Physical Chemistry

New Types of Halogen-Free, Eco-Safe Fire-Extinguishing Composite Powders and Evaluation of Their Efficiency

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ABSTRACT. Elaboration of new types of halogen-free, eco-safe, inexpensive, highly effective fire-extinguishing composite powders and evaluation of their efficiency are discussed in the article. Such powders will be made by mechanical blending of local mineral raw materials, which do not require modification with expensive, halogen-containing hydrofobizative additives. The optimal dispersity were selected so, that caking capacity to be minimal and homogeneous action of combustion products on the flame as well as a heterogeneous inhibition of combustion process to take place. Powder efficiency was evaluated with consideration of both effects. The technology for the production of obtained fire-extinguishing powders differs from the serial production technology. Such powders, will be made by mechanical blending of local mineral raw materials: zeolites, perlites and clay shales, which does not require additional chemical processing and modification with expensive, halogen-containing hydrofobizative additives, what makes the extinguishing materials far cheaper than imported analogues. Received fire-extinguishing powders are characterized with high operating characteristics as well as high fire-extinguishing capacity and values of recombination coefficients of atomic oxygen. Thus, they are non-halogen, eco-safe, inexpensive, highly effective and universal. *© 2015 Bull. Georg. Natl. Acad. Sci.*

Key words: *halogen-free, eco-safe, high efficiency, fire-extinguishing powders.*

At present the most effective fire-extinguishing matters are powder fire extinguishers, which are characterized by high effectiveness and universality. They are most widely used in cases when it is not advisable to use traditional fire-extinguishing matters. Fire-extinguishing powders represent the fine dispersed mineral salts with expensive, halogen containing hydrophobizative additives. Thus, most of them are halogen-containing and do not meet the contemporary demands, first of all with the view of effective, and universal use. Therefore, elaboration of halogen-free, eco-safe fire extinguishing powders is one of the most important problems in the world [1-3].

The aim of the presented investigation is the elaboration of new types of halogen-free, eco-safe, composite fire-extinguishing powders on the basis of local mineral raw materials and evaluation of their efficiency.

The technology for production of these fire-extinguishing powders differs from the serial production technology. Such powders will be made by mechanical blending of local mineral raw materials, which does not require additional chemical processing and modification with expensive, halogen-containing hydrofobizative additives, what makes the extinguishing materials far cheaper than imported analogues.

Raw materials: zeolite, clay shale and perlite were selected according to their high operating properties and due to the factors indicating the reduction of burning processes. As it is well known, such raw materials are mainly of silicate origin and contain alkali and alkaline-earth metal carbonates, bicarbonates, silicates, oxalates, also Fe, Al and alkali metal hydroxides and crystallization water. Therefore, at their intensive heating incombustible gases, water steam and metal oxides are separated. Released incombustible gases and water steam in flame zone are functioning as phlegmatizer and in surface zone cause formation of swallen layer. Protective film of metal oxides, swallen and coke layer create “fire-limiting” effect [4].

The effectiveness of powder depends on their dispersity, inhibition properties and on their operating characteristics as well. The most important operating properties are: the tendency to consolidation and caking, moisture adsorption, powder flow and storage duration. Experimental researches showed, that zeolites are characterized by lower caking ability, but higher moisture capacity compared to perlites and clay shales, while composite powders produced for admixture zeolites, perlites and clay shales are characterized by low moisture capacity as well as caking ability [5]. This indicates that zeolite in composite powders play the role of hydrophobizators. Therefore, we can surmise that introduction of amophos and dolomites, which are hygroscopic but are characterized by high inhibition properties, in zeolite containing composite powders of raw materi-

