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Physical Chemistry

Raw Materials for Fabrication of New Type, Environmentally Safe Fire-Extinguishing Powders and Evaluation of their Efficiency

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Selection of local mineral raw materials for production of new type, environmentally safe, highly effective fire-extinguishing powders are discussed in the paper. As is known, the commonly produced fire-extinguishing powders mostly are halogen containing and cannot satisfy the modern demands, in the first place from the viewpoint of effective, non-toxic and environmentally safe using. Therefore, development of halogen free, non-toxic, environmentally safe fire-extinguishing powders is currently a very important problem. Local mineral raw materials – zeolite, clay shale, perlite, dolomite, barite-calcite and ammophos are taken as the basis for receiving such powders. Raw materials were selected according to their high performance properties and due to the factors indicating the reduction of combustion processes, which can be predicted using the results of chemical and thermal gravimetric analysis. Such raw materials mainly contain alkali and alkaline-earth metal carbonates, bicarbonates, oxalates, silicates, Fe, Al and alkali metal hydroxides, crystallization water. At their Intensive heating incombustible gases, water steam and metal oxides are separated. Incombustible gases and water steam in flame zone are functioning as phlegmatizer and in surface zone are causing the formation of swelled layer. Protective films of metal oxides, swelled and coked layer cause a strong "fire-limiting" effect. This indicates the fact that they are characterized by high inhibition properties. It is stated, that zeolites in composite powders can act as efficient hydrophobizing agents. It allows to create a wide range of zeolite-containing fire-extinguishing powders on the basis of local mineral raw materials. *© 2020 Bull. Georg. Natl. Acad. Sci.*

Halogen free; non-toxic; highly effective; fire-extinguishing powder; inhibition properties

Traditionally fire-extinguishing means (CO_2, water and foam), are not universal, neither environmentally safe and less efficient [1-3]. Nowadays, fire-extinguishing powders are considered to be the most efficient fire-extinguishing agents due to their universality (they can be used for extinguishing of different class standard fires) and high efficiency. Unlike traditional fire extinguishing means, powders are characterized by homogeneous action of combustion products on flame, as well as

