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PHYSICO-MECHANICAL AND PHYSICO-CHEMICAL HARDENING PROCESS CHANGING RESEARCH IN GYPSUM BINDER AND TRANSITION IN GYPSUM-CEMENT BINDER AND THEN TO GYPSUM-CEMENT-POZZOLANIC USING WITH MECHANICAL TESTS AND X-RAY SPECTROSCOPY

Abstract

Gypsum-Cement-Pozzolan binder (GCPB) has been invented in 60-s of last century in USSR by group of scientists under Mr. A. Volzhenskiy leadership. In that time in USSR and actually in US construction technological processes of civil and industrial buildings increasing a lot. So demand of cement for heavy concretes as a main component high up day to day, year to year. But realisation of that idea in practical way wasn't easy thing because as we know from «Material science» course – cement is hydraulic binder which hardening in moisture condition or in must cases in water and if we see about gypsum is an air binder. That means gypsum is hardening and gets its high compression strength in air condition and losing that strength in moisture condition or under influence of water. After analysing knowledge that have been written above about GCPB we may stay some problems in front of us: 1) First problem connect with modern theoretical physical-mechanical and physical-chemical researches absence, when GCPB hardening process have been described by modern X-Ray spectroscopy and mineralogical analysis. All what we have found in internet resources is basic and theoretical issue with some mechanical tests. 2) Also the main problem when we start see on that researches and mechanical tests, there are some conflicting things as links for technical requirements of GCPB through ages, storage conditions before tests. So according by what we have said above we choose some targets of our research: a) How gypsum binder's physical-mechanical characteristics going to change as it would be main stuff for GCPB preparing. And also transition process gypsum binder (GB) in gypsum-cement binder (GCB) and then in gypsum-cement-pozzolan binder (GCPB); b) How gypsum binder's physical-chemical characteristics going to change during transition process in GCB and then into GCPB with X-Ray spectroscopy analysis.

Key words: gypsum binder, gypsum-cement binder, gypsum-cement-pozzolan binder, creep factor, softening factor (K_s).

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ГИПС-ЦЕМЕНТТІ ТҮТҚЫРЛЫҚҚА, АЛ ОДАН ГИПС-ЦЕМЕНТТІ-ПОЗЦОЛАНДЫ ТҮТҚЫРЛЫҚҚА АУЫСА ОТЫРЫП, ГИПСТІ ТҮТҚЫРЛЫҚ ҚАТАЮЫНЫҢ ФИЗИКА-МЕХАНИКАЛЫҚ ЖӘНЕ ФИЗИКА-ХИМИЯЛЫҚ ПРОЦЕСТЕРІНІҢ ӨЗГЕРУІН ФИЗИКА-МЕХАНИКАЛЫҚ СЫНАҚТАР МЕН РЕНТГЕНОФАЗАЛЫҚ ТАЛДАУ АРҚЫЛЫ АЛЫНҒАН ДЕРЕКТЕР НЕГІЗІНДЕ ЗЕРТТЕУ

Андатпа

Гипсоцемент-поззолан байланыстырғышының (ГЦПБ) пайда болуы өткен ғасырдың 60-жылдарында КСРО-да А.В. Волженский басқарған ғалымдар тобының жұмысы нәтижесінде пайда болды. Куйбышева (қазіргі кезде МГСУ им. Куйбышева). Айта кету керек, сол жылдары КСРО – да қарқынды өнеркәсіптік және азаматтық құрылыс жүрді. Ол портландцементке өте қажет бетон өндірісінің байланыстырушы негізі, ол көбінесе жеткіліксіз болды. Алайда, бұл қызықты идеяны іс жүзінде жүзеге асыру портландцемент гидравликалық байланыстырғыш, яғни тұтқыр, ылғалды жағдайда және тіпті суда қатайып, гипс байланыстырғыш (құрылыс гипсі немесе алебастр деп аталады) әуе байланыстырғышымен шектелді. Яғни, тұтқыр, тек құрғақ ауа жағдайында максималды беріктікке ие бола алады және ылғалды пайдалану жағдайында осы беріктігін жоғалтады.

