Efficient technologies for making gypsum binders

A I Gabitov\textsuperscript{1,*}, A S Salov\textsuperscript{1}, V A Ryazanova\textsuperscript{1}, A A Timofeev\textsuperscript{1} and
V A Timofeev\textsuperscript{1}

\textsuperscript{1}Ufa State Petroleum Technological University, 1 Kosmonavtov St., Ufa, 450064, Russia

*E-mail: gabitov.azat@mail.ru

Abstract. A number of various proposed options and flow charts applied for the production of gypsum binders are considered herein. Large volumes of inorganic waste amount to millions of tons therefore the phosphogypsum utilization to get effective gypsum binders is an urgent issue. The production of phosphogypsum binders both in our country and abroad is indicated to go in three main directions - burnt, autoclaved and anhydrite (hard-burnt) binders.

One of main methods for phosphogypsum utilization is the production of gypsum binders characterized by a wide variety of the proposed options and flow charts being implemented. The production of phosphogypsum binders both in our country and abroad goes in three main directions, i.e. burnt, autoclaved and anhydrite (hard-burnt) binders [1-3].

The production of phosphogypsum binders is associated with certain difficulties due to chemical composition and physical and mechanical properties of the raw materials. The moisture content of the material, as well as phosphoric and sulfuric acid residues found in phosphogypsum, the soluble salts thereof and other impurities complicate the dehydration process negatively affecting the final properties of gypsum binders [3].

Analysis of the dehydration of unwashed phosphogypsum being made in a wide range of acidity thereof has shown that one of reasons for the deterioration of binding properties is unstable phase composition thereof, in particular, formation of a lot of insoluble anhydrite influenced by acidic phosphate and fluoride compounds.

The hemihydrate obtained by dehydration of “reagent grade” calcium sulfate in a solution of pure phosphoric acid is hydrating far more slowly as compared to the hemihydrate obtained by dehydration of chemically pure gypsum in distilled water. Delayed hydration and, accordingly, low strength characteristics of the binder are due to the formation of phosphate films on the crystal surface that are slowing down the hemihydrate dissolution, with the concentration of hemihydrate in the solution of the hardening mixture being reduced more than twice from 7-8 to 3 g/l [4].

The activity of impurities was also due to formation of complex slightly soluble salts, “poisoning” of active centers of the growing crystal with impurity ions, formation of impermeable films on the crystal surface, and fixation of impurities on the surface of faces during nucleation and growth of crystals [1,5].

According to P.F.Gordashevsky’s studies the content of phosphoric acid in an amount of 0.1-0.3% of the mass of the binder is slightly increasing the setting time. Just like dibasic calcium phosphate has little effect on the setting time either, causing the hydration acceleration. The addition of soluble phosphates up to 0.5% even slightly increases the binder strength. Fluorine compounds have a pronounced effect on the properties of the binder producing the acidic environment of the sludge along with phosphoric and sulfuric acids. The addition of soluble fluorides and fluoroisilicates NaF and Na$_2$SiF$_6$ amounting even to 0.1% is reducing the strength of the gypsum binder, while an increase in the content thereof to 0.4% is reducing almost twice the strength properties of the binder. The content of soluble fluorides also increases the normal density and decreases the compressive strength of the
samples. The emission of fluorine gases at the heat treatment is complicating the technology, thereby resulting in the increased corrosion of the equipment due to higher acidity of the material. Organic impurities found in phosphogypsum make the resulting gypsum dark and reduce the strength thereof. Salts of sodium and potassium are likely to appear on the surface of drying products as efflorescence.

Low strength properties of the binder obtained by burning phosphogypsum are also associated with the high water demand during tempering (over 100%). According to P.F. Gordashevsky the main reason for the high water demand of the phosphogypsum binder is the large internal porosity of dehydrated gypsum and the crystalline structure thereof resulting in high content of extended needle-shaped crystals. A significant reduction in the water demand of the binder is achieved by phosphogypsum grinding (from 130 to 60%) [5,6].

There are different views on impurities affecting the hardening mechanism of phosphogypsum binder. Anyway, despite the different views the majority of scientists unanimously think that it is unlikely to obtain a binder with satisfactory properties without prior purification of phosphogypsum from impurities [7].

The maximum total amount of Na⁺ and K⁺ should not exceed 0.15%. The content of P₂O₅ impurity (aqueous) according to various sources should not exceed 0.1-0.5% depending on the method of phosphogypsum processing and the requirements for the binder properties.

The known methods of phosphogypsum purification from impurities to be actually used may be divided into the following types: 1 - washing of phosphogypsum with water; 2 - adding of neutralizing additives; 3 - thermal method.

Methods of the first and second groups and the combination thereof provide a high degree of purification. Additional washing of phosphogypsum with water is the most common method for extracting soluble impurities.

