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DEMONSTRATION OF METASTABLE PARAGENESIS IN THE PROCESS OF SOLID PHASE INTERACTION IN THE SYSTEM OF $\text{CaO} - \text{Al}_2\text{O}_3 - \text{SiO}_2$

A short characteristic of new type of foreign dental cements Mineral Trioxide Aggregate (MTA) for root canal dressing is presented. The results of experimental researches dealing with the development of the composition and method of producing of the national dental cement of the similar purpose. The effect of modifying additions (CaF_2 , P_2O_5 , Bi_2O_3 , MgO) on the sintering process of clinkers was studied and the demonstration of metastable paragenesis in the of solid phase interaction in the system $\text{CaO} - \text{Al}_2\text{O}_3 - \text{SiO}_2$ was found. The obtained results provide more reliable designing of the mineralogical composition of cement clinker.

Introduction. This work is a systematic research carried out at the Department of Chemical Technology of Binding Materials of Belarusian State Technological University in collaboration with the Department of General Dentistry of Belarusian State Medical University devoted to the the development of dental materials for various purposes.

There is a need for surgical treatment to save the tooth at a time of the high prevalence of Belarusian patients dental caries (15-year-old population tooth decay is 91.7% and 35–44 years age group reaches 100%). The success directly depends on the right choice of filling material [1].

Theoretically the filling material must guarantee the tight root canal insulation. It must prevent the penetration of infection from the cavity. But it doesn't have to cause any irritation to the surrounding tissue, to dissolve under the influence of tissue fluid. It must be easily removed from the channel because in the case of treatment failure may be required a second sealing.

Over the years amalgam, zinkoksideugenol, polimeric, glass ionomer cements, sealers containing calcium hydroxide, polydimethylsiloxanes, etc were used for these purposes. But none of them doesn't fully meet all the requirements for dental materials of the mentioned destination. A common shortcoming of all of these materials is their hydrophobicity. That's why it is necessary to provide a completely dry workspace when they are used. But the problem is that quite often it cannot be achieved in the process of surgery root perforations, retrograde fillings, etc. [2].

New material Mineral Trioxide Aggregate (MTA) has been developed in 1993 in the USA. This material represents the calcialuminosilicate cement capable harden and gain strength in wet conditions [3, 4].

Such kinds of cements are not being produced in Belarus, so the demand for them is met by the imported materials like "ProRoot MTA" (Dentsply USA), "Trioksident" ("VladMiVa" (Russia)), "Restapex" (Ukraine), etc.

However the experience of application of these cements in dental clinics of the Republic of Belarus has shown that they do not fully meet the growing requirements. Thus the major shortcomings of the material "Trioksident" (Russia) is a long-time of the final curing (24 h) which makes it impossible to root canal fillings within one patient visit. It also contains some large particles of the radiopaque filler (100–150 μm). It is also typical for "Restapex" (Ukraine). Thus it makes difficult the penetration of cement paste into the narrow curves of root canals and the necessary seal isn't provided.

Time of the final "ProRoot MTA" (USA) cement hardening is 4–6 h. But its operating time takes only 4–5 min. It is not sufficient for good sealing. In addition it doesn't have the necessary plasticity.

Therefore the aim of this research is the development and manufacturing process of receiving as well as holding technical and clinical testing of this type of dental cement. That is free of the mentioned drawbacks of similar foreign analogs.

Main part. Literature and patent analysis of the data showed that the composition of MTA cement contains such minerals as $(3\text{CaO} \cdot \text{SiO}_2, 2\text{CaO} \cdot \text{SiO}_2, 3\text{CaO} \cdot \text{Al}_2\text{O}_3)$. Being mixed with water they can be subjected to the hydrolysis and hydration with subsequent conversion to the lithoid material. Therefore three-component system $\text{CaO} - \text{Al}_2\text{O}_3 - \text{SiO}_2$ was taken as a base for their production.