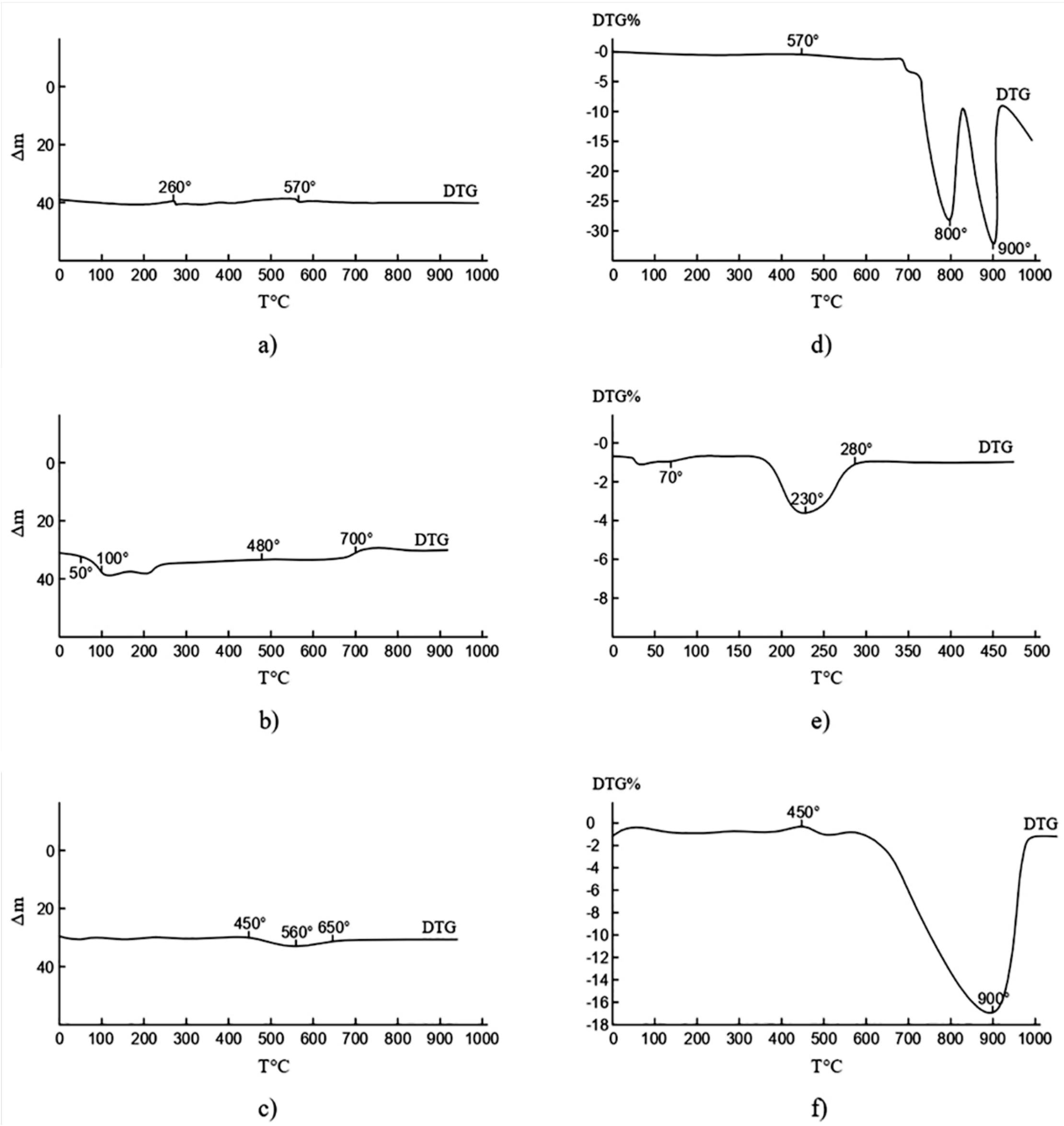

Fig. 1. Derivatogrammes of raw materials: a) Perlite; b) Zeolite (clinoptilolite); c) Clay shell; d) Dolomite; e) Ammophos; f) Barite-calcite.

heterogenic inhibition of burning process. Homogenous effect means heating, evaporation and destruction of powder particles, when there happens emission of incombustible gases and metal oxides performing burning processes inhibition. But it is known that if powder particles dimensions exceed 50 μ then such particles have no time to be heated to ignition temperature, therefore homogeneous mechanism of extinguishing is less effective and heterogeneous mechanism has leading role, which means heterogeneous removal of reaction active centres (atoms and radicals) on the surface of solid particles of the powder [4, 5].

Serial production of fire-extinguishing powders mainly represents fine dispersed mineral salts with different additives. All they are multicomponent heterogeneous systems and their fire-extinguishing capacity (as well as other performance properties) is mainly determined by the chemical composition and powder dispersion degree. It should also be mentioned, that high-dispersive powders are characterized with lower performance properties (mainly, by high caking capacity). In order to improve performance properties of salts (mainly, to decrease the caking capacity) water absorbing additives are used for hydrophobization of powders. As an additives halogen containing, organic origin hydrophobizators are mainly used. Thus, most of them are containing halogen and do not satisfy the modern demands, in the first place from the viewpoint of effective, environmentally safe and universal using. Therefore, at present one of the most important problems is the elaboration of halogen-free, environmentally safe fire-extinguishing powders [6-9].

Considering the above said, the aim of this research is the selection of local mineral raw materials for production of new type, halogen-free, environmentally safe, highly effective and universal fire-extinguishing powders.

Materials and methods. The local mineral raw materials – zeolite (Clinoptilolite, a deposit in the Caspian region), clay shale (deposit in the Duruji Gorge), perlite (Paravani deposit), dolomite (Kareli district deposit), barite-calcite (barite ore in the Chordy) and ammophose are taken as the basis for receiving such powders. Such raw materials are selected according to their high performance properties and due to the factors indicating the reduction of burning processes, based on chemical and thermal gravimetric analysis. The thermal gravimetric measurements were performed using a derivatograph of Paulic, Paulic & Erdey (Hungary). Measurements were carried out in the temperature range 20÷1000°C, at a heating rate -10°C/min. Experimental data is given in Fig.1. In order to study performance properties of powders: powder dispersity, specific surface areas, tendency to