Жоғарыда келтірілген мәліметтерді талдай отырып, сіз осы байланыстырғышты зерттеумен байланысты қазіргі зерттеушілердің алдында туындайтын бірқатар мәселелерді анықтай аласыз: 1) Бірінші мәселе қазіргі заманғы рентгенофазалық және минералогиялық талдаулармен расталған ГЦПБ-да қатаю кезінде пайда болатын физика-химиялық және физика-механикалық процестерді қазіргі заманғы теориялық зерттеулердің жоқтығымен байланысты. Табуға болатын барлық нәрсе-бұл негізінен әртүрлі дәрежеде Сығылған жалпы акпарат немесе белгілі бір жергілікті ГЦПБ-ның бірқатар физикалық-механикалық сипаттамалары туралы кейбір мәліметтер келтірілген қолданбалы сипаттағы жұмыстар. 2) Сонымен қатар, соңғы жағдайда да, яғни қолданбалы сипаттағы жұмыстарда авторлар бірқатар мәселелер бойынша өте қарама-қайшы мәліметтер келтіреді. Мысалы: әр түрлі жылдардағы ГЦПБ-ға қойылатын техникалық талаптарға сілтемелер, сынақ алдында үлгілерді сақтау шарттары мен мерзімдері және т. б. Жоғарыда айтылғандарға сәйкес, жоғарыда аталған олқылықтардың орнын толтыру мақсатында осы жұмыстың алдына келесі міндеттер қойылды: а) гипсцементтік тұтқырлыққа (ГЦБ) және гипсцементтік-поззоландық тұтқырлыққа (ГЦПБ) ауыса отырып, ГЦПБ негізі болып табылатын гипстік тұтқырлықтың (ГБ) келесі физикалық-механикалық сипаттамалары қалай өзгеретінін қадағалау; б) гипсцементтік тұтқырлыққа (ГЦБ), ал одан гипсцементтік-поззоландық тұтқырлыққа (ГЦПБ) ауыса отырып, қатаятын тасты рентгенофазалық, химиялық және минералогиялық талдау арқылы алынған деректер негізінде гипсцементтік-поззоландық тұтқырлыққа (ГЦПБ) қатаюдың физика-химиялық процестері қалай өзгеретінін қадағалау.

Тірек сөздер: гипс байланыстырғыш, гипс цемент байланыстырғыш, гипс цемент-поззолан байланыстырғыш, сығылу (creep factor), жұмсарту коэффициенті (Кж).

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ИССЛЕДОВАНИЕ ИЗМЕНЕНИЯ ФИЗИКО-МЕХАНИЧЕСКИХ И ФИЗИКО-ХИМИЧЕСКИХ ПРОЦЕССОВ ТВЕРДЕНИЯ ГИПСОВОГО ВЯЖУЩЕГО С ПЕРЕХОДОМ К ГИПСОЦЕМЕНТНОМУ ВЯЖУЩЕМУ, А ОТ НЕГО К ГИПСОЦЕМЕНТНО-ПУЦЦОЛАНОВОМУ ВЯЖУЩЕМУ НА ОСНОВЕ ДАННЫХ, ПОЛУЧЕННЫХ ПОСРЕДСТВОМ ФИЗИКО-МЕХАНИЧЕСКИХ ИСПЫТАНИЙ И РЕНТГЕНОФАЗОВОГО АНАЛИЗА

Аннотация

Появление гипсоцементно-пуццоланового вяжущего (ГЦПВ) произошло в 60-х годах прошлого столетия в СССР в результате работы группы ученых, возглавляемых А.В. Волженским в МИСИ им. Куйбышева (в настоящее время – МГСУ им. Куйбышева). Необходимо отметить, что в те годы в СССР шло интенсивное промышленное и гражданское строительство, которое остро нуждалось в портландцементе – вяжущей основе для производства бетонов, которого часто попросту не хватало. Однако реализация этой заманчивой идеи на практике ограничивалась тем, что портландцемент является гидравлическим вяжущим, то есть вяжущим, твердеющим во влажных условиях и даже в воде, а гипсовое вяжущее (так называемый строительный гипс, или алебастр, как его тогда называли) – воздушным вяжущим. Анализируя вышеприведенные сведения по ГЦПВ, можно наметить ряд проблем, связанных с исследованием этого вяжущего, возникающих перед современными исследователями: 1) Первая проблема связана с практически полным отсутствием современных теоретических исследований физико-химических и физико-механических процессов, протекающих в ГЦПВ во время его твердения, подтвержденных современными рентгенофазовым и минералогическим анализами. Все, что удалось найти, – это преимущественно общая сжатая в разной степени информация или работы прикладного характера с приведением некоторых данных по ряду физико-механических характеристик того или иного местного ГЦПВ. 2) При этом даже в последнем случае, то есть в работах прикладного характера, авторы приводят очень противоречивые данные по ряду вопросов, например, таких как ссылки на технические требования к ГЦПВ разных годов, условия и сроки хранения образцов перед испытаниями и др. В соответствии с вышесказанным с целью некоторого восполнения вышеуказанных пробелов в исследовании ГЦПВ перед данной работой ставились следующие задачи: а) проследить, как меняются следующие физико-механические характеристики гипсового вяжущего (ГВ), являющегося основой ГЦПВ с переходом в гипсоцементное вяжущее (ГЦВ) и гипсоцементно-пуццолановое вяжущее; б) проследить, как меняются физико-химические процессы твердения гипсового вяжущего с переходом к гипсоцементному вяжущему, а от него к гипсоцементно-пуццолановому вяжущему на основе данных, полученных посредством рентгенофазового, химического и минералогического анализов твердеющего камня.