To define the scope of the clinker formation the reagents CaCO_3 (class "p"), $\text{Al}(\text{OH})_3$ (class "c.p.") and $\text{SiO}_2 \cdot n\text{H}_2\text{O}$ (class "c.p.") some experimental mixtures have been prepared. The molded samples pills with diameter 50 mm and height 5 mm have been formed from the batch mixture by semi-dry pressing. Burning has been carried out in an electric furnace in the temperature range of 1,300–1,450°C for 4 h. It was followed by rapid cooling of obtained sinters (clinker) in air.

The concentration limits of oxides (wt %): $\text{CaO} - 75-85$; $\text{SiO}_2 - 15-25$; $\text{Al}_2\text{O}_3 - 5-25$

forming clinkers under heat treatment have been established during the first stage of the experimental work

To estimate the binding properties the fired clinkers were finely grinded in a ball mill. It ensured the passing of cement through the sieve N 0045 without a trace. The grinded cement mixed with the distilled water of water-cement ratio of 0.45. It helped to obtain the necessary consistency of cement paste that was molded into cubes with an edge of 10 mm. The compressive strength of the hardened material in accordance with ISO 9917 was measured at 3 and 28 days.

Table 1 shows the cement characteristics which are derived from clinkers fired at 1,450°C and possess the best strength properties.

The Table shows that the cement production as a strength (23.3 MPa) as well as working time (6.0–6.5 min) is inferior to foreign analogs whose compressive strength is 65 MPa (“Pro-Root MTA”) and working time is 10–15 min (“Trioksident”).

That’s why the the next stage of the experimental work was to improve the service properties of dental cement. To effect it we had to intensify the process of clinker formation.

Fe₂O₃ is known to improve the STI-calcination of cement clinker in industry. It is widely and effectively used for these purposes. Being a smooth it substantially reduces the temperature of clinker formation. However in addition to dental material strength high requirements are lodged for its whiteness. The dark color cement is not suitable from an aesthetic point of view. Therefore the efficient qualities of the mentioned addition cannot be used in this case.

Therefore, CaF₂, P₂O₅, Bi₂O₃ were taken as modifiers for the 3-component system. Their selection was based on the following reasons. Calcium fluoride is known to accelerate the processes occurring between the components of a calcinable

mixture, to lower the temperature of the formation of the basic eutectic melt. Thereby it reduces the clinker melt viscosity. The mobility of the ions is increased, the diffusion processes are accelerated. The formation of clinker is speeded up. Phosphorus pentoxide stabilizes β-C₂S and C₃S thereby increasing their hydraulic properties. It should be explained by their loosening under the influence of ion P⁵⁺ and corresponding increasing of the supply of the potential energy of the crystal lattice of silicates [5–8]. As bismuth oxide is a low-melting (870°C) it simultaneously provides radiopaque of dental cement.

The results of the experimental data (Table 2) showed that the separate addition of the CaF₂ and Bi₂O₃ failed to achieve lower burning temperature (up 1,340°C) because clinkers spillage occurred in the process of cooling as a result of their silicate disintegration, i.e. the transformation of the active hydraulic dicalcium silicate β-2CaO · SiO₂ to the inactive modification γ-2CaO · SiO₂. With the addition of P₂O₅ and burning temperature 1,340°C this effect was avoided but the strength of the cement based on such clinker was minimal. It happened because the melt process of clinker formation was slowed down in deficiency of the resulting eutectic melt.

Reducing of the clinker formation temperature up to 1,340°C was achieved by the addition both V₂O₅ and CaF₂. To prevent further silicate decay P₂O₅ was additionally added. Besides to increase the strength properties of dental cement MgO was added, since magnesium ions partially replaced in the crystal lattice of Ca²⁺ make the high-temperature forms of tricalcium silicate more stabilize that can best contribute to the increase in the strength of cement.

Table 2 shows that the cement received by the simultaneous addition of mineralizing adds has the highest strength characteristics. However the dental cement should also have the necessary time of final curing and working time.