Table. Performance properties

Materials	Powder dispersity range, X (mm)	Specific surface areas, S (cm^2 /kg)	Powder fluidity, Q (kg /s)	Capacity of moisture absorption W%	Tendency to consolidation and caking, C%
Clay shale	# 0.1 # 0.1-0.2 # 0.2-0.3	7270 5530 5100	- 0.19 0.18	1.2 0.2 0.18	50 7.5 1.2
Zeoloite (Clinoptilolite)	# 0.1 # 0.1-0.2 # 0.2-0.25	5530 4640 4280	- 0.17 0.17	4.6 4.2 3.6	20 0.6 0
Perlite	# 0.1 # 0.1-0.2 # 0.2-0.25	2540 1295 1093	- 0.14 0.14	0.8 0.7 0.7	18 0.1 0
Dolomite	# 0.1 # 0.1-0.2 # 0.2-0.25	6440 5384 4550	- 0.18 0.17	1.4 0.9 0.7	30 6.5 1.0
Ammophos	# 0.1 # 0.1-0.2 # 0.2-0.25	5240 4195 3852	- 0.21 0.22	10.8 9.7 8.8	60 8.2 2.4
Barite-calcite	# 0.1 # 0.1-0.2 # 0.2-0.25	6650 5580 4850	- 0.17 0.18	1.3 1.1 0.9	25 6.1 0.8
Zeolite + Clay shale + Perlite + Dolomite + Barite-calcite	# 0.2-0.25	-	0.16	0.08	0.016
Zeolite + Clay shale + Perlite + Dolomite + Barite-calcite + Amophos	# 0.2-0.25	-	0.19	0.12	0.07

consolidation and caking, capacity of moisture absorption and powder fluidity laboratory standard methods are used (Normative Documents, NPB 170-98* General purpose fire extinguishing powders. General technical requirements. Test methods. 1998, Russia). Experimental results of performance factors of raw materials and composite powders are given in Table 1.

Results and Discussion. On the basis of thermal gravimetric analysis of zeolites, perlites, clay shales, dolomites, barite-calcites and ammophos it is stated that their destruction goes on by stages. Zeolite and ammophos destruction begin at considerably low temperature (50÷70°C) than that of clay shales, perlites, dolomites and barite-calcites (250÷450°C). Peak profile on DTG curve indicates, that the mass loss for zeolite in temperature range of 50÷480°C is 11-15% and for ammophos in temperature range of 70÷280°C is 12-17%. It is supposed that at first adsorbtion water is separated and water containing silicates are dehydrated, then crystallization water, hydroxyl groups, nitric and phosphoric oxides are removed, which results in material amorphization. In temperature interval of 480÷700°C zeolites are somehow stable, do not undergo structural changes, which is proved by the growth of adsorption properties of gases. Therefore, in this interval mass loss is gradually decreased, while above 700°C the mass begins to increase because of gases adsorption. At this stage simultaneous decomposition and oxidation process takes place. Presumably there happens decomposition of hydrocarbonates and hydroxides and further oxidation of oxides received by decomposition and burning out of admixtures. For clay shales, perlites, dolomites and barite-calcites the loss of adsorbed water is not noticed. Their destruction begins at relatively high temperature – 250÷450°C. At the first stage the mass losses are insignificant, which supposedly correspond to crystallization water separation and decarbonization. In the temperature interval of 450÷800°C the mass loss increases (12÷32%) and more than 800°C such raw materials are somehow stable. At the same time, it should be noted, that destruction of dolomite and barite-calcite begins at high temperature, but undergoes the process more extensively (mass loss 28-32%) compared to perlites and clay-shales, which is due to their chemical composition.

Proceeding from the above said, at high temperatures above 800°C for zeolites, as well as, for clay shales, perlites, dolomites, barite-calcites and ammophos is characteristic the creation of protective film of metal oxides and coke layer on material surface. At this time the material begins to soften, the closed pores are formed near the surface, which prevent the separation of gases and material begins to rise. Thus, separation incombustible gases and water steam in flame zone act as phlegmatizers while in surface zone they cause the formation of risen layer. The risen layer, metal oxides protective film and coke layer create the “fire restricting” effect. This indicates to the fact, that such raw materials are characterized by high inhibition properties.