Ключевые слова: гипсовое вяжущее, гипсоцементное вяжущее, гипсоцементно-пуццолановое вяжущее, ползучесть (creep factor), коэффициент размягчения (K_c).

Introduction

Gypsum-Cement-Pozzolanic binder (GCPB) has been invented in 60-s of last century in USSR by group of scientists under Mr. A. Volzhenskiy leadership. In that time in USSR and actually in US construction technological processes of civil and industrial buildings increasing a lot. So demand of cement for heavy concretes as a main component high up day to day, year to year. According to that there were lots of deficiency of many construction materials and cement has been stayed on 1-st place. Being truth many countries have tried find decision of reducing role of cement in construction industry, and USSR was one of them and as an idea for some low-floor buildings, which contain one or two floors, was replace to use cement binder for gypsum binder instead. All the more so that prime cost gypsum stuff is cheaper at least 5 times comparing with cement. But realisation of that idea in practical way wasn't easy

thing because as we know from «Material science» course – cement is hydraulic binder which hardening in moisture condition or in most cases in water and if we see about gypsum is an air binder. That means gypsum is hardening and gets its high compression strength in air condition and losing that strength in moisture condition or under influence of water. That negative side of gypsum binder may be explained in high level of creeping (creep factor) and low range of softening factor in gypsum binder comparing with cement binders and concretes. For our readers we may remind that creeping (creep factor) is an effect when hardened binder display high plastic deformations under influence of loading and moisture makes that process get more fast[1 P.2]. Creeping (creep factor) has private connection with softening as creep factor also may be explained as losing strength properties of hardened and dry binder after moisture influence. Level of softening may be described as softening factor(K_s), which may be calculate as strength of water-saturated binder samples dividing on strength of dry binder samples[1 P.2-3]. Using easy explanation – ratio of strength sample in high wet condition to strength sample in dry condition. According softening factor(K_s) we may estimate that factor as water resistance. Water resistance or softening factor(K_s) gypsum binder stay in range 0,3 – 0,45 and cement binder – 0,6 – 0,8 [2 P.6]. So to find some decision of that problems as creeping and softening factor(K_s) of gypsum binder Mr. A. Volzhenskiy's researches and his followers has been dedicated at last century. During 20 years since 60-s to end of 80-s some scientists have made some researches as Mr. A. Palagin, and Mr. M. Kurotsapov[3] has described influencing 3-10% of cement by gypsum mass. Also water resistance, softening factor(K_s) and compression strength has been determined. Increasing water resistance also have been noticed by Mr. P. Budnikov, and Mrs. L. Gulnova and S. Torchinskaya[4], when 10% of cement have been added in dihydrate gypsum. Positive side of influence on water resistance after adding cement in gypsum binder may be explained by low water resistance level in hardening gypsum and its high water-solubility level which stay in range 2g/l[5 P.3]. During hydration process in two-component binder – gypsum-cement binder(GCB) we have two hydration ways: gypsum hydration from hemihydrate gypsum to dihydrate gypsum; and hydration cement minerals. That two process comes hand in hand and during that low-soluble compounds start appear in solution as calcium hydrosilicate and on gypsum dehydrate surface low-soluble film appearing in same time which prevent gypsum molecules by high solubility. After some researches gypsum-cement binder's(GCB) stuff, real results have been taken which shows two things. The water resistance has been grown up but not so much. The second one – after some time samples of gypsum-cement binder(GCB) start being under internal deformation, which leads to strength losing on 1-3 months later after hardening[6 P.462]. In some cases there are crush of samples. And that negative side of GCB may be explained because a special mineral start appear inside the structure or if we may say like this inside solid body of GCB sample. According to chemistry is three-sulphate form of calcium hydro-sulphoaluminate but according to mineralogy that mine calls ettringite. That ettringite appear from calcium hydroaluminate with gypsum dehydrate reaction. By easy words it may be explained three calcium aluminate from cement plus calcium sulphate from gypsum equal ettringite in whole hardening system during 1-3 months after hardening[6 P.462]. Here we must remind that we have two types of ettringite: first and secondary. The first one appear fast in solution after water addition. The secondary start appear in system after hardening, inside of solid sample. Also the most important thing is concentrations of ions as Ca^{+2} and SO_4^{-2} . In two-component binder GCB there are high concentration and many of them comes by gypsum side reacting with three calcium aluminate from cement side and moisture, or extra moisture from atmosphere increase speed of that process, start from pores of solid sample where ettringite start its way. Appearing ettringite is a process of crystallization in pores, which comes with volume increasing, and that means increasing of tension. When that tension inside pores high up day to day cracks start appear in solid body and in the end of case sample has crushed by tension and cracks. Only that may be explained why we have compression strength losing during the time and It's negative side of ettringite appearing. So to demolish that negative ettringite side in two-component binder three-component – Gypsum-Cement-Pozzolanic binder(GCPB) have been invented by Mr. A. Volzhenskiy and his group of scientists. Under Mr. A. Volzhenskiy leadership some researchers have been made that shows, if we put some pozzolan additives in two-component binder we would achieve kind of stability of system with strength increasing in air and water conditions without