Table 1

Composition of experimental cements and their properties

Composition number	Oxides mass content, wt %			Compressing strength, MPa, at the age, 24-hour period		Worktime, min
	CaO	Al ₂ O ₃	SiO ₂	3	28	
22	60	20	20	12.7	22.7	1.5
22.1	65	15	20	14.5	21.3	2
21	70	20	10	12.4	17.8	3
21.1	75	5	20	8.3	10.8	6.5
21.2	75	10	15	10.65	16.2	4.5
21.3	65	10	20	6.2	19.5	4
21.4	70	5	25	13.2	23.3	6

Table 2

Strength of cement depending on the input of additives and firing temperature

Mineralizer		Addition mass content, wt %	Compressing strength, MPa, at burning temperature, °C					
			1,300		1,340		1,400	
			at the age, 24-hour period		at the age, 24-hour period		at the age, 24-hour period	
			3	28	3	28	3	28
P ₂ O ₅		0.6	4.2	8.57	4.7	9.2	12.4	24.4
CaF ₂		1.5	9.7	18.1	10.3	19.4	14.6	27.1
Bi ₂ O ₃		5.0	6.7	18.3	12.5	20.2	16.4	28.2
Combined introduction	P ₂ O ₅	0.8	10.1	19.2	12.9	24.3	18.6	29.8
	CaF ₂	1.5						
	Bi ₂ O ₃	3.0						
Combined introduction	P ₂ O ₅	1.0	11.5	22.8	14.9	29.4	21.4	32.1
	CaF ₂	1.5						
	Bi ₂ O ₃	3.0						
	MgO	0.3						

As you know the paramount influence on the properties of cement has its mineral composition. Therefore for the structurally-controlled synthesis, i.e. the formation of the desired mineral composition it was necessary to examine the sequence of formation of the crystalline phases in the dynamic conditions like those that are used in the cement industry.

There is no any information on this subject in the literature. At the same time, we know that the sequence of the formation of crystalline phases during the “top” crystallization taking place on cooling magmatic melt the effect of metastable paragenesis appears. It refers to natural co-location of minerals connected by general physico-chemical and thermodynamic conditions of formation [9].

Thus the establishment of a metastable paragenesis in the case of the “bottom” crystallization would establish a physical-chemical basis for the structure-controlled synthesis of dental cement clinkers.

Relatively recently performed researches presented in the doctoral dissertation of E. N. Potapova [10] show that the cement properties (compressive strength, working time, setting time, etc.) do not only depend on the mineralogical composition of the clinker, but also on its melting history. Therefore for a more reliable design of clinker composition to produce dental cement it was necessary to establish on its base the genetic relationship in a line “charge → clinker → melt” and its effect on phase formation in the silicate system.

Predict the sequence of formation of phases in the solid phase reactions and their realization allowed the results of thermodynamic calculations

and experimental data on the determination of the phase composition of cakes (clinker) at different burning temperatures by X-ray fluorescence analysis (XFA).

The direct reactions of interaction with CaCO₃ can take place at temperatures up to 800°C in the absence of CaO [11].

At temperatures above 800°C when CaCO₃ decarbonization takes place, Al₂O₃ and SiO₂ react with CaO and with some formed elementary low-basic compounds with subsequent saturation to a highly-basic ones.

Analysis of changes of the Gibbs energy of solid phase reactions shows that the formation of the main clinker phases (3CaO · SiO₂, 2CaO · SiO₂, 3CaO · Al₂O₃) is the most probable through the intermediate phase.

In reality the process of clinker formation can be traced by X-ray diffraction study. The analysis of samples obtained at different temperatures showed that their phase composition differs from the state showed on the diagram. It was found that the crystallization process of compositions in non-mineral phase in non-equilibrium conditions affect neighboring phases formed at lower temperatures.

Fig. 1 shows a fragment of the constitution diagram of CaO – Al₂O₃ – SiO₂ illustrated with studied composition points and location of the phase composition depending on the burning up temperature of the samples (Table 3).

