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New Cements and Composite Materials Based on Them for Atomic Industry

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1. Introduction

New cements contains double oxides and aluminates of calcium, barium, stroncium. The date obtained allow to classify new cements as high-property fire-proof, quick-hardening and high-strength binders. The synthesis of cement clinker takes place through solid phase reactions. The newer developed cements of the higest fire resistance show only insignificant loss of strength when being heated (15% to 20% by weight), which can be accounted for by formation of high temperature - proof epitaxial contacts between the new hydrate formations and double oxides grains.

The aim of this work is to enlarge our knowledge about this new cements and hightemperature composites on them and find answers to questions about the optimum application of this product in severe industrial conditions and to analyse how this material performs in high temperatures.

The composite before trials investigated with the help of roentgen - structural and roentgen - spectral of the analyses, optical and raster electronic microscopy on standard techniques.

2. The using of high temperature composites based on zirconia's cement in recycling and catcher of fuel

For coating of high temperature gas - dynamic of channels (> 2000 °C) used high temperature composites based on zirconia's cements. The properties and structure of a material are adduced in table 1, 2. The erosive and temperature stability of a material on a bench, special energies heat treatment channel a bench was previously evaluated. The test specifications are adduced in table 3.

Complex three-component source structure, durables maintenance at temperatures exceeding not only temperature of a sintering, but also the melting aluminates of barium (-2100K) and the sintering of a dioxide of a zirconium, intensive of component's evaporation making of cement in a combination to large gradients of temperature result in steep changes on width of lining of a structure and structure of a material. It, naturally, is reflected in strength and reliability of maintenance of lining, that stipulates necessity of a detail research of a formed structure, in particular for detection of zones destruction.

No	Water to solids, % by weight	Setting time, min		Strength, N/mm2		
	solids, 70 by Weight	start	end	2nd	4 th	8 th
				day	day	day
1	15	25	55	550	880	1050
2	15	55	90	400	540	900
3	15	65	98	190	400	520
4	13	70	105	170	280	330
5	13	86	120	150	200	240
6	12	29	63	180	280	480
7	12	62	98	150	250	290
8	12	75	110	140	240	350
9	12	79	130	120	240	320
10	15	30	98	600	910	1100
11	15	60	90	450	600	950
12	15	70	105	210	450	600
13	13	78	115	200	310	350
14	12	91	125	180	250	270

Table 1. Properties of zirconia's cements.

Properties		Content of binder / mass - %			
_	10	20	30		
Baddeleyite (ZrO2)	90	80	70		
Refractoriness, K	2673	2473	2073		
Compression strength cold, MPa	38	45	65		
Compression strength, MPa					
burnt at 120°C	29	38	57		
burnt at 300°C	17	34	39		
burnt at 500°C	19	32	46		
burnt at 800°C	23	37	44		
burnt at 1000°C	36	39	63		
burnt at 1200°C	38	44	52		
burnt at 1400°C	39	45	50		
burnt at 1600°C	40	47	56		
burnt at 1750°C	42	45	58		
Linear change, 1750°C, mass-%	1.1	1.7	2.0		
Temperature of initial deformation under load, °C, no less	1750	1660	1560		
Thermal shocr resistance 1300 - water heat changes, no less	16	15	11		

Table 2. Physical and technical properties of composites materials based on zirconiur cements.

The composite material from a dioxide of a zirconiumipn cement contains a filler from stabilized cubic ZrO_2 and cement including 30 mass-% of monoaluminates and 70 % of zirconat. A dioxide of a zirconium making 80 % of concrete, is represented by three fractions: large (0.2 – 2.5 mm), average (0.1 – 0.5 mm), small-sized (are more small-sized (more finely) than 0.1 mm), including with the linear sizes of partials 1-5 microns. Used in experiments a dioxide of a zirconium was stabilized 6-7 mass-% oxide yttrium.

