

One of primary synthesized cyclododecaphosphates, e.g Cs₃ Ga₃ P₁₂ 0₃₆, Cs₃ Sc₃P₁₂ 0₃₆, Cs₃In₃P₁₂0₃₆ have been obtained by us [9 - 11] (see also detailed and interesting publication [6]). These achievements, including the successful synthesis of the first representatives of double cyclooctaphosphate classs – K₂Ga₂P₈O₂₄ and Rb₂Ga₂P₈O₂₄ are noted and distinguished by many scientists / authors in the important publications [1, 2, 6, 8].

So, by crystallization from melts of polyphosphoric acids at the temperature range of 120 – 650 °C we are obtaining more than 85 double condensed phosphates of alkali and trivalent metals; all compounds, or practically almost entities were identified by roentgen phase analysis and investigates thermo gravimetrically [3 - 5], many compounds was wholly examined by X-ray structural techniques, described in works [1, 7 - 9, 12].

The physical and chemical properties of phosphates are evaluated. In addition, detailed investigation of system $M^{I_2}O-M^{III_2}O_3-P_2O_5-H_2O$ at 150 – 350 °C, where M^{III} = Tl is on the stage of examination.

Discussing about the range of $M^{I}M^{III}(PO_3)_4$ compounds' structures where M^{I} is constantly alkali or any other monovalent metal and where M^{III} is any of trivalent metals such as gallium, indium, scandium and others, even rare earth elements, it can be concluded: while the radius of M^{3+} decreases, the polyphosphate chain identity period increases, due to complication of its form-factors; the cycles slowly appears, the number of structural types increases caused by correlation of average distances between (M^{III} –O) and (M^{I} –O). Less is the correlation / ratio, more is the probability of big cycle formation.

Concerning geopolymers: the commercial application of these materials can be used in the production of fire-retardant and heat-resistant coatings and sealants, in medicine, in high-temperature ceramics, for the encapsulation of new types of fibrous, toxic, and radioactive waste components, and as a component of cement and concrete. The properties of geopolymers have been studied in many scientific and industrial disciplines [13 - 22], and examined by various researchers [23 - 29], and taking into account these aspects we have considered experimenting: by adding a certain amount of condensed phosphates synthesized by us to geopolymers in order to increase their binder properties.

By citing Dr. E. Shapakidze, "Geopolymers are an innovative materials, and they are progressively turning to a partial or complete alternative to Portland cement in the fabrication of concrete, which is presently considered one of the main causes of ecological system degradation and destroys the sustainable development model" [30 - 34]. In view of the reasons, mentioned above, the production of new environmentally friendly and economically viable materials from local industrial waste is of great importance, especially since adding very small quantities of the new condensed phosphates synthesized by us gives the hope of anticipating the improvement of their qualities [33, 34].

The influence of chemical, thermal and mechanical activation on the formation of structure and processes of curing of geopolymeric binders will be studied during future experiments as soon as possible.

Having reconsidered and resuming the above it is very interesting to study the possibility of obtaining new geopolymer binders based on metallurgical dump slags and phosphoric acid and also by adding to the geopolymers a smaller quantity of condensed phosphates obtaining the alternatives to portland cement – geopolymers with improved

properties. The first steps to obtain the desired materials have been taken. Heat-insulating porous geopolymer materials were obtained under laboratory conditions **[33, 34]**. Studies of the possibilities of obtaining new geopolymer binders on the basis of industrial waste and phosphoric acid were conducted. When selecting the ratio of dump slag to sand, it is possible to regulate the properties of the binder, for example, porosity and mechanical strength **[34]**.