any plastic(crush) deformations[6 P.462]. According by Mr. A. Volzhenskiy's proposal in three-component binder(GCPB) hardening role of pozzolana explained as reducing $\text{Ca}(\text{OH})_2$ concentration in water conditions to that level when system hasn't got any circumstances of calcium hydroaluminate existence as $4\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 13\text{H}_2\text{O}$ and $3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 6\text{H}_2\text{O}$; which qualify as highly-basic, and start redistribution process in low-basic consistence. During cement minerals hydration $\text{Ca}(\text{OH})_2$, or lime, start appearing and then react with pozzolana additive (SiO_2) and in the end of case calcium hydrosilicate forms in system as CSH(B). By other words low-basic calcium hydrosilicate start appear, which works as protective film for dehydrate gypsum, covering its, during his hydration from hemihydrate, and prevent his high solubility, increasing water resistance in whole three-component system. According by Mr. A. Volzhenskiy's opinion that kind of processes, which we have described above, demolish circumstances calcium three-sulphate hydroaluminate form, by easy words ettringite $3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 3\text{CaSO}_4 \cdot 31\text{H}_2\text{O}$, appearing in first and secondary time. Instead of that one-sulphate hydroaluminate form start appear - $3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{CaSO}_4 \cdot 12\text{H}_2\text{O}$, hydro grenades - $3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot n\text{SiO}_2 \cdot (6-2n)\text{H}_2\text{O}$, gypsum $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, hydrosilicoaluminate $3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{CaSiO}_3 \cdot 12\text{H}_2\text{O}$ and their hard solutions. Transition three-sulphate hydroaluminate form in one-sulphate form comes with volume decreasing in 1,5 times of original stuff. That situation decrease critical tension by ettringite appearing. That process comes by reaction: $3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 3\text{CaSO}_4 \cdot 31\text{H}_2\text{O} \rightarrow 3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{CaSO}_4 \cdot 12\text{H}_2\text{O} + 2\text{CaSO}_4 \cdot 2\text{H}_2\text{O} + 15\text{H}_2\text{O}$. By other words when we demolish any circumstances of ettringite appearing(cement bacillus) in three-component binder (GCPB) we may achieve system stability in long-time hardening. Water resistance and hydro-hardening(hardening in water) may be explained as low-solubility compounds appearance in must cases, calcium hydrosilicate which protect dehydrate by water soluble action. According by Mr. A. Volzhenskiy's view that protection action start with 15-20% cement consistence in three-component binder[6 P.465].

By that author's work and their researches consistence of gypsum-cement-pozzolanic binder may consist by percentage of mass(%):

- Hemihydrate gypsum : 75 – 50
- Cement: 15-25
- Pozzolanic additives(with 200mg/g activity): 10-25

Main provisions

Target of research we may see in title and meaning of that is to catch connection physical-mechanical properties changing as water requirement, setting time, compression strength in 2 hours age, compression strength after whole natural drying system(7 days, 14 days – depend of ratio actually), compression strength after steaming chamber, water resistance(Softening factor K_s); during transition gypsum binder to gypsum-cement binder and then to gypsum-cement-pozzolanic binder. Not seeing at this extra target of research have been X-Ray spectroscopy results examining by gypsum-cement binder and gypsum-cement-pozzolanic binder for three-sulphate and one-sulphate calcium hydrosulfoaluminate form which have been described by Mr. A. Volzhenskiy.

Materials and methods

In that work some materials have been used for ratios preparing:

- Gypsum binder – construction gypsum by “Alinex” KZ company, G-5 according to GOST 125-2018[7].