Parameter	Tank of the combustion chamber (CC)	Site a channel		
Expenditure of products of combustion of natural gas, kg/s	2-5			
Volumetric share of oxygen in an oxidizer, mass - %	40			
Temperature of a heating of an oxidizer, K	1100			
Coefficient of excess oxidizer	0,85-1,05			
Temperature of products of combustion, K	2600 - 2700	2500 - 2650		
Flow velocity, m/s	80	700		
Pressure (absolute), MPa	0,25	0,25-0,15		

Table 3. Specification of a test of lining.

The zirconium cement in an outcome of interaction with a water is subjected hydratation with derivation of a number of connections (BaAI₂O₄·6H₂O, BaAI₂O₄·7H₂O, BaAI₂O₄·2H₂O, Ba₂AI₂O₅·5H₂O), carrying on which among are two and six-water aluminates of barium. The accretion of chips of hydrat phases results in creation of a frame ensuring strength of a material at room temperature. The developed link between partial's of cement and filler at this stage is absent. The porosity of a material after hardening makes 15-2 mass-%.

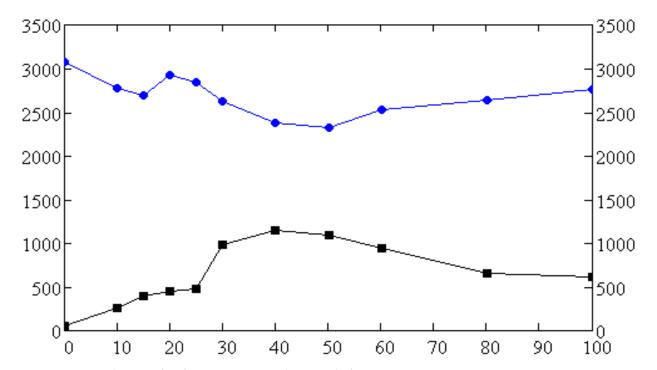


Fig. 1. Dependence of refractoriness and strengh from contents.

At temperatures is lower 400 K a material does not undergo changes. In remaining sites happens dehydratation knitting. Above 1400 T is observed a sintering of a material. Thus in a zone, which hot boundary corresponds to temperature 1700 K, the sintering happens mainly at the expense of development of contacts between partials of cement, in a zone up to 2150 K - at the expense of link of partials of cement among themselves and to grains of a

filler, in a more high-temperature layer the direct contacts of partials dioxide of a zirconium develop. In intermediate area (between the poorly changed zone and by a sintering layer) the structure of a material is determined by a degree dehydratation knitting, accompanying by destruction source hydro aluminates of barium. In a zone, from the cold side to sintering to a layer, where has a place practically full loss of a water, the destruction of a frame derivates, and, as a corollary it, recession of strength of a material happens. It is necessary to mark, that while in service destructions of lining on this zone, as a rule, does not happen, probably, by virtue of design features of a wall.

The width sintering of a layer depends on a level of temperature on a hot surface. At the temperature of about 2200 K the width sintering of a layer makes 20-25 mass-% from width of lining (for linings by width hS =12-60 mm), at 2300 - 2350 K 0,45 hS - 0.6 hS (on the profile of temperature partial transparency of a material) essentially influences. In a hot part sintering of a layer a sintering of a material increasing at the expense of derivation of a melt aluminates of barium. The rnelt partially quits on a firing surface of lining. The selection of a melt on a firing surface of a material during first 0,5-1 h of unisothermal heating immediately was observed during trials.

In bounds of a sintering layer it is possible to select some zones. Immediately zone adjoins to a hot surface, which distinctive feature is the presence only in the extremely minor amount (less than 1 %) components of cement. The cold boundary of this zone approximately coincides an isotherm 2200 K. by a Dominating phase a sintering layer is trie cubic hard solution because of dioxide of a zirconium. Aluminates and zirconate of barium register as separate of inclusions. Aluminates making is represented in main inclusions Al_2O_3 . The average content BaO in a sintering layer makes 0.2 – 0.4 mass-%, Al_2O_3 0.3 – 0.4 mass-%.

The structure of a material of a hot layer, going to a firing surface, shows, that during trials it in main loses components of cement. Zirconat of barium is partial in other zones, is partially decomposed with selection as an independent phase Al₂O₃. The loss of components of cement carries on to growth of a porosity of a material in a hot layer on 5 mass-% - 8 mass-% in comparison with source.