Fig. 1 shows that the composition points of the experimental compositions in the crystallization field of the same phase depending on the location (center or periphery) will differ. The mode of samples burning up also influence on it.

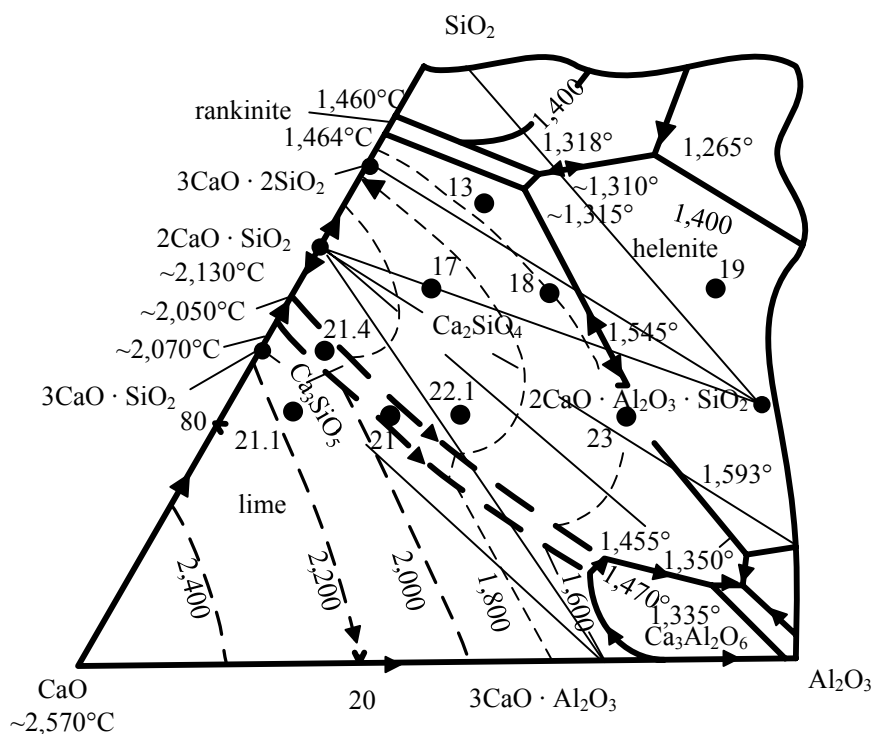


Fig. 1. Constitution diagram of CaO – Al₂O₃ – SiO₂ illustrated with experimental composition points

Table 3

Changes of the phase composition depending on the burning up temperature

Composition number	Crystallization field on the constitution diagram	Phase composition in the process of burning up, °C		
		1,300	1,400	1,450
19	H	H	H	H
17	C ₂ S	C ₂ S, A	C ₂ S, C ₃ A	C ₂ S, C ₃ A, C ₃ S
13	C ₂ S – R	R, C ₂ S, A, H, P	R, C ₂ S, H, P	R, C ₂ S, H
18	C ₂ S – H	H, C ₂ S, A	H, C ₂ S	H, C ₂ S
23	C ₂ S – H	C ₂ S, H, A	C ₂ S, H	C ₂ S, H, C ₃ S
22	C ₂ S	C ₂ S, H, A, C ₃ A	C ₂ S, C ₃ S, C ₃ A, G	C ₂ S, C ₃ S, C ₃ A
22.1	C ₂ S – C ₃ S	C ₂ S, H, A, C ₃ A	C ₂ S, C ₃ A, C ₃ S	C ₂ S, C ₃ S, C ₃ A
21.4	C ₃ S	C ₂ S, C ₃ A, C ₃ S, M	C ₂ S, C ₃ S, C ₃ A	C ₃ S, C ₂ S, C ₃ A
21	C ₃ S – CaO	C ₂ S, C ₃ A, C ₃ S, H	C ₂ S, C ₃ A, C ₃ S	C ₃ S, C ₂ S, C ₃ A
21.1	C ₃ S – CaO	C ₂ S, C ₃ A, H, M	C ₂ S, C ₃ A, C ₃ S	C ₃ S, C ₂ S, C ₃ A

Notes. H – helenite; A – anorthite; R – rankinite; P – pseudowollastonite; M – mullite; C₃S – 3CaO · SiO₂; C₂S – 2CaO · SiO₂; C₃A – 3CaO · Al₂O₃.