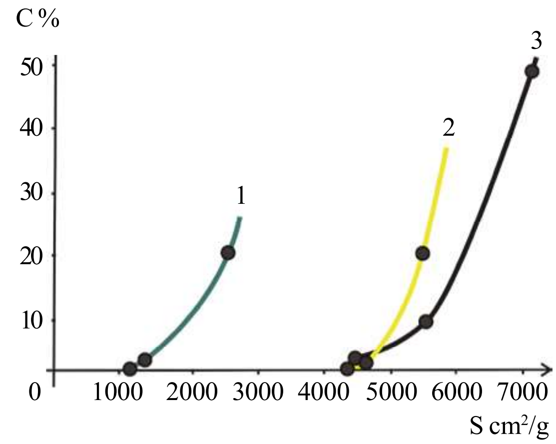

Fig. 1. The relation of powder caking and specific surface areas 1 – Zeoloite, 2 – Perlite, 3 – Clay shale.

als will not cause significant changes of operating characteristics, but will considerably increase fire-extinguishing capacity.

The least desirable operation property is the tendency to consolidation and caking, which complicates and conclusively cancel the fire-extinguishing ability of the powder. The main reason causing consolidation and caking is humidity and medium temperature. The powder absorbs moisture from air, that is to say, solid particles are dissolved in condensate water forming saturated solution of the solid phase. By further increase of humidity the solution becomes supersaturated and at the contact surfaces of supersaturated and saturated particles the crystallization out of solid phase takes place. Formation of phase contacts is possible only in the conditions of new coagulation. An average hardness of elementary contacts of individual particles depends on the hardness of powder structure, which is dependent on particles dispersity, settling and compaction degree. It has been established, that the tendency to consolidation and caking increases with increasing dispersity.

By experimental studies it was established that for different powders even at identical dispersions the specific surface area sharply differs. Because the powder caking is conditioned of solid phase crystallization on the touch surface of the particles, their caking will be significantly different. Considering all this, we determined the specific surface area of the powders

Table 1. Operating properties of raw materials

	Materials	Powder dispersity, S (μ)	Specific surface areas, S (cm^2/kg)	Powder fluidity,Q (kg/s)	Moisture content and tendency to humidity, W%	Tendency to consolidation and caking, C%
1	Clay shale	# 0.1 # 0.1-0.2 # 0.2-0.3	7270 5530 5100	_ 0.17 0.17	0.17 0.18 1.2	50 7.5 2.0
2	Zeoloite	# 0.1 # 0.1-0.2 # 0.2-0.3	5530 4640 4280	_ 0.16 0.16	3.6 4.6 4.6	20 0.6 0
3	Perlite	# 0.1 # 0.1-0.2 # 0.2-0.3	2540 1295 1093	_ 0.14 0.14	0.7 0.7 0.8	18 0.1 0

with different dispersity and established the dependence of powder caking on specific surface area (Tab. 1 and Fig. 1). In order to define specific surface area air-penetrating method device ADP -3 is used. The analysis of experimental data shows that the caking capacity of high-dispersive powders sharply increases with increasing dispersity, while the caking capacity of lower-dispersive powders insignificantly changes with changing dispersity. For example, when powder dispersity < 100 μ the caking capasity is 30–40%; when dispersity is within 100–200 μ caking capacity rapidly decreases to 0.2 – 0.4% and when dispersity - 200–300 caking capacity drops to 0%.

Proceeding from it, optimal dispersity (to 200 μ) was selected in such a way that caking capacity to be minimal, powder feed to be convenient and particle measures to be suitable for their rapid heating and destruction, that is to say, a homogeneous action of combustion products on the flame as well as a heterogeneous inhibition of combustion process must take place. Homogenous effect means heating, evaporation and destruction of powder particles, when there happens emission of incombustible gases and metal oxides inhibit the burning processes. 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 centers on the surface of solid particles of the powder. At the same time it should be mentioned that by heterogeneous mechanism powder fire-extinguishing capacity is estimated not by mass consumption of powder in volume unit (*G*), but by the area of powder particles total surface in unit volume, or by „surface" concentration (*Cn•S*), which can be determined by product of mass concentration on powder specific surface area [4]. So, for the complex evaluation of extinguishing effect special characteristics were selected:

- Reciprocal value of extinguish "surface" concentration - 1/Cn·S

- Coefficient of atomic oxygen recombination - γ_0

The coefficient of atomic oxygen recombination (γ_0) was determined by Electro Paramagnetic Resonance (EPR) methods. In order to determine fire-ex-

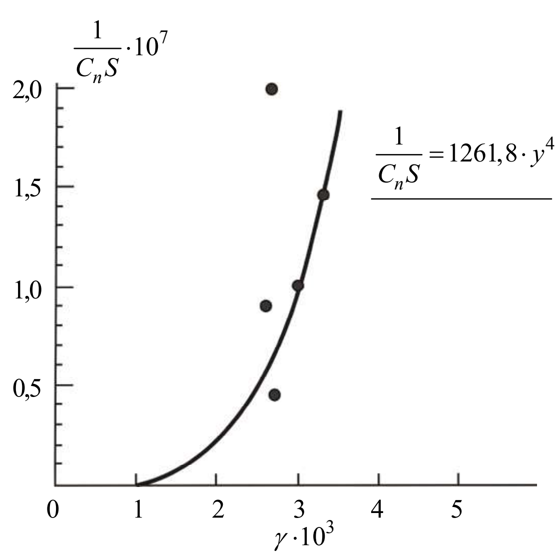

Fig. 2. The relation of fire-extinguishing capacity and recombination coefficient of atomic oxygen.

Table 2. Fire-extinguishing ability

	Material	Class of fire	Time of fire-extinguishing, t_{cr} (sec)	Minimum consumption per unit area, G (kg/m^2)	Minimum mass concentration, Cn (kg/m^3)	Powder special surface area, S (sm^2/kg)	1/Cn·S	Coefficient of atomic oxygen recombination, γ_0
1	Clay shale	A	18	4.1	8.2	$4.5\cdot10^6$	$0.027\cdot10^{-6}$	$6.5\cdot10^{-3}$
		B	12		7			
2	Zeolite	A	15	2.6	5.2	$4.28\cdot10^6$	$0.045\cdot10^{-6}$	$2.7\cdot10^{-3}$
		B	8		4.8			
3	Perlite	A	12	2.2	4.4	$1.09\cdot10^6$	$0.20\cdot10^{-6}$	$2.6\cdot10^{-3}$
		B	8	2.0	4.0			
4	Zeolite + Clay shale + Perlite	A	10	1.8	3.6	$1.9\cdot10^6$	$0.146\cdot10^{-6}$	$3.3\cdot10^{-3}$
		B	7		2.0			
5	Zeolite + Clay shale + Perlite + Amophos	A	6	1.1	2.2	$4.5\cdot10^6$	$0.1\cdot10^{-6}$	$3.0\cdot10^{-3}$
		B	5		1.1			
6	Zeolite + Clay shale + Perlite + Dolomite	A	8	1.4	2.8	$3.9\cdot10^6$	$0.09\cdot10^{-6}$	$2.6\cdot10^{-3}$
		B	6		1.3			
7	Standard powder	A	7	1.5	2.5	$4.1\cdot10^6$	$0.1\cdot10^{-6}$	$2.5\cdot10^{-3}$
		B	6		1.3			

tinguishing ability the polygon testing methods are used, which consider extinguishing of different class standard fires with the help of fire extinguishing constructions [6]. The results of experimental researches are given in Table 2 and Fig. 1.