The structure of a hot layer of lining by width 0.14 hS- 0.16 hS (here and further at the temperature of of working surface is higher 2300 K) represents sintering porous ceramics because of dioxide of a zirconium. The character of a structure, formed in this layer, is determined by a level of temperature and amount of a liquid phase at the first phase of a sintering. In to a going firing surface a layer (the hot part of a zone of porous ceramics) happens heavily division of source grains of a filler into more small-sized fragments. Present here at initial stage of trials the melt aluminates of barium, which amount can be increased at the expense of arrival from more cold sites, promotes both process dispergation, and reallocation of products dispergation and partials of a small-sized fraction on size. The partials of a small-sized fraction dioxides of a zirconium are intensive decristallisation. In an outcome in to a hot surface a layer the material loses obviously expressed division into large and small-sized fractions and acquires a rather homogeneous structure.

In more cold sites of a zone of porous ceramics an amount of a liquid phase present to not initial stage of trials and capable to ensure a regrouping, of a capable, much below, than in of surface area. Dispergation of grains of a filler with derivation of free interfaces between blocks is not accompanied by essential reallocation of derivate partials on size.

Because of grains of a filler will be derivates of partials dioxide of a zirconium, inclu a grain and going to it a partial of a small-sized fraction.

In accordance with transition to even more cold sites the decrease of the size of grains, of the filler which has undergone dispergation is observed. Dispergation of large grains of a filler happens in a hot part, which width makes approximately 60 - 65 mass-% from width of a zone of porous ceramics. In underlying zones in large grains of a filler the increase S of a porosity registers in comparison with source. In more small-sized grains the growth of a porosity is combined with splitting on blocks. The latter will be realized(sold) mainly near to boundaries of a grain of a filler. As well as in hotter sites, in a material the developed contacts of grains of a filler with decristallisation by partials of a small-sized fraction are observed.

The link between large by dispergation grains of a filler implements derivations of a complex configuration generated from partials of average and small-sized fractions dioxide of a zirconium. A structure of these derivations, number and quality of contacts, explicating between them and large grains of a filler, largely determine strength of a material in a zone of porous ceramics because of dioxide of a zirconium. Their most characteristic variants of allocation of structural units in intervals between large grains it is necessary to mark a structure, in which the primary orientation is absent.

The hot part of a zone of porous ceramics differs from hot sites less by rectangular distribution of a material and large size of vacuum in intervals between grains of a filler. Thus the fair quantity porosity, oriented along a hot surface is observed. In some cases the concentration such nop on approximately one horizon happens, the depth makes 0.12 hS – 0.14 hS. The rise of concentration porosity carries on to lowering strength of a material on appropriate horizon. At availability change, of temperature in this area the cracks, carrying on to destruction linings can develop.

As already it was marked, a dominating phase in a zone of porous ceramics is the cubic hard solution because of dioxides of a zirconium. The concentration of the stabilizing "component Y_2O_3 in a layer, which adjoins to a hot surface, makes 3 - 4 mass-% (molar shares) ambassador 50 hours of trials. The same level of concentration of the component registers through 200 - 250 hours after a beginning of trials. In accordance with transition to more steep layers of this zone concentration Y_2O_3 the gradually is increased and near to cold boundary of a zone of porous ceramics receives a reference value. The not stabilized dioxide of a zirconium either is absent, or registers in an amount less than 1 %. The absence of the not stabilized dioxide of a zirconium shows, that in a hot part of this zone the reallocation of the component Y_2O_3 between a source cubic hard solution and not stabilized ZrO_2 , selected happens at decomposition zirconat barium.

The link of particles of a dioxide of a zirconium in a zone of porous ceramics implements mainly direct contacts ZrO_2 - ZrO_2 . The part of contacts will be realized by means of films by width a micron and less, containing oxide of a aluminum.