- Cement binder – white portlandcement M500-A0 by “ChemTrade”

- Pozzolanic additive – microsilica mark “MKH - 95” by “Tau-Ken Temir” with 100 mgCaO/g activity.

Gypsum-cement binder(GCB) compound was consist: hemihydrate gypsum – 75%; white cement – 25% as we see here is proportion 3:1. In same proportion have been kept in gypsum-cement-pozzolanic binder(GCPB) but after pozzolana addition by whole mass percentage: hemihydrate – 62%; white cement – 20%; pozzolana – 18%. Increasing pozzolana percentage comparing with Mr. Volzhenskiy's compound may be explained by its activity 100 mgCaO/g which is half according by Mr. Volzhenskiy's compound(200 mg CaO/g). Physico-mechanical tests of gypsum binder, GCB, GCPB have been based on GOST 23789 – 2018 «Gypsum binder. Test methods» with changing with few cases. According by GOST

23789 – 2018 some characteristics have been determined as standard consistence, using with Suttard's cylinder, setting time, for strength checking beams 160x160x40 mm have been prepared. After 15 ± 5 minutes hardening samples have been leaving in air conditions $t = 22 \pm 2^\circ\text{C}$. Some pieces have been tested in 2 hours age, other pieces have been tested after steaming chamber keeping – 2 hours increasing to 75°C and then 6 hours steaming. Third group of beams have been leaving for 7 days strength tests. Half of piece have been tested in 7 days, second piece have been put in water for softening factor (softening coefficient K_s) determination, after 2 days keeping in water. Softening factor (K_s) have been calculated as proportion – compression strength 7 days drying plus 2 days lying in water divided by compression strength in 7 days age. That kind of methods have been used in every rations: gypsum binder (GB), gypsum-cement binder (GCB), and gypsum-cement-pozzolan binder (GCPB). One turning in GCB and GCPB, we use two methods of sample keeping – water conditions (moisture 100%) and hydro-both, during 7 days and then air conditions as in gypsum binder. That kind of methods described in TC 21-31-62-89 «Gypsum-cement-pozzolan binder. Technical conditions». After tests experiment few grams have been taken for X-Ray spectroscopy with using «Drone - III» machine, for sulphate forms checking.

Results and discussion

Results of research have been shown in table 1 by three rations GB, GCB, GCPB.

As we may see from table 1 results water requirement was the same at each ratio, 52% by mass of compound. Flow test by Suttard's cylinder also same for GB and GCB but have been decrease for GCPB, which may be explained microsilica presence – 18% by mass of ratio. Here we have dependence – if we increased water we would keep mixture flow and vice versa if we kept water proportion our flow would change. Comparing setting time of three rations we may see that there weren't any changings, that ability have been inherited by gypsum binder.

The second point is setting time in GCB and GCPB totally the same as beginning and ending. For explaining that effect we must remember that in hemihydrate – $\text{CaSO}_4 \cdot 0,5\text{H}_2\text{O}$ we also have impurities, as dehydrate – $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ and anhydrite – CaSO_4 .

Table 1 – Mechanical tests

Type of binder	Water requirement	Setting time	Compression strength N/mm ²				K_s
	Flow	<u>begining</u> <u>ending</u>	2 hours age	After drying	After water inf.	Steaming chamber	
1	2	3	4	5	6	7	8
GB	52 %	12 min.	5,08	14,5	4,75	4,2	0,327
	188 – 190 mm.	22 min.					
GCB	52 %	9 min.	5,02	13,21	5,91	6,21	0,447
	185 mm.	14 min.		11,75			
GCPB	52 %	9 min.	4,00	16,04	12,84	7,87	0,8
	120 mm.	13 min.		12,59			

NOTE: According to column 5 for GCB and GCPB rations in numerator have shown results that's we take after hydro-both keeping during 7 days and then drying in air conditions. In denominator have shown results which have been taken after 7 days water keeping (moisture 100%) and then drying in air conditions.

According to this dehydrate phase in that involves for setting time, organise kind of dotes which work as central of crystallization hemihydrate to dehydrate transformation. So as much dehydrate impurities in hemihydrate as many crystallization centres would be and as fast setting time would be. In our case dehydrate quantity have been increased also by dehydrate from cement. As a result of that addition was central crystallization increasing and setting time of GCB and GCPB became faster than GB. The same beginning time may be explained as proportion keeping between cement and gypsum. According by compression strength in 2 hours age we may see gypsum binder influence in every rations. As an example

