Refractories and Industrial Ceramics *Vol. 45, No. 3, 2004*

UDC 666. 764.3:666.3.022.66

DISPERSING (DEFLOCCULATING) ALUMINAS

Yu. E. Pivinskii,[1] **Pav. V. Dyakin,**[1] **and P. V. Dyakin**[1]

Translated from Novye Ogneupory, No. 3, pp. 29 – 38, March, 2004.

The rheological properties of aqueous suspensions of a reactive alumina and high-alumina cements have been studied, and a method for evaluating the thinning effect due to agents used to deflocculate ceramic casting systems has been developed; a classification of thinning agents is proposed. Alumina dispersants make it possible to decrease the moisture content of Al_2O_3 suspensions by 50 – 60 rel.% and increase their volume concentration from 0.50 to 0.65. The characteristics of dispersing aluminas used for the thinning (deflocculation) of new refractory castables containing Al_2O_3 (76 – 96%) and organic deflocculants are given. Suspensions based on four types of dispersants (with a moisture content of 19 – 25%) exhibiting a thixotropic flow behavior are considered.

1. GENERAL CHARACTERIZATION AND RHEOLOGICAL PROPERTIES OF SUSPENSIONS BASED ON DISPERSING ALUMINAS

Superior rheotechnological properties and minimum water content — these two conditions have been and continue to be a major challenge for the production technology of a new generation of refractory materials — zero-cement ceramic castables and low- and ultralow-cement shotcrete castables. As is known, the porosity and physicomechanical properties and, correspondingly, performance characteristics of castables are directly related to the moisture content (water demand) of the molding mixture [1 – 3]. In past years, much effort has been devoted to the development and selection of thinning (deflocculating), plasticizing, or stabilizing agents, which assured the required fluidity of concrete mixes at a minimum content of the dispersion medium (water) under controlled setting and hardening conditions [1 – 10].

Characterization of precursor materials. There has been much interest in the so-called dispersing aluminas developed by, and available from, Alcoa World Chemicals Co. [1, 11, 12]. The specific features and thinning efficiency of dispersing alumina are as follows. The traditional thinning and dispersing additives for low-cement castables contained chemicals in small amounts — phosphates (hexametaphosphate, tripolyphosphate), citric acid, sodium citrate, and organic additives. They were added, as a rule, in amounts not exceeding 0.2%, which posed problems with their uniform distribution in dry concrete mixes.

Dispersing alumina is a highly-disperse reactive alumina containing organic components — thinning additives. These additives account for 10 – 20 wt.%. Therefore the total of them in the concrete mix is about 1%. Thus, the dispersing alumina plays the role of a carrier of organic thinning agents. Using dispersing alumina increases the total additive mass by a factor of 5 – 10, which allows its more uniform distribution over the concrete mix. Dispersing alumina contains also additives that serve to control the hardening rate (decelerating or accelerating). The dispersants are prepared by grinding dry mixtures of reactive alumina and additives (organic components, B_2O_3, etc.). Most refractory castables are compositionally based on corundum or Al_2O_3, and the high-disperse alumina is a component of their matrix system. Thus, the dispersing aluminas are complex organomineral additives that are used to control the rheological and technological properties of the percursor molding mixtures; to some extent, they affect the properties of the end product.

In [13], effects due to an alumina-based dispersing additive (0.4% ADS 3 + 0.6% ADS 1) and traditional additive (0.05% phosphate + 0.03% citric acid) were compared. With the complex dispersant added to low-cement corundum castables containing 6% high-alumina cement (SA-14S grade), the moisture content of the molding mixture could be reduced from 5.5% to 4.6% (that is, by 16 rel.%). This notwithstanding, vibratory spreadability of the castable was observed to increase. The compressive strength of the castable held for 24 h at 20°C increased from 8 to 31 MPa.

Five types of dispersing alumina are commercially available from Alcoa Co. [12, 14]; relevant characteristics are given in Table 1. ADS 1 and ADS 3 dispersants are used to thin out microsilica-free corundum castables and to retard

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[1] Kerambet R&D Joint-Stock Co., Belgorod, Russia; St. Petersburg State Technological Institute (Technical University), St. Petersburg, Russia.