Near to cold boundary of a zone of porous ceramics the increase of number of * inclusions zirconat of barium is observed. On depth 0.14hS – 0.16hS the sharp increase of a content zirconat of barium up to 20 - 25 mass-% (figure 1) happens, that considerably exceeds the source value - about 14 mass-%. Zirconat of barium in this area will derivate congestions on

a surface of particles dioxide of a zirconium, fills in the porosity and crack in grains of a filler. The particles zirconat of barium forming on boundaries of grains dioxide of a zirconium, have the linear sizes 2-50 microns and differ by dense stacking. Sometimes such are be surrounded by a film Al_2O_3 . The content Al_2O_3 in a zone of synthesis zirconat of barium makes 1.5-1.7 mass-%. Thus an amount aluminates of barium makes 1 %.

The useful increase of an amount zirconat of barium allows to assume, that the part a pair(vapour.couple) BaO selected at decomposition zirconat of barium in a zone of porous ceramics, acts to space in more cold zones, where is condensed and enters response with a dioxide of a zirconium with derivation secondary zirconat of barium. It is necessary to marRrTRaT the derivation BaZrO₃ in a considered zone is also in case of absence zirconat of barium in source concrete. Thus the amount synthesized during trials zirconat of barium does not exceed 3-4 %.

The material of a zone enriched zirconat of barium, after trials is saturated with cracks. The development of cracks should be promoted by the volumetric extension accompanying synthesis zirconat of barium. The link of particles of a dioxide of a zirconium implements both by means of direct contacts, and through inclusions zirconat of barium.

In a cold part of a zone of synthesis zirconat of barium the number of inclusions aluminates of barium accrues. The amount of the latter spasmodically increases on depth 0,24hS - 0,26hS. The underlying layer by width about 0,07hS differs by an increased content aluminates of barium (12 - 15 mass-%), essentially exceeding a source level (6 mass-%). In a hot part of a zone enriched BaZrO₃, aluminates of barium in a combination to particles BaZrO₃ will derivate interlayer up to 150 microns on boundaries of grains of a filler. The content zirconat of barium is close a reference value. The particles of cement differ by rather dense stacking. Their linear sizes make in main 3-15 microns. The direct contacts of particles dioxide of a zirconium here practically are absent. At the same time in this area the development of contacts of particles dioxide of a zirconium both with zirconat and with aluminates of barium is provided. The material of lining in a considered layer differs in increased density in comparison with the poorly changed zone. It is possible to assume, that the derivation of this packed zone is stipulated by arrival of a melt aluminates of barium from hot layers of lining and it a chip.

From the cold side the layer adjoins to a zone with increased density, in which the content of components of cement is identical source. The sintering of cement in this zone flows past rather actively and is accompanied of the linear change. In an outcome in intervals between grains of a filler the including also small-sized particles of a dioxide of a zirconium will be derivated densely stacked of particles of cement. The structure of a material here is identical to a structure of concrete, in isothermal conditions at 1900 -2000 K.

In accordance with deleting from a zone saturated aluminates of barium, the size of particles of components of cement of a gradually decreases, the quality of link between a filler and particles of cement is worsened. At the same time the linear change within the limits of a small-sized fraction hinders with derivation of a continuous frame of cement, that in a combination to not enough developed contacts a filler - the cement carries on to lowering strength of a material in this zone. At cooling of lining the explicating in a material of power result in derivation of trunk cracks in a cold part of a circumscribed above zone on depth, making 0.3hs - 0.4hs.

In more cold sites down to cold boundary of a layer the sintering of cement happens without obviously expressed the linear change. Recristallisation of particles of cement is expressed poorly. In a material the continuous frame of cement is formed. Thus the link between a filler and cement is advanced poorly. As already it was marked, the cold boundary sintering of a layer passes on depth 0.45hs – 0.6hs.

The circumscribed above zones in a sintering layer are present at the rather developed form in 2 hours after a beginning of trials. The more durables trials do not result in increase of width of a sintering layer and zones, composing it. With rise of duration of trials the zone of porous ceramics because of dioxides of a zirconium in a greater degree is cleared of inclusions containing barium and aluminum. Besides the more expressed character is acquired with concentration of the poores in a cold part of a zone of ceramic porous.