GB – 5,02 N/mm², GCB – 5,08 N/mm². Not so big difference, as from cement minerals in that time only three-calcium aluminate being in reaction with dehydrate. But if we see on GCPB we may notice 4,00 N/mm² strength in 2 hours age which had fallen down and may be explained that mineral additive – microsilica hasn't started to work yet. Compression strength which have been shown in 5-th column almost the same GB – 14,5 N/mm², GCB – 13,2 N/mm², and GCPB – 16,04 N/mm². And that kind of results may prove theory that properties of GCB and GCPB more close by gypsum which share was 75% and 62% respectively. According to above paragraphs we may conclude that during application GCB and GCPB where gypsum and cement stay in 3:1 proportion physico-mechanical properties would't change so much as compression strength increasing and others as water requirement, setting time, strength in 2 hours age also would be inheriting by gypsum binder. Now let's try to understand differences between GCB and GCPB according to table 1 results. At first one is storage conditions. As we may know by material science gypsum is an air binder – a binder which after water addition and hardening increase and keeps its strength in air conditions – moisture 55±5 % and loose strength in water. But in our research work when we have prepared GCB and GCPP samples we have combined storage conditions: 1) some samples have been kept in hydro-both; 2) others have been kept in water conditions – moisture 95±5%(for one sample at each condition). After 7 days keeping samples was took out and here we have change conditions still keep its in air condition drying until constant mass(7 days or 14 days – depend to ratio). At conclusion of this we may notice that GCB and GCPB are not air binders they are hydraulic binders as they may be leaving and increasing its strength in water. The second point, which may prove that theory, is experiments in steaming chamber – table 1, column 7-th. Gypsum binder in that case have been shown 4,2 N/mm² which proves creping factor of that material – after water influence it start loose strength. And here wasn't only water influence, it was boiling water – steam and temperature 85±5° C. With GCB and GCPB was vice versa, as we may see from table 1, 7-th column – GCB – 6,21 N/mm², comparing with 2 hours age – 5,02 N/mm². Gypsum-cement-pozzolan binder after steaming chamber – 7,87 N/mm² comparing with 2 hours age 4,00 N/mm². Here we have second evidence which describe them(GCB and GCPB) as hydraulic binders. The third point of differences between GB on one side and GCB, GCPB on the other side was softening factor(softening coefficient - K_s) – 8-th column. According to gypsum binder(air binder) $K_s = 0,327$; to gypsum-cement binder – $K_s = 0,447$ which may qualified as middle water resistance material ($K_s = 0,45-0,6$). Comparing results GCPB where $K_s = 0,8$ and may qualified as water resistance material and also we may notice here that K_s of cement stay in rang 0,6-0,8. Also we may add some observations when our beams have drying until constant mass, as an example for GB and GCB that process was coming 7 days(7 days in water + 7 days in air conditions for GCB) there weren't internal moisture at all. Beams from GCPB which have been half for pieces after 7 dry-days was in 2/3 of internal moisture and drying process have been finished in 1/3 area of sample only on edges. The others 2/3 have been dried extra 10 days. That mean for GCPB binder 7 days in water + 17 days in air conditions – $t = 20 \pm 2^\circ \text{C}$, moisture 55 – 60. That effect may be explained as – lime $\text{Ca}(\text{OH})_2$, which appearing from cement hardening start react with pozzolana additive(SiO_2) and organizing calcium hydrosilicates – CSH(I). That element form kind of film which cover gypsum dehydrate molecules, increase water resistance, decrease diffusion and water molecules evaporation outside of sample. Also we need notice here some important moments. At first one is that samples GB, GCB and GCPB as in 2 hours age and as after steaming chamber was in moisture condition that's explain numbers of compression strength. During drying process until constant mass, which we still keep after steaming chamber(steaming chamber process + drying until constant mass) that results have changed: GB – 10,34 N/mm²; GCB – 13,41 N/mm²; GCPB – 13,83 N/mm². Comparing with 5-th column results, which also have been prepared and drying, but without steaming process, we may see one thing: GB – 14,5 N/mm²; GCB 13,21 N/mm²; GCPB – 16,04 N/mm², so according to this gypsum binder loose its strength – 28,7 %. Meanwhile GCB and GCPB after steaming chamber + drying was the same as normal hardening. According to this we may conclude that hardening process of GCB and GCPB may come with two ways: 1) normal hardening – moisture 95±5 %, $t = 20 \pm 2^\circ \text{C}$; 2) fast hardening – steaming chamber $t = 85 \pm 5^\circ \text{C}$ for 6 hours. The secondary are differences between GCB and GCPB in storage conditions. As an example 7 days in hydro-both and 7 days in water may explain our results difference in compression strength. Everything have shown in 5-th column from what we may conclude – the most effective circumstances of storage conditions wasn't in water it was in hydro-both as it has shown better

compression strength. That effect may be explained by one thing – when we keep our samples in water there is lime $\text{Ca}(\text{OH})_2$ leaching in water, as we may see that our water had became with white powder around. According to this calcium hydrosilicates in water samples were weaker than in hydro both. The most noticeable it was in GCPB hardening. By this we may conclude that extra calcium hydrosilicates, which appearing after $\text{Ca}(\text{OH})_2$ and pozzolana (SiO_2) reaction, make a positive effect for GCPB strength.