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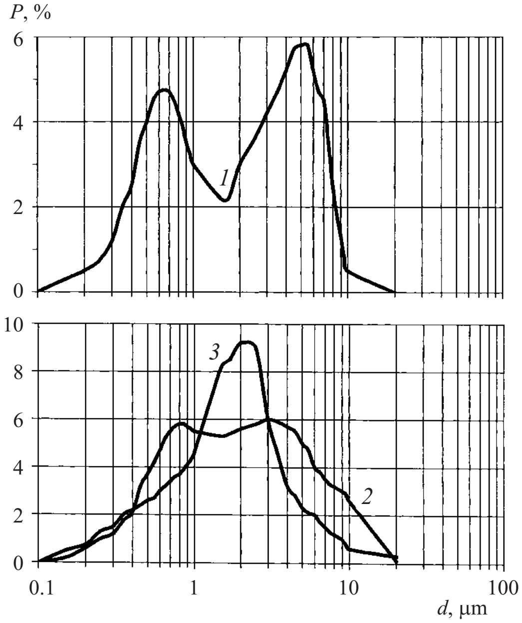

Fig. 1. Differential particle size distribution curves for dispersing (*1*) and reactive aluminas of grade CTC-30 (*2*) and CTC-20 (*3*).

their hardening. ADW 1 dispersant is used to accelerate hardening. In castables containing microsilica, M-ADS 1 and M-ADW 1 are used to retard or accelerate hardening, respectively. The data in Table 1 show that the dispersing aluminas differ in composition: Al_2O_3 from 76 to 96%, Na_2O from 0.1 to 1.4%, B_2O_3 from 0.03 to 2.8%, and CaO from 0.02 to 1.8%. The dispersants (Table 1) differ also in calcination loss Δm_{calc} that characterizes the content of organics in them. The differential grain distribution curves for the dispersants are shown in Fig. 1.

The differential curves in Fig. 1 show that the precursor powders are characterized by a bimodal particle distribution. Here the first peak corresponds to particles of diameter 0.6 μm (d_m), and the second peak — to particles of diameter 5 – 6 μm (d_b). The ratio $d_b/d_m \sim 10$ implies that the packing of particles in the system is sufficiently high. The median diameter d_{50} for all dispersing aluminas is 2.3 μm (Table 1). Evaluated in terms of d_{50} and d_{90}, the dispersants in question are similar to other reactive alumina available from Alcoa Co. (for example, of grade CTC-30 [15]).

TABLE 1. Characterization of Dispersing Alumina*

Characteristic	ADS 1	ADS 3	ADW 1	M-ADS 1	M-ADW 1
Contents, %:					
Al_2O_3	80	76	80	91	96
Na_2O	0.1	0.1	0.1	1.40	0.1
B_2O_3	0.80	2.80	0.03	1.3	0.55
CaO	1.8	1.8	1.8	0.02	0.02
Δm_{calc} at 1050°C, %	18.0	20.0	18.0	7.0	2.7

* Median particle diameter d_{50} and particle diameter d_{90} in all specimens are 2.3 and 7.5 μm, respectively.

In this work, we present results obtained in a study of four dispersing alumina — ADS 3 (hardening retarder), ADW 1 (hardening accelerator), and M-ADS 1 and M-ADW 1. The bulk density for ADS 3 and ADW 1 is 0.9 and 0.8 g/cm^3, respectively. With allowance for the density of dispersants and the amount of organic components contained in them, one may assume that their weight concentration of 18 – 20% corresponds to a 45 – 50% volume concentration.

The dispersants differ in B_2O_3 content — 2.80% for ADS 3 and 0.03% for ADW 1. Correspondingly, their concentrated suspensions prepared using distilled water likewise differ in medium pH: 6 – 6.5 for ADS 3 and 7.5 – 8.0 for ADW 1.

Dispersants M-ADS 1 and M-ADW 1 (recommended for SiO_2-containing castables) were primarily on bauxite HCBS (highly concentrated ceramic binding suspensions) containing additions of highly-disperse quartz glass (HDQG) [1, 2]. These additives have a bulk density of 1.0 – 1.2 g/cm^3 and, judging from the Δm_{calc} value, contain organic components in amounts appreciably smaller than those in ADS 3 and ADW 1. The pH values of aqueous suspensions based on M-ADS 1 and M-ADW 1 were in the range 6.60 – 8.0.