Fig. 2 shows the change of the composition of clinker N 21.4 at the center of crystallization 3CaO · SiO₂ depending on the burning up temperature.

Fig. 3 and 4 show the percentage of phases of clinker N 21.4 depending on the burning up temperature and input supplements.

It can be seen that some intermediate phases are formed at lower temperatures. They convert to the basic ones at higher temperatures. By studying the change in the ratio of clinker phases depending on the burning up temperature and the introduction of additions you can get dental cement which will have the necessary properties.

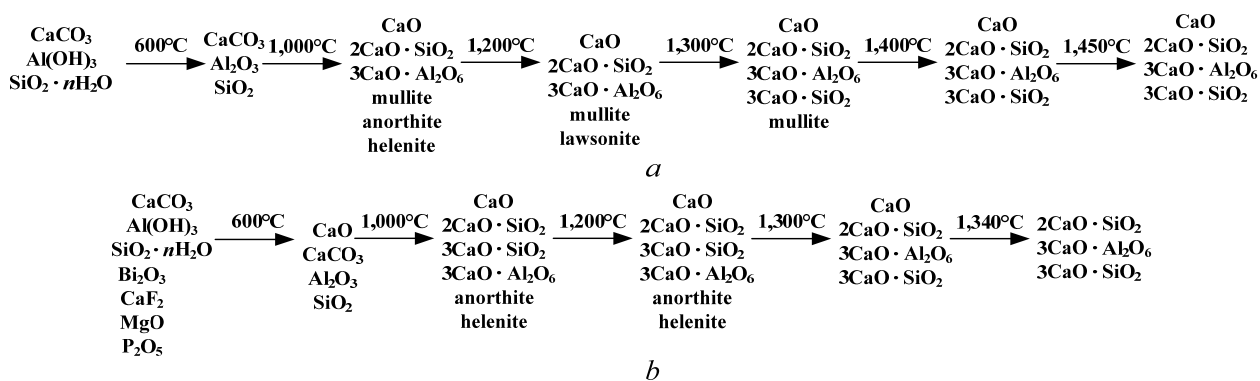


Fig. 2. Sequence of crystal phase formation:
a – composition N 21.4; *b* – modified P_2O_5 , CaF_2 , Bi_2O_3 , MgO