The extinguishing powders not only should effectively extinguish fire, but they should maintain their performance properties. The least desirable performance property is caking capacity, which complicates and conclusively cancels the extinguishing ability of the powder. Experimental results of performance factors of raw materials and composite powders show that zeolites are characterized by low tendency to consolidation and caking but high capacity of moisture absorption, which considerably decreases at admixture of clay shales, dolomites perlites, and barite-calcites. Thus, zeolite-containing composite powders are characterized by both low capacity of moisture absorption and caking capacity. Proceeding from the above said, that such composite powders are characterized by higher performance properties than these raw materials utilized separately. At the same time it has been established that introduction a small amount of ammophos (which are hygro-scopic, but characterized by inhibition effect of burning products) in zeolite-containing composite powders do not cause significant changes in performance properties, but considerably increase inhibition effect. All this indicates that zeolites in composite powders can act as efficient hydrophobizing agents and zeolite-containing composite powders do not require the addition with expensive halogen-inclusive hydrophobizators. It allows to create a wide range of zeolite-containing fire-extinguishing powders on the basis of local mineral raw materials. It should also be mentioned, that performance properties of powder depend on their dispersity. Caking capacity of high dispersive powders sharply increases with the increase of dispersity, while the caking capacity of low dispersive powders insignificantly changes with changing dispersity, and when powder dispersity is within – 200-250 μm the caking capacity drops to zero. Therefore, for the increase of efficiency of powder, optimal dispersity (up to 250 μ) we selected in such way that caking capacity to be minimal, powder feed be convenient (high-disperse powder direct feeding into ignition place creates many problems) and a homogeneous action of combustion products on the flame as well as a heterogeneous inhibition of combustion process take place.

Conclusion. Raw materials: zeolite, clay shale, perlite, dolomite, barite-calcite and ammophose are characterized by high performance as well as high inhibition properties. At their destruction at high temperatures the emission of asphyxiating gases and toxic matters does not happen. Thus, they can be effectively used for production of new type, halogen-free, environmentally safe and inexpensive fire-extinguishing powders.

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მინერალური ნედლეული ახალი ტიპის, ეკოლოგიურად უსაფრთხო ცეცხლმაქრი ფხვნილების დასამზადებლად და მათი ეფექტურობის შეფასება

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ნაშრომში აღწერილია მინერალური ნედლეული (ცეოლითი, თიხა-ფიქალი, პერლიტი, დოლომიტი, ბარიტ-კალციტი და ამოფოსი), რომელთა საფუძველზე შესაძლებელია ახალი ტიპის, ეკოლოგიურად უსაფრთხო ცეცხლმაქრი ფხვნილების დამზადება. ნედლეული შერჩეულია მათი მაღალი ექსპლოატაციური თვისებების შესაბამისად და იმ ფაქტორების გათვალისწინებით, რომლებიც მიუთითებენ წვის პროცესების შემცირებაზე. ამის საშუალებას იძლევა მათი მინერალოგიური შედგენილობა და თერმოგრავიმეტრიული ანალიზი. დადგენილია, რომ აღნიშნული ნედლეული არის სილიკატური წარმოშობის, უჰალოგენო და ეკოლოგიურად უსაფრთხო. მათი დესტრუქციისას ადგილი არა აქვს ტოქსიკური ნივთიერებებისა და მხუთავი აირების გამოყოფას. დესტრუქციისას ძირითადად გამოიყოფა უწვადი გაზები, წყლის ორთქლი და მეტალთა ოქსიდები. ეს კი ხელს უწყობს წვის პროცესების ინჰიბირებას ალის ზონაში და აფერხებს ალის გავრცელებას ზედაპირულ ზონაში, რაც იმაზე მიუთითებს, რომ ისინი ხასიათდებიან მაღალი ინჰიბიტორული თვისებებით. ამიტომ შესაძლებელია მათი გამოყენება ეკოლოგიურად უსაფრთხო ცეცხლმაქრი ფხვნილების დასამზადებლად.

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