The rheological properties of suspensions containing the dispersants in question and the effect of these on the properties of a number of high-disperse suspensions used in the technology of low-cement refractory castables were also studied. Concrete mixes are usually tested for spreadability by the slump cone method [1]. It is a known fact that the rheological properties of concrete mixes are primarily determined by the structure of their matrix [1, 2 – 5, 7, 8]. For example, a relationship was established between viscosity and yield limit of matrix systems (suspensions) and the spreadability of self-flow zero-cement corundum-based castables [2, 7, 8].

A concept of matrix advantage system (MAS) has been developed by Alcoa Co. [11, 12] that is based on the selection of matrix modular systems using new raw materials. The concept in question consists in optimizing the composition of castables of different type (self-flow, vibration-placed, for gunning purposes). The best binder for these castables was CA-270-grade high-alumina cement (available from Alcoa Co.).[2] According to data from [15, 16], the cement contains 25 – 27% CaO and 71.5 – 73.5% Al_2O_3; the total of Na_2O, SiO_2, and Fe_2O_3 does not exceed 0.75%, which is a factor essential for the high-temperature strength of the castable [2]. The cement's polydispersity characteristics are: $d_{50} = 4 – 7$ μm, and particles larger than 45 μm across account for 10 – 15%. The initial setting time is 310 min and final setting time is 480 min [15, 16].

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[2] Data on this material will be reported elsewhere.

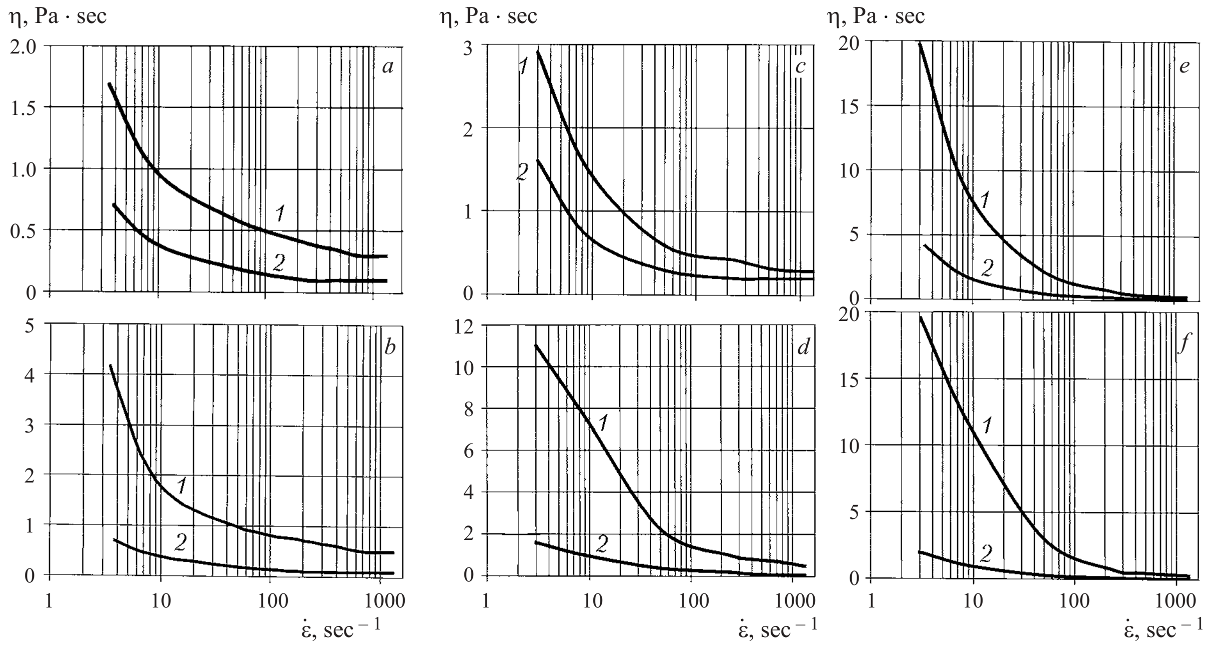

Fig. 2. Effective viscosity η plotted as a function of the shear velocity $\dot{\varepsilon}$ for suspensions based on the dispersing alumina ADS 3 (*a*) at moisture content of 18.8 (*1*) and 22% (*2*); ADW 1 (*b*) at moisture content of 19 (*1*) and 24.3% (*2*); mixture (*c*) ADS 3 (50%) + ADW 1 (50%) at moisture content of 19.4 (*1*) and 25.2% (*2*); M-ADW 1 (*d*) at moisture content of 19.4 (*1*) and 23.4 % (*2*); M-ADS 1 (*e*) at moisture content of 19.4 (*1*) and 25% (*2*); mixture (*f*) M-ADS 1 (50%) + M-ADW 1 (50%) at moisture content of 19.4 (*1*) and 24% (*2*).