X-Ray spectroscopy results in gypsum-cement binder and gypsum-cement-pozzolanic binder compounds. After hardening some samples have been taken for X-Ray analysis. GCB results have been shown on «GCB 7 + 7» X-Ray Graph (Figure 1) and GCPB results have been shown on «GCPB steaming» X-Ray Graph. Here we must say that GCPB on X-Ray analysis have been tests after steaming chamber + 7 days dry process. As we said later the main goal of X-Ray spectroscopy was – calcium hydroaluminate(ettringite) – $3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 3\text{CaSO}_4 \cdot 31\text{H}_2\text{O}$ availability. And that's for GCB but if we say about GCPB, we have searched for one-sulphate form - $3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{CaSO}_4 \cdot 12\text{H}_2\text{O}$, which have been described by Mr. A. Volzhenskiy in middle of 60-x.

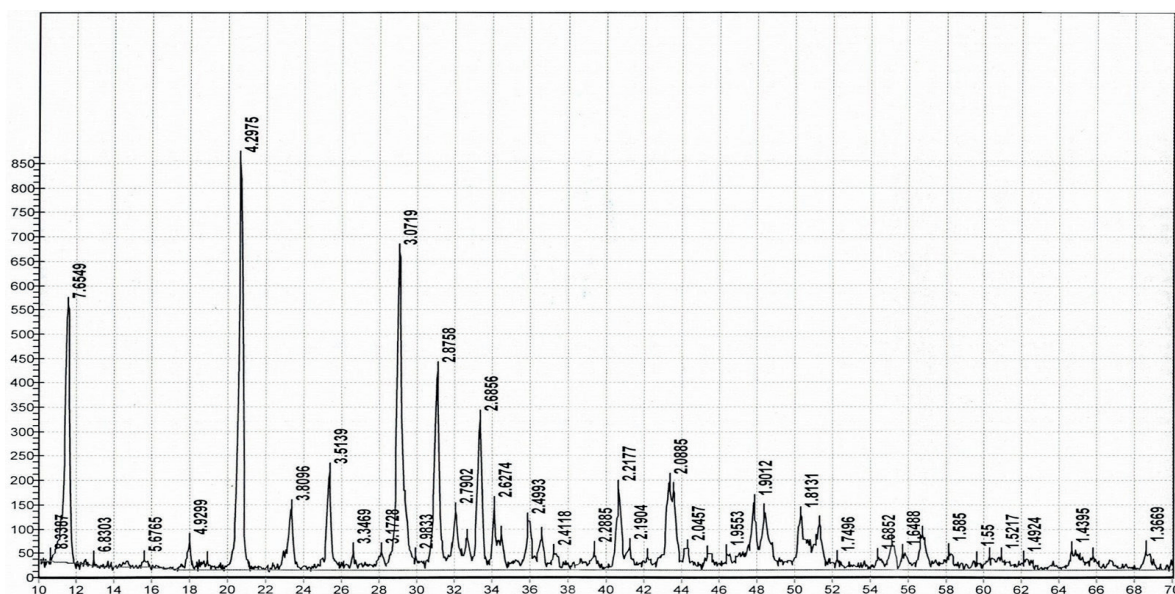


Figure 1 – “GCB 7 + 7” X-Ray Graph

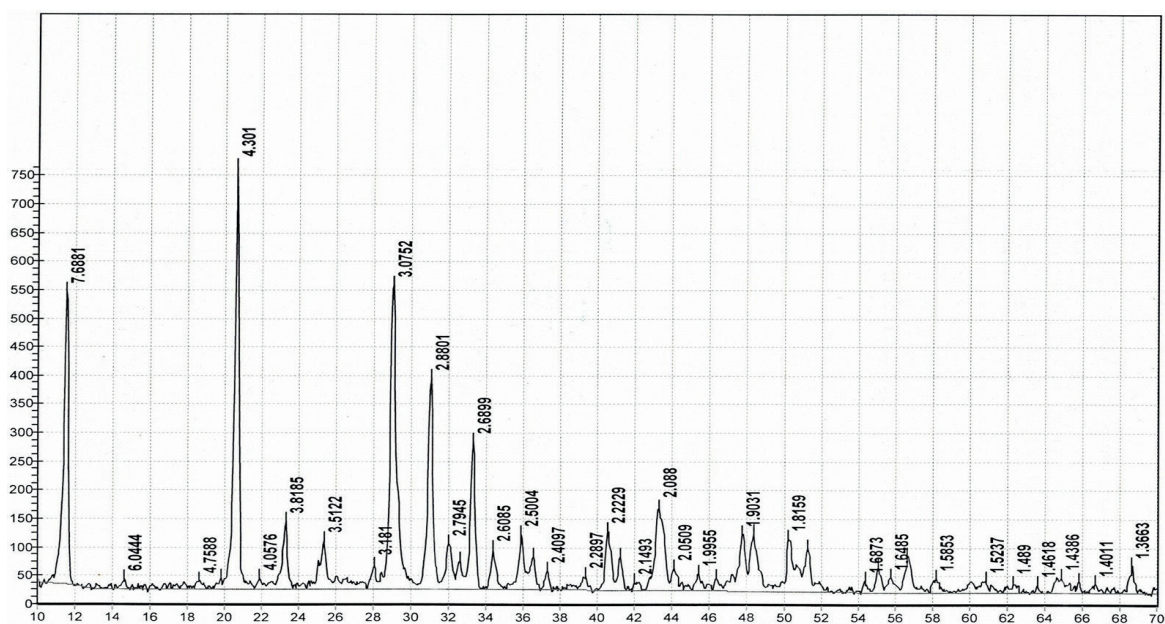


Figure 2 – “GCPB steaming” X-Ray Graph

Comparing the graphs we may see same high diffraction maximums with high intensity d , Å: 7,65(7,68); 4,29(4,30); 3,071(3,075) and more weaker as 3,80(3,81); 2,87(2,88); 2,68(2,68) which explains dehydrate $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ availability (GCPB – number in brackets, GCB number outside of brackets). Our qualification that mine the same as in resource [10 P.196]. The others diffraction maximums have low intensity line and may be qualified as cement mines. That low intensity may be explain by concentration of cement in any compound – GCB(25%)? GCPB(20%). On GCB X-Ray graph (Figure 2) we may notice low-lines which may be qualify as ettringite (three-sulphate form $3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 3\text{CaSO}_4 \cdot 31\text{H}_2\text{O}$) d , Å: 5,67(5,61); 4,93(4,98); 2,79(2,733); 2,627(2,616); 2,288 (2,230) (ettringite – number in brackets, GCB graph number outside of brackets) [10 P.285]. GCPB X-Ray graph have shown on picture 2, where we haven't see any low-lines