Is conducted about 20 launches of installation for trial of materials by duration from 50 till approximately 400 o'clock. During trials temperature on a surface of lining (both in the combustion chamber is fixed, and in gas-dynamic a channel), as a rule, 2250 -2400 K, in separate experiments it was possible to reach temperature 2600 K.

The rise of temperature of a surface of lining Ts is precisely fixed at decrease of a share of a firing surface occupied by copper edges and at increase of width of lining h (from Ts \approx 2000 K at x \approx 0,15 and h=10 mm up to Ts \approx 2400 K at x \approx 0 and h=25-30 mm). Is marked, that at Ts >2200 K defining a role in creation of a thermal mode of a firing surface begins to play of walls among themselves (density of a heat flow \geq 1 MW/m2 at density of a convective heat flow \leq 0.4 MW/m2).

At temperatures a surface of concrete is higher 2150 T concrete lining on zirconia's cement in a upper layer well conglomerated in first 2-6 hours of installation, that provided to lining high erosive stability purely erosion of a material during trials was less than 1 micron / hour.

Is clarified, that the lining on zirconia's cement allows conduct fast (for 20 - under 60 min.) heating of an outline of installation. Moreover, such heating even is preferable to concrete (acceleration of a sintering of a high layer results in decrease of initial erosion of concrete).

3. The using of zirconia's cement composite in coating of quartz glass tanks

The new cements and composite based on then can be used in the coating of quartz glass tanks. In contact with glass there are used refractories made of natural baddeleyite without stabilizing oxides. The coating of this material showed good characteristics under thermal shock and quartz glass penetration resistance properties.

3.1 Red mud

Red mud is a waste material which results from alumina production during the Bayer process. Approx. 35-40% of the bauxite ore processed goes into waste as red mud. This is a cheap source of raw material for the manufacture of low-cost ceramic products such as building blocks, floor and wall tiles, sanitary ware and as an additive for cement. The chemical composition of red mud is as follows (Table 4).

Oxidic Compounds	Content [Mass - %]	
Fe_2O_3	38.1	
$A1_2O_3$	27.01	
SiO_2	14.15	
TiO ₂	5.01	
Na ₂ O	6.03	
K ₂ O	0.36	
CaO	2.26	
MgO	1.01	
CO_2	4.02	7
SO_3	2.05	

Table 4. Cemical composition of the calcined red mud.

Red mud is a very complex material. It is a mixture of several oxides and minerals such as hematite, sodium aluminum silicates, and rutile. These make the mud a potential raw material for the production of additives for cements.

The particle size analysis of the calcined red mud showed that 85% of the particles are <10um (Figure 2). The calcined red mud ranged in size from 35 to 5 urn average particle diameter. The particle size analysis of the calcined red mud is given in Figure 3.

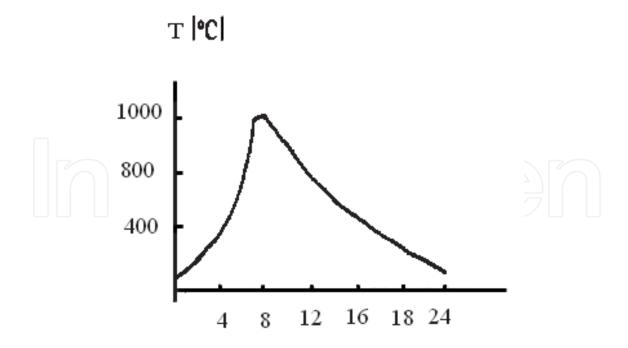


Fig. 2. The firing treatment of red mud. The treatment of red mud n dependent on temperature and time.

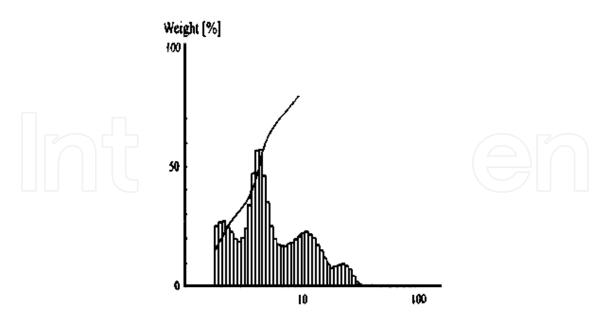


Fig. 3. The particle size analysis of calcined red mud. X-Ray diffraction results of the calcined red mud.