The CTC-30-grade[2] reactive alumina has also found wide use in matrix systems [15, 17]. Its typical characteristics are: 99.8% Al_2O_3, 0.09% Na_2O, multimodal particle distribution (see Fig. 1), specific particle surface 3.8 m^2/g, median particle diameter 1.6 μm, and maximum particle diameter 11 μm.

The CTC-30-grade reactive alumina is mainly used for preparation of vibration-placed castables, and the CTC-20-grade alumina[2] (analogous to the former in chemical composition) — for preparation of self-flow castables. The latter alumina has a smaller specific surface (2.1 m^2/g) and a different modal particle distribution (see Fig. 1). The high-efficient refractory castables of corundum-spinel composition have also found wide application [1 – 3, 18]. The matrix system in many castables of this class has a component AR-78-grade magnesium aluminate spinel[2] (available from Alcoa Co.) [15, 19] composed of 22.0 – 23.0% MgO, 0.22 – 0.26% CaO, 76 – 77% Al_2O_3; median particle diameter 3.0 μm, and maximum particle diameter 20 μm.

Rheological properties of dispersant-based suspensions. The rheological properties of precursor dispersant suspensions, high-alumina cements, reactive alumina, and magnesium aluminate spinel (with and without dispersants added) were examined using a Rheotest-2 viscosimeter (Germany). The measurements were mostly carried out with the gap between the coaxial cylinders in the viscosimeter set at a width of 0.38 mm. which made it possible to measure viscosity over a wide range of the relative shear velocity $\dot{\varepsilon}$, from 3 to 1312 sec^{-1}. Knowledge of the rheological properties of dispersing alumina suspensions is important considering that they control the rheological and technological properties of both matrix and molding systems in the production of castables.

Rheological curves showing the dependence of viscosity on shear velocity for suspensions based on ADS 3 dispersants with two moisture contents — 18.8 and 22% — are shown in Fig. 2*a*. The suspensions display a thixotropic flow character. It is seen in curve *1* that as the shear velocity $\dot{\varepsilon}$ increases from 3 to 1000 sec^{-1}, the viscosity η decreases roughly by a factor of 5; a similar relationship is characteristic of the suspension of lower concentration (Fig. 2*a*, curve *2*). The behavior of the suspension based on the ADW 1 dispersant is analogous to the former (Fig. 2*b*). This suspension likewise displays a thixotropic flow character, even more pronounced at comparable values of viscosity η. For example, viscosity η at $\dot{\varepsilon} = 3 - 10\ sec^{-1}$ (Fig. 2*b*, curve *1*) is about twice that for the ADS 3-based suspension at the same moisture content (see Fig. 2*a*, curve *1*).

In practice, binary dispersants have found application in the preparation of low-cement corundum castables [12]. Therefore of help would be a knowledge of the rheological properties not only for suspensions of individual dispersants, but also for their binary mixtures. The relationship η versus $\dot{\varepsilon}$ for a binary system composed of ADS 3 and ADW 1 is shown in Fig. 2*c*. Similar to their parent suspensions, the binary suspensions are characterized by a thixotropic rheology.

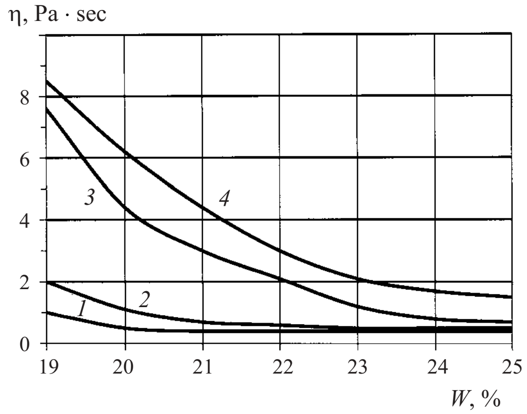

Fig. 3. Effective viscosity η at $\dot{\varepsilon} = 9\ \text{sec}^{-1}$ plotted as a function of moisture content for suspensions based on ADS 3 (*1*), ADW 1 (*2*), M-ADW 1 (*3*), and M-ADS 1 (*4*).