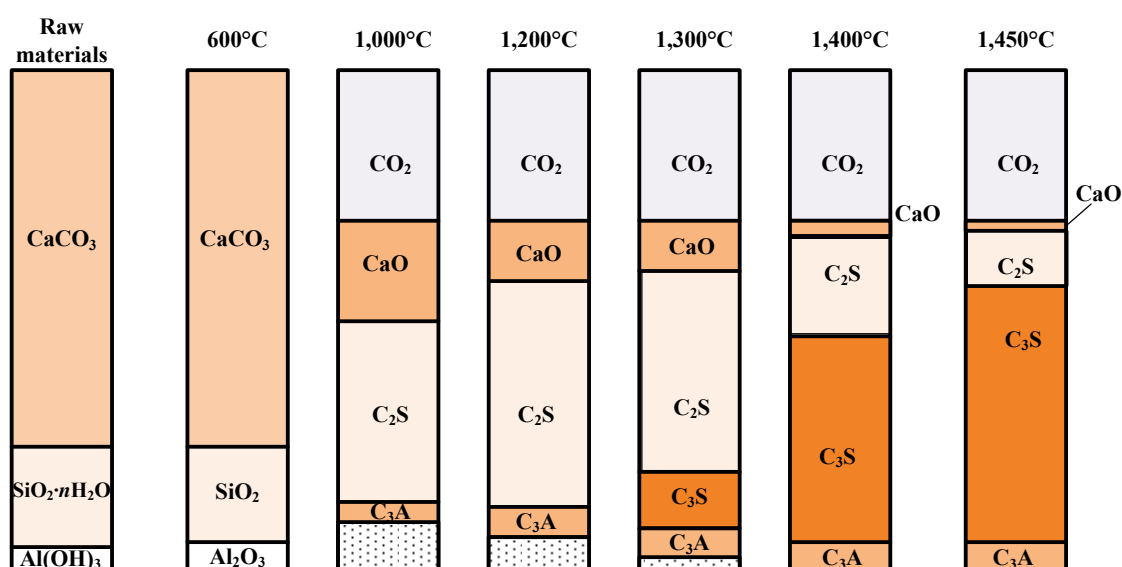


Fig. 3. Sequence of phase composition formation of sample N 21.4

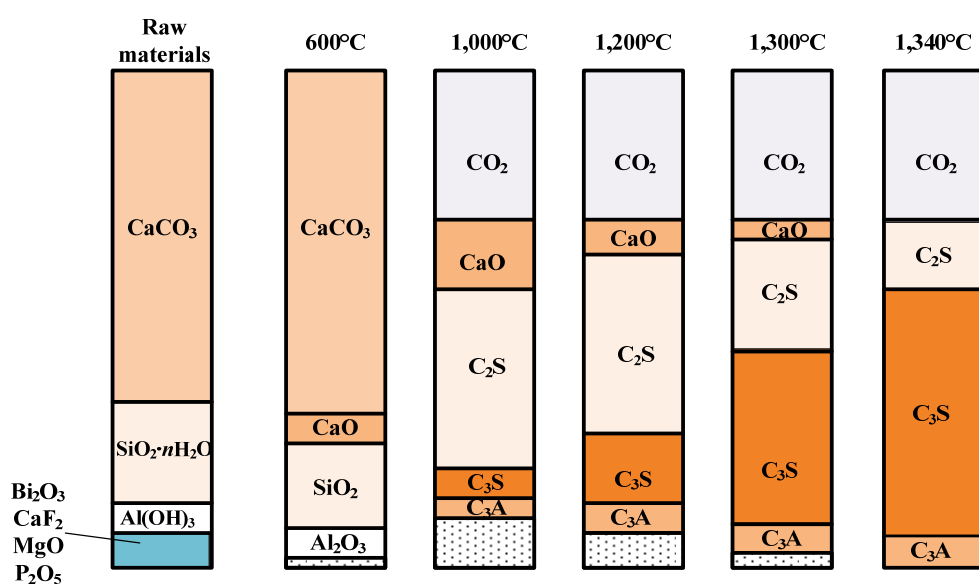


Fig. 4. Sequence of phase composition formation of sample N 21.4,
 modified P_2O_5 , CaF_2 , Bi_2O_3 , MgO : $\text{C}_3\text{S} - 3\text{CaO} \cdot \text{SiO}_2$; $\text{C}_2\text{S} - 2\text{CaO} \cdot \text{SiO}_2$; $\text{C}_3\text{A} - 3\text{CaO} \cdot \text{Al}_2\text{O}_3$;
 [stippled box] – silicates and calcium aluminates

Conclusion. Based on the systematic investigations of solid-phase interaction in the system $\text{CaO} - \text{Al}_2\text{O}_3 - \text{SiO}_2$ as well as the modified CaF_2 , P_2O_5 , Bi_2O_3 , MgO the dental cement to seal the root canal was developed. It possesses all best properties of the foreign analogues.

The results of thermodynamic calculations and experimental data on the phase formation by XRD revealed the manifestation of metastable paragenesis during crystallization in dynamic environments. It was the basis for the development of the parameters of the structural-controlled synthesis of dental cement.

The production of this cement will allow to expand assortment of domestic dental materials produced by JSC GIAP and to provide import substitution.

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