3.2 Clays nonconditional caolins

Ukraine has a great number of clay deposits. These clays can be used for traditional ceramics production and for production as an additive to cement. The physicoceramic date revealed that, in general, the clays sensitive to drying from this area, have significant plasticity (between 30 and 58%) and relatively high total shrinkage (between 6 and 21%) (Figure 4), have good to very good capability, average water adsorption (between 9 and 16%) good to very good mechanical resistance (compressive strength between 325 and 355 daN/cm²) (Figure 5), and bending strength between 90 and 460 daN/cm².

Plasticity and Total Shrinkage of the Studied Clay Samples

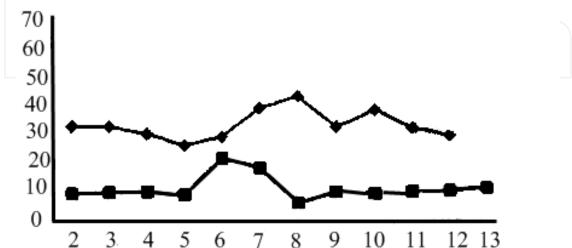


Fig. 4. The Augustinic diagram of use of the clay deposits.

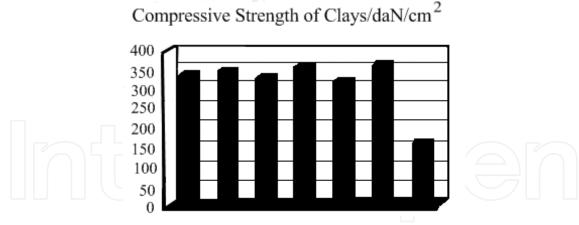


Fig. 5. Comparative diagrams of physico-mechanical characteristics of clay deposits.

The red mud sample was supplied by Nicolayew Plant(Ukraine), Kaolin wastes(region of Donetsk), Nepheline wastes(Atschinsk, Russia).

The chemical analysis of the sample was accomplished by using an atomic absorption spectrophotometer or digital photometer and wet chemical methods (Table 5). X-Ray diffraction studies on the sample were undertaken using a Philips X-Ray diffraction unit. The particle size distribution of the sample was measured by using a Sedigraph (5000D Micrometrics). The photographs of the samples were taken with an optical microscope (Olympus BH2-IMA).

Working zones		Distance from hot face, mm		Contents			
	SiO ₂	$A1_{2}O_{3}$	Fe ₂ O ₃	MgO	Na ₂ O	CaO	K ₂ O
1	68.11	14.85	5.6	0.91	0.14	0.96	0.57
2	69 52	15	4.6	0.6	3.75	1.68	0.75
3	52	31	8	0	2.1	0	2.3
4	54.6	23 19	2.1	1.6	0.3	0.6 2.03	2.6
5	58.38	19	6.6	1.85	0.95	2.03	
6	64	14.4	6.7	1.1	1.13	2.14	1.27
7	57.03	18.57	7.37	2.22	1.04	2.16	2.88
8	64.88	12.51	5.13	2.29	1.63	5.99	2.1
9	65.07	16.48	6.08	1.18	0.74	1.18	1.66
10	51.62	27.97	3.92	1.09	1.59	0.76	1.59
11	14.76	26.94	37.6	1.01	5.83	2.06	0.34
12	57.21	20.02	1.44	0.94	0.55	1.96	3.2
13	53.43	32.07	5.82	2.06	0.05	2.14	0.19
14	59.1	25.64	7.1	1.28	0.06	2.27	0.85
15	50.12	29.78	5.04	1.00	0.04	0.45	0.7
16	43.02	27.68	3.09	0.6	11.62	2.04	9.34
17	6.86	35.9	0.9	4.39	0.15	48.9	0.06

Table 5. Trend of contents of coating after working (153 days).

The obtaining of additives from alumina wastes is based on a theoretical study of the system CaO - AI2O3 - SiO2 - Fe2O3, MgO - CaO - AI2O3 - SiO2 [Figures 6, 7].