At comparable moisture contents, the viscosity of a binary suspension takes an intermediate position with respect to the viscosity of the parent suspensions. So, at $\dot{\varepsilon} = 9\ \text{sec}^{-1}$ and a moisture content of 19%, the viscosity η for the original suspensions is 1.0 and 1.9 Pa · sec (Fig. 2*a* and *b*), whereas for the binary suspension it is 1.5 Pa · sec (Fig. 2*c*).

As compared to the above suspensions, the viscosity of suspensions based on M-ADS 1 and M-ADW 1 dispersants is appreciably higher at comparable moisture contents. The suspension based on M-ADW 1 with a moisture content of 19.4% and density of 2.59 g/cm^3 show a significant thixotropy (Fig. 2*d*, curve *1*). As the shear velocity $\dot{\varepsilon}$ increases from 3 to 48 sec^{-1}, the viscosity η decreases by a factor greater than 4; at $\dot{\varepsilon} = 1312\ \text{sec}^{-1}$, the decrease is 22-fold. The increase in moisture content to 23.4% (with C_V decreasing from 0.55 to 0.46) at $\dot{\varepsilon} > 80\ \text{sec}^{-1}$ is accompanied by a decrease in η by a factor of 7 – 8 (Fig. 2*d*, curve *2*).

The M-ADS 1-based suspensions at a moisture content comparable with that of the M-ADW 1-based suspensions are characterized by a substantially higher viscosity (Fig. 2*e*). The underlying factor is as follows. The dispersants in question differ in organics content, which is seen from their values of Δm_{calc} (7.0% for M-ADS 1 and 2.7% for M-ADW 1). Therefore the solid-phase densities and, correspondingly, the volume concentrations of suspensions at the same moisture content were quite different. Furthermore, a significant air entrapment occurred in the M-ADS 1 at a moisture content of 19.4% (Fig. 2*e*), which might lead to an increase in viscosity [2]. This suspension exhibited high values of η (up to 19 Pa · sec) in the region of small values of $\dot{\varepsilon}$. The viscosity of the disturbed thixotropic structure (at $\dot{\varepsilon} = 1312\ \text{sec}^{-1}$) as compared with η at $\dot{\varepsilon} = 3\ \text{sec}^{-1}$ decreases by a factor of 100. The increase in moisture content to 25% is accompanied by a decrease in viscosity under retained thixotropic flow conditions.

It follows from Fig. 2*f* that high thixotropy is likewise characteristic of the mixed suspension (50% M-ADW 1 + 50% M-ADS 1). The viscosity of this mixture at a moisture content of 19.4% is the same as that of the suspension M-ADS 1 (Fig. 2*e* and *f*, curve *1*).

The viscosities for all the suspensions studied at $\dot{\varepsilon} = 9\ \text{sec}^{-1}$ are plotted in Fig. 3. In order of increasing viscosity, the suspensions are arranged as ADS 3 → ADW 1 → M-ADW 1 → M-ADS 1. A rheological analysis shows that the maximum possible concentration for suspensions ($C_V = 0.55 – 0.60$, $W = 17 – 19\%$) lies within a concentration range typical of amorphous HCBS [2]; the suspensions retain thixotropic flow characteristics.

2. THINNING EFFECT AND A METHOD FOR ITS EVALUATION

The thinning (deflocculation) of suspensions and various casting systems is an operation rather frequently used in the technology of ceramics and refractories. However, until the present no general method for evaluating the efficiency of this process has been proposed. In analogy with the classification adopted in the technology of structural concretes [21, 22], it would be advisable to work out a similar classification for thinning agents (deflocculants) to be able to evaluate their efficiency for ceramic casting systems.

Methods for evaluating the thinning effect and classification of additives. In conformance with State Standard GOST 24211–80 “Additives for concretes. Classification,” in the technology of structural concretes the additives that are used to plasticize (thin out) concrete mixes are classified into superplasticizers and plasticizers. Two methods are used to evaluate the plasticizing (thinning) effect. In one method, the slump of a standard cone (300 mm height) of concrete mix is determined. This method is used to determine the flowability, that is, the ability of a concrete mix to spread under the pull of gravity. Additives that make it possible to achieve a cone slump ≥ 20 cm are classified as category *I* superplasticizers. For plasticizers of categories *II* – *IV*, the rated cone slump is 14 – 19, 9 – 13, and ≤ 8 cm, respectively (see Fig. 4). This method is used to compare concrete mixes with the same (constant) original moisture content. The consistency evaluated in terms of the cone slump by this method is a variable parameter.