The analysis of experimental data shows that between fire-extinguishing capacity (1/Cn·S) of the received powders and recombination coefficient of atomic oxygen (γ_0) there is symbatic relation (Fig. 2). The growth of γ_0 rapidly increases the fire-extinguishing ability. The mentioned relation can be expressed with the following equation:

$$1/\mathrm{Cn}\,S = 1262.8\,g$$

The deviation from the average value is detected for some of them. For ezxample: γ_0 value for perlites ($2.6\cdot10^{-3}$) is close to zeolites ($2.7\cdot10^{-3}$), while perlite fire-extinguishing ability ($0.20\cdot10^{-6}$) exceeds that of zeolites ($0.20\cdot10^{-6}$), which in our opinion, is caused by the fact that perlites at high temperature are characterized by blowing-up of particles and with additional homogeneous effect of powder fine particles on the flame. The positive correlation shows the priority of heterogeneous mechanism in fire-extinguishing action. While significant deviation notices for clay shales. Particularly high value of γ_0, which 2.0-2.5 times exceeds the values of recombination coefficient of zeolites and perlites corresponds to low value of fire-extinguishing capacity. This is basically conditioned with high specific weight, high dispersion and specific surface area of clay shales, which results in the increase of powder mass consumption and surface concentration. Hence, recombination coefficient of powder received with introduction of clay shales in zeolite and perlite composite powders are somehow increased, while fire-extinguishing capacity (1/Cn·S) changes insignificantly or approaches the values of fire-extinguishing capacity of zeolites and perlites.

All the above said suggests that composite fire-extinguishing powders based on zeolites, perlites and clay shales are characterized with high fire-extinguishing capacity and values of recombination coefficients of atomic oxygen. Thus, such composite powders are characterized by high fire-extinguishing effect.

It should be noted, that the efficiency of the received powders isn't less than the standard powders of serial production, but unlike them they are non-halogen, eco-safe and inexpensive (1.2-2 times cheaper).

ფიზიკური ქიმია

ახლი ტიპის, უჰალოგენო, ეკოლოგიურად უსაფრთხო ცეცხლმაქრი ფხვნილების დამზადება და მათი ეფექტურობის შეფასება

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(წარმოდგენილია აკადემიის წევრის შ. სამსონიას მიერ)

ნაშრომში აღწერილია ახალი ტიპის, უჰალოგენო, ეკოლოგიურად უსაფრთხო, იაფი და მაღალეფექტური ცეცხლმაქრი ფხვნილების დამზადებისა და მათი ეფექტურობის შეფასების გზები. ფხვნილები მზადდება მინერალური ნედლეულის მექანიკური შერევით და არ საჭიროებს ძვირადღირებული, ჰალოგენშემცველი ჰიდროფობიზატორების დამატებას, რის გამოც მიღებული ფხვნილები გაცილებით იაფია იმპორტულ ანალოგებთან შედარებით. მინერალური ნედლეული: თიხაფიქალი, ცეოლიტი, პერლიტი შერჩეულია მათი მაღალი ექსპლოატაციური თვისებების შესაბამისად და იმ ფაქტორების გათვალისწინებით, რომლებიც მიუთითებენ წვის პროცესების შემცირებაზე. ოპტიმალური დისპერსულობა (200 მკმ-მდე) შერჩეულია ისე, რომ ფხვნილის კოშტვადობა იყოს მინიმალური, და ამავე დროს ადგილი ჰქონდეს როგორც წვის პროდუქტების ალზე ჰომოგენურ ზემოქმედებას ასევე წვის პროცესის ჰეტეროგენულ ინჰიბირებას. აქედან გამომდინარე, ორივე ეფექტის გათვალისწინებით, ცეცხლმაქრი ფხვნილების ეფექტურობის შეფასებისათვის შერჩეულია მახასიათებლები: ქრობის "ზედაპირული" კონცენტრაციის შებრუნებული სიდიდე — $1/CnS$ და ატომური ჟანგბადის რეკომბინაციის კოეფიციენტი — γ_0. შესწავლილია ამ მახასიათებლებს შორის დამოკიდებულება, რომლის საფუძველზეც მიღებული ფხვნილებისათვის დადგენილია ქრობის მექანიზმი.

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