References

- [1] M.-Th. Averbuch–Pouchot, A. Durif. Topics in Phosphate Chemistry, 1996, World Scientific.
- [2] A. Durif. The development of cyclophosphate crystal chemistry. Solid State Sci., 2005, 7, 6, 760-766.
- [3] I. Grunze, K. K. Palkina, N. N. Chudinova, M. A. Avaliani, L. S. Guzeeva. Structure and thermal transitions of double Cs–Ca phosphates. Inorg. Mater., 2009, 23, 4, 539-544.
- [4] M. Avaliani. Investigation and thermal behaviour of double condensed compounds of gallium, scandium and silver. Nano Studies, 2018, 17/18, 21-24.
- [5] M. Avaliani, E. Shapakidze, N. Barnovi, D. Dzanashvili, G. Todradze, V. Kveselava, N. Gongadze. Regiocontrolled synthesis of double condensed oligo-, poly-, and cyclo-phosphates, their characterization and possible solid-state applications. Nano Studies, 2019, 19, 273-284.
- [6] E. V. Murashova, N. N. Chudinova. Double condensed phosphates of caesium–indium. Inorg. Mater., 2001, 37, 12, 1521-1524.
- [7] M. Avaliani. Synthesis and Investigation of Condensed Phosphates of Gallium and Indium (PhD Thesis), 1982, Moscow, N. Kurnakov Inst. Gen. Inorg. Chem.
- [8] A. Oudahmane, D. Avignant, D. Zambon. Dipotassium dialuminium cyclooctaphosphate. Struc. Rep., 2010, 2, 7, 149-150.
- [9] M. Avaliani, E. Shapakidze. Areas of crystallization of double condensed phosphates of Ag and trivalent metals and regularities of their formation. In: Abs. 5th Int. Conf. Org. Inorg. Chem. "Strategic Approach and Future Generation Advancements in Organic and Inorganic Chemistry", 2018, Paris, Poster, DOI: 10.13140/RG.2.2.11335.19364.
- [10] M. Avaliani, V. Chagelishvili, E. Shapakidze, M. Gvelesiani, N. Barnovi, V. Kveselava, N. Esakia. Crystallization fields of condensed scandium-silver and gallium-silver phosphates. Eur. Chem. Bull., 2019, 8, 5, 164-170.
- [11] M. Avaliani, M. Gvelesiani. Areas of crystallization of condensed scandium and caesium phosphates and regularities of their formation. Proc. Georgian Natl. Acad. Sci. (Chem. Ser.), 2006, 32, 1/2, 52-58.
- [12] K. K. Palkina, S. I. Maksimova, V. G. Kuznetsov, N. N. Chudinova. Structure of crystals of double octametaphosphate Ga₂K₂P₈O₂₄. Dokl. Acad. Sci. USSR, 1979, 245, 6, 1386-1389.
- [13] M. L. Gualtieri, M. Romagnolia, A. F. Gualtieri. Preparation of phosphoric acid-based geopolymer foams using limestone aspore forming agent – Thermal properties by *in situ* XRPD and Rietveld refinements. J. Eur. Ceram. Soc., 2015, 35, 11, 3167-3178.
- [14] A. S. Wagh. Chemically bonded phosphate ceramics A novel class of geopolymers. Ceram. Trans., 2005, 165, 107-116.