In the other (second) method, the moisture contents of concrete mixes of similar flowability (viscosity) are compared; here the variable factor is optimum working (technological) moisture content which is controlled by the plasticizer added. Plasticizers are classified in terms of the decremental amount of water ΔW_{rel} (%) needed to reach an equal flowability of concrete mixes. For superplasticizers of category *I*, the value of ΔW_{rel} should be not less than 20%; for plasticizers of categories *II*, *III*, and *IV*, it is ≥ 10, ≥ 5, and < 5%, respectively. The generalized data presented in Fig. 4 show the efficiency of plasticizers of different categories — the higher the value of ΔW_{rel}, the higher the cone slump.

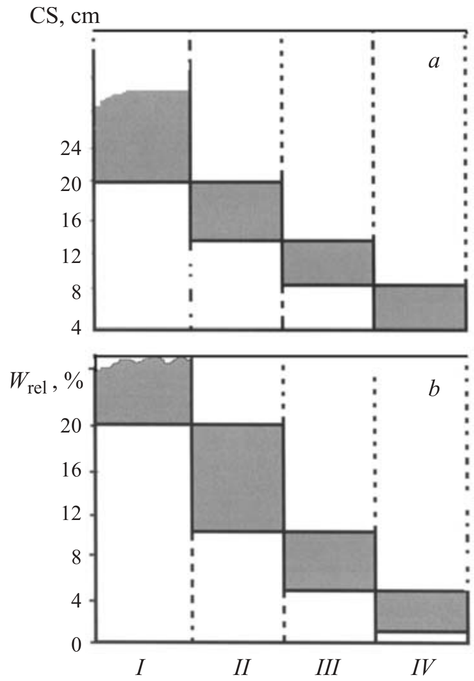

Fig. 4. Schematic diagram showing the cone slump height (CS) (*a*) and relative moisture decrement ΔW_{rel} (*b*) for superplasticizers of category *I* and plasticizers of categories *II* – *IV* in concrete mixes of similar flowability.

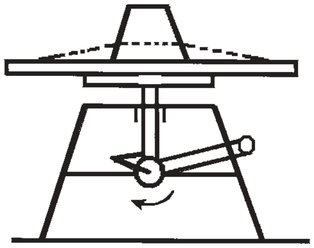

Fig. 5. Schematic diagram of a shaking table for the slump cone test.

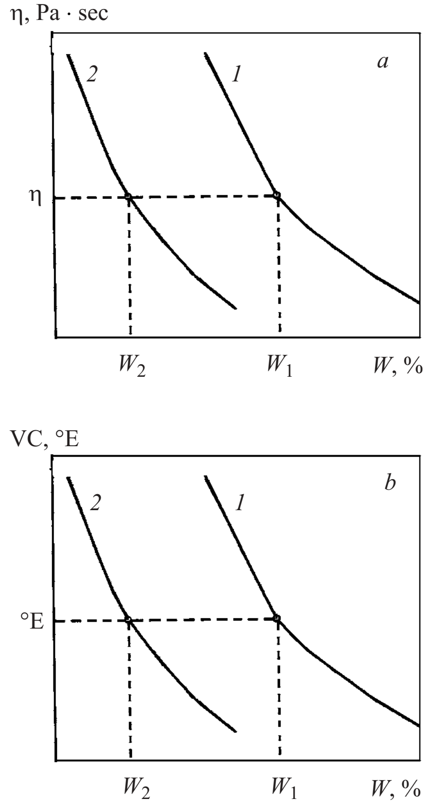

Fig. 6. Schematic diagrams illustrating the effective viscosity η (*a*) and conventional viscosity VC (*b*) as a function of the moisture content *W* for suspension in the intact (*1*) and deflocculated state (*2*).

To test cements (or structural concretes) for mortar consistency, a method is used in which the slump cone in placed on a shaking table (Fig. 5). A similar method using a truncated cone of height 40 mm, bottom diameter 70 mm, and top diameter 60 mm was employed to test processing properties of self-flow castables of silica and mullite-corundum composition [2]. The flowability (otherwise, spreadability) *