The most promising technologies are those where the harmful impurities of phosphogypsum are neutralized by putting them into slightly soluble or insoluble compounds.

Most of the third group methods are based on burning phosphogypsum to soluble anhydrite with further hydration thereof and repeated burning to hemihydrate. They are not widely used since the increased energy cost and scarce additives are required therefor, and also the constancy of the binder properties is not provided under the changing phosphogypsum composition.

The high moisture content and dispersion of phosphogypsum were the prerequisites for the processing thereof in an autoclave as a pulp with constant mixing. The phase transition in an autoclave is used for cleaning the binder and reducing the impurities included in the crystal lattice of the dihydrate. The main problem in the autoclave method of pulp processing is the formation of dense isometric crystals of α-hemihydrate, providing the binder with low values of normal density and high strength indicators. The hydrothermal method of dehydration of gypsum under pressure with active additives i.e. hemihydrate crystallization regulators (HCR - according to P.F. Gordashevsky) is currently more widely used [8,9]. The analysis of dependence of the crystallization character, and α-hemihydrate properties on the HCR nature and concentration, the process temperature and the acidity of the medium has been made.

A number of companies like ICI (England), Mitsubishi (Japan), “CdF Chimie” (France) [8] and others were involved in the development of the technology for producing high-quality gypsum binders. Currently, the α-hemihydrate is generally made from phosphogypsum by “Giulini Chemie GmbH” method (Germany), being applied in Germany (“Babcock BSchH”, “Knapsak”, etc.), France, Scotland, Ireland, Russia (Voskresensk Industrial Group “Minudobreniyu”) and others. The manufacturing process includes: phosphogypsum washing; making of working pulp; autoclave pulp processing; autoclaved product filtration; drying and grinding of the finished product. Carboxymethylcellulose is used as an active additive therein [10].

There are actually no fundamental differences in industrial versions of process flow for making autoclave binders from phosphogypsum. There are slight differences in the methods and equipment for washing, filtration and drying. The additives recommended for regulating the growth of hemihydrate crystals also differ [11].
VNIIstrom named after P.P. Budnikov has developed an efficient method for making a high-strength water-proof binder from phosphogypsum. Phosphogypsum is dehydrated in an autoclave with a hydraulic component (Portland cement), therewith the calcium hydroxide being released in the autoclave under hydration of the hydraulic component is neutralized by acidic impurities of phosphogypsum, i.e. the latter act as a pozzolanic additive preventing hydrosulfoaluminate destruction of the system, thereby enabling Portland cement use with no extra addition of pozzolanic additives thereto, and no prior washing of phosphogypsum [12,13].

However, the high cost of the resulting binder and the complicated technological process prevent from wide application of the autoclave method for processing phosphogypsum into a binder.

Adequate studies on the technology of processing phosphogypsum into anhydrite binders were made in the USSR more than 30 years ago. An anhydrite binder with a breaking strength up to 25 MPa (with sodium sulfate addition - 2%) was obtained after 7 days, with the phosphogypsum being burnt in 8m furnace at 600-1000°C [14].

Paper [61] indicates that S^{6+} ion may be substituted by P^{5+} ion, and a higher hydration activity and the strength of the anhydrite formed with P_2O_5 are noted. Under the results of analyzing the properties of anhydrite binders, it was concluded that the unwashed phosphogypsum may be used for making anhydrite binders, although according to other paper [15] a slight strength reduction of the binder was found with more than 0.2% of fluorine or more than 0.8% of P_2O_5.

The development of phosphogypsum processing production therewith is prevented by the need for high-temperature burning, as well as by the related disadvantages of phosphoanhydrite binders i.e. delayed setting and the need to use hardening activating additives.

The wide-scale industrial production of anhydrite binders in some countries mainly was on the basis of natural anhydrite and fluoroanhydrite i.e. hydrofluoric acid production waste, when mechanochemical activation of raw materials only is required for obtaining a finished binder [16].

The most process operations for binders making from phosphogypsum are complicated, resulting in the fact that phosphogypsum binders often cannot compete in cost with a binder obtained from natural gypsum raw materials [17, 18]. “Knauf” experts consider that phosphogypsum binders will have advantages under the following conditions:

- remote location of phosphogypsum processing enterprises from deposits of natural gypsum feedstock;

- arranging the binder production in a phosphoric acid plant thereby solving the problem of transport and discharge of wastewater, as well as agreement of the phosphogypsum processes with the phosphoric acid production;

- close location of potential consumers.