- [15] M. L. Gualtieri, M. Romagnoli, S. Pollastri, A. F. Gualtieri. Inorganic polymers from laterite using activation with phosphoric acid and alkaline sodium silicate solution: Mechanical and microstructural properties. Cem. Concr. Res, 2015, 67, 259-270.
- [16] D. S. Perera, J. V. Hanna, J. Davis, M. G. Blackford, B. A. Latella, Y. Sasaki, E. R. Vance. Relative strengths of phosphoric acid-reacted and alkali-reacted metakaolin materials. J. Mater. Sci., 2008, 43, 6562-6566.
- [17] L.-P. Liu, X.-M. Cui, S.-H. Qiu, J.-L. Yu, L. Zhang. Preparation of phosphoric acid-based porous geopolymers. Appl. Clay Sci., 2010, 50, 600-603.
- [18] A. Katsiki, T. Hertel, T. Tysmans, Y. Pontikes, H. Rahier. Metakaolinite phosphate cementitious matrix: Inorganic polymer obtained by acidic activation. Materials, 2019, 12, 3, 442, 1-15.
- [19] H. K. Tchakoute, C. H. Ruscher. Mechanical and microstructural properties of metakaolin-based geopolymer cements from sodium waterglass and phosphoric acid solution as hardeners: A comparative study. Appl. Clay Sci., 2017, 140, 81-87.
- [20] S. Louati, S. Baklouti, B. Samet. Geopolymers based on phosphoric acid and illitokaolinitic clay. Adv. Mater. Sci. Eng., 2016, 2016, 2359759, 1-7.
- [21] H. Celerier, J. Jouin, V. Mathivet, N. Tessier–Doyen, S. Rossignol. Composition and properties of phosphoric cid-based geopolymers. J. Non-Cryst. Solids, 2018, 493, 94-98.
- [22] H. Douiri, S. Louati, S. Baklouti, M. Arous, Z. Fakhfakh. Enhanced dielectric performance of metakaolin–H₃PO₄ geopolymers. Mater. Lett., 2016, 164, 299-302.
- [23] Y. Han, X. Cui, X. Lv, K. Wang. Preparation and characterization of geopolymers based on aphosphoric-acid-activated electrolytic manganese dioxide residue. J. Clean. Prod., 2018, 205, 488-498.
- [24] A. V. Sarukhanishvili, L. Shashek, E. V. Shapakidze, I. A. Sarukhanishvili. Waste materials from the production of electrolytic manganese dioxide in the glass-container industry. Glass Ceram., 1992, 49, 161-163.
- [25] F. F. Wu, X. P. Li, H. Zhong, S. Wang. Utilization of electrolytic manganese residues in production of porous ceramics. Int. J. Appl. Ceram. Technol., 2016, 13, 511-521.
- [26] B. Du, C. B. Zhou, Z. K. Luan, N. Duan. Preparation and characterics of steamautoclaved bricks produced from electrolytic manganese solid waste. Constr. Build. Mater., 2014, 50, 291-299.
- [27] A. S. Wagh. Recent progress in chemically bonded phosphate ceramics. ISRN Ceram., 2013, 2013, 983731, 1-20.
- [28] A. S. Wagh, S. Y. Jeong. Chemically bonded phosphate ceramics: III. Reduction mechanism and its application to iron phosphate ceramics. J. Am. Ceram. Soc., 2003, 86, 1850-1855.
- [29] Н. А. Ерошкина, М. О. Коровкин. Геополимерные строительные материалы на основе промышленных отходов, 2014, Пенза, Изд. Пензенского Гос. унив. архитектуры и строительства.
- [30] ე. შაფაქიძე, მ. ნადირაშვილი, ვ. მაისურაძე, ი. გეჯაძე, ე. ხუჭუა, თ. პეტრიაშვილი. ახალი სახის მჭიდების – გეოპოლიმერების მიღების შესაძლებლობის კვლევა ბრძმედის ნაყარი წიდის და ბუნებრივი ქანის საფუძველზე. საქართველოს მეცნ. ეროვ. აკად. მაცნე (ქიმიის სერ.), 2016, 42, 2, 206-211.

- [31] E. Shapakidze, M. Nadirashvili, V. Maisuradze, I. Gejadze, T. Petriashvili, M. Avaliani, G. Todradze. Elaboration of optimal modefor heat treatment of shales for obtaining metakaolin. Eur. Chem. Bull., 2019, 8, 1, 31-33.
- [32] E. Shapakidze, M. Nadirashvili, V. Maisuradze, I. Gejadze, M. Avaliani, T. Petriashvili. Production of geopolymer binders using local raw materials. Abstracts of thr 5th International Scientific-Practical Conference on Up-to-Date Problems of Geology: Power of Geology is the Precondition for Regeneration of Economics, 2019, Georgian Technical University, 125-127.
- [33] E. Shapakidze, M. Avaliani, M. Nadirashvili, V. Maisuradze, I. Gejadze, T. Petriashvili. Geopolymers based on local rocks as a future alternative to portland cement. Mater. Sci. III, 2020, 25, DOI: 10.13140/RG.2.2.28081.12644.
- [34] ე. შაფაქიძე, მ. ავალიანი, მ. ნადირაშვილი, ვ. მაისურაძე, ი. გეჯაძე, თ. პეტრიაშვილი. გეოპოლიმერული მჭიდა მასალების მიღება თერმულად მოდიფიცირებული საქართველოს თიხოვანი ქანების საფუძველზე. Nano Studies, 2020, 20, 43-52.