intensity which may prove ettringite availability. But here we may see one-sulphate form ($3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{CaSO}_4 \cdot 12\text{H}_2\text{O}$) low-lines as d , Å: 2,88(2,87); 2,79(2,73); 2,409(2,41); 1,815(1,82); 1,648 (1,66) – one-sulphate form – number in brackets, GCPB graph number outside of brackets [10 P.284]. According by this Mr. A. Volzhenskiy's theory, one-sulphate form of calcium hydrosulphoaluminate appearing in GCPB instead of ettringite (three-sulphate form), have been proved in our research. And also we may highlight one difference between GCB and GCPB graphs. In GCB there are $\text{Ca}(\text{OH})_2$ low-lines availability d , Å: 4,93(4,93); 2,627(2,63); 1,95(1,93) and there aren't in GCPB X-Ray graph ($\text{Ca}(\text{OH})_2$ – number in brackets according to [10 P.292], GCB X-Ray graph with $\text{Ca}(\text{OH})_2$ lines – number outside of brackets) [10 P.292]. According to this we may conclude that we haven't got any “galos” by amorphous microsilica as mineral additive and that means there were reaction between $\text{Ca}(\text{OH})_2$ and SiO_2 in GCPB, but in GCB $\text{Ca}(\text{OH})_2$ has still stay in three way.

Conclusion

In conclusion we may say in that work we have proved Mr. A. Volzhenskiy's two theories about gypsum-cement-pozzolanic binder.

1) Gypsum-cement-pozzolanic binder compound – hemihydrate – 62%; cement (white cement) – 20%; mineral additive with 10 mg CaO/g activity – 18%. Every properties have been inherited by gypsum binder but it's not air binder as they increase its strength in water, in steaming process and in air-moisture conditions – hydro both. That kind of hydro-binder, which hardening process comes in water and in steaming conditions, have higher softening factor (K_s) which same as cement.

2) In GCPB there isn't any circumstances for ettringite appearing, internal tensile and future system damage during water and sulphate influence as it comes for gypsum binder.

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