The obtaining of cements is based on a theoretical study of the system CaO, SrO, BaO - Al_2O_3 - SiO_2 - Fe_2O_3 , MgO-CaO- Al_2O_3 -SiO₂.

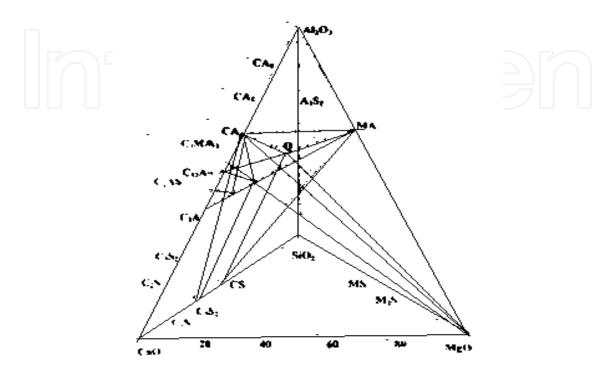


Fig. 6. Optimum region for obtaining of special cements. Subsolidus structure of the system CaO - Al_2O_3 - Fe_2O_3 - SiO_2 .

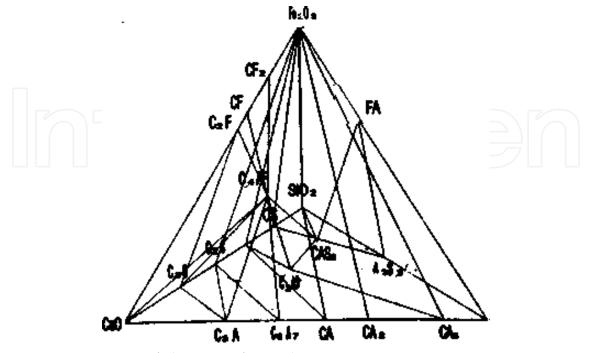


Fig. 7. Optimum region of obtaining of special cements.

It was found that pseudocuts containing double oxides and binder compounds (C₂S, C₃S, CA) have greater binder activity. The initial stage of hydration begins with leaching the surface atoms and active chemical adsorption of water molecules due to presence at active centres followed by their relation through forming OH hydroxide groups and a surfactant layer having specific surface area (to 2*10A6 sq.m/kg) and consisting of aluminum hydroxide. At the next stage the surfactant layer of double oxides adsorbs ions Ca⁺². Chemical adsorption of the cations decelerates nucleation and promotes formation of epitaxy contacts on the surface of the double oxides as well as oriented growth of hydrate formations of hydroaluminates hydrosilicates of calcium. As a result of chemical adsorption process and oriented crystallization 01 hydrates around the double oxides grains there is formed a contact zone that is significantly higher than that of pure cement stone. This determines the high strength of the double oxides containing cement.

4. Conclusion

The development of new high temperature composites based on zirconium cements for the application in various consuming industries has been illustrated and is well documented in terms of performance improvements. They are meant to protect units from influence of temperature more than 2073 K. They are used for coating of high temperature headtreatment, in coating of fuel - construction, in coating of furnace for making fuel, carbon-reactor, H_2 - Furnace, petrochemistry reactors.

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Materials are important to mankind because of the benefits that can be derived from the manipulation of their properties, for example electrical conductivity, dielectric constant, magnetization, optical transmittance, strength and toughness. Materials science is a broad field and can be considered to be an interdisciplinary area. Included within it are the studies of the structure and properties of any material, the creation of new types of materials, and the manipulation of a material's properties to suit the needs of a specific application. The contributors of the chapters in this book have various areas of expertise. therefore this book is interdisciplinary and is written for readers with backgrounds in physical science. The book consists of fourteen chapters that have been divided into four sections. Section one includes five chapters on advanced materials and processing. Section two includes two chapters on bio-materials which deal with the preparation and modification of new types of bio-materials. Section three consists of three chapters on nanomaterials, specifically the study of carbon nanotubes, nano-machining, and nanoparticles. Section four includes four chapters on optical materials.

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