The Research and Educational Center for Innovative Technologies at the Architectural and Construction Institute of the Ufa State Petroleum Technical University is currently making active research in this area. ACI USPTU specialists make R&D support and quality control of materials and work done on the most of the construction sites in the city of Ufa and the Republic of Bashkortostan.
Figure 1. The Research and Educational Center for Innovative Technologies

Innovative laboratory-tested concrete compositions with the application of waste, by-products and end products of chemical and petrochemical industries with high performance properties modified by a number of multifunctional chemical additives and modifiers developed and patented by the University staff are being introduced. Today, the alternative binders, nano-based fillers and compositions of effective superplasticizers are being developed under significant expansion of the composition selection automation. Certificates of registration of programs enabling optimization and evaluation of the quality of the materials applied were obtained [19-20].

References
[1] Mirsayev R N, Babkov V V, Yunusova S S, Kuznetsov L K, Nedoseko I V and Gabitov A I 2004 Phosphogypsum waste of the chemical industry in the production of walling items (Moscow: Chemistry)
[2] Ermilova E Yu, Kamalova Z A and Rakhimov R Z 2016 The study of the composite cement effect with a complex mineral additive on the physical and mechanical and other operational properties of mortars News of KazGASU 1 (35) pp 165-171
[3] Udalova E A, Gabitov A I, Shuvaeva A R, Nedoseko I V, Chernov A R and Yamilova V V 2016 Actual status and promising opportunities for application of phosphogypsum for the binder making History and Education of Natural Science 4 pp 55-58
[4] Ivanitsky V V, Klassen P V, Novikov A A et al. 1990 Phosphogypsum and application thereof (Moscow: Chemistry)
[5] Gabitov A I, Udalova E A, Salov A S, Chernova A R Pyzhjanova D V and Yamilova V V 2017 Historical aspects of production and application of hollow ceramic blocks History of science and technology 6 pp 58-65
[6] Ermilova E Yu, Kamalova Z A, Rakhimov R Z and Gulyaeva R I 2017 The study of the effect of complex additives based on carbonate rocks and thermally-activated polimimal clay on the composition of hydration products of composite cement stone News of KazGASU 1 (39)
[7] Mirsayev R N, Akhmadulina I I, Babkov V V, Nedoseko I V, Gaitova A R and Kuzmin V V 2010 Gypsum slag compositions from industrial waste in construction technologies // Construction materials 7 pp 4-6
[8] Narkevich I P and Pechkovsky V V 1984 Utilization and disposal of waste in the inorganic substance technology (Moscow: Chemistry) 239
[9] Salov A S, Chernova A R and Kuzmina A Yu 2015 Problems of concrete quality at cast-in-situ construction Current topics of technical, humanities and science Papers of the International Science and Technology Conference pp 71-74
[10] Meshcheryakov Yu G and Fedorov S V 2007 Industrial processing of phosphogypsum (St.-Petersburg, Stroyizdat SPb Publ) 104
[11] Rakhimov R Z 2008 Ways for reducing the cement intensity of construction products Popular Concrete Science. St.-Petersburg - LLC "Stroybetony" 107 (21) pp 24-28
[12] Babkov V V, Sakhibgareev R R, Chuikin A E, Terekhov I G and Salov A S 2005 Physical and chemical aspects of cement composites hardening at late stages Bashkir Chemical Journal 12 (4) pp 124-129
[13] Gaitova A R, Akhmadulina I I, Pechenkina T V, Pudovkin A N and Nedoseko I V 2014 Nanostructural aspects of hydration and hardening of gypsum and gypsum-slag compositions based on calcium sulfate dihydrate Construction materials 1-2 pp 46-51
[14] Ratinov V B and Stekanov D I 1984 Physical and chemical fundamentals for making high-strength cast stones Construction materials 11 pp 6-7
[15] Khaliullin M I, Rakhimov R Z, Sabanina Yu V, Nurieva E M, Korolev E A and Bakhtin A I 2006 The influence of aging on the physical, mechanical and structural properties of multiphase gypsum binders News of higher educational institutions. Construction 10 pp 25-29
[16] Khaliullin M I, Altykis M G and Rakhimov R Z 2000 Composite anhydrite water-resistant binders Construction materials 12 pp 34-35
[17] Anisimova S V, Korshunov A E and Emelyanov D N 2016 Properties of gypsum suspensions with water-soluble acrylic polymers Construction materials 7
[18] Shelikhov N S, Rakhimov R Z, Sagdiev R R and Stoyanov O V 2016 The influence of mineral additives on properties of the low-temperature burning hydraulic binders Bulletin of Kazan Technological University 5
[19] Pudovkin A N, Gabitov A I, Salov A S and Chernova A R 2018 Program for calculating the grain size and grain composition of sand Certificate of state registration of the computer program No. 2018617134 / right holder FGBUU from UGNTU; claimed 24/04/2018; reg. 19.06.2018
[20] Sinitsyna E A, Pudovkin A N, Nedoseko I V and Salov A S 2020 The program for calculating the specific surface area of the raw mixture and the average surface particle size Certificate of state registration of the computer program No. 2020663812/ right holder FGBUU from UGNTU; claimed 26.10.2020; reg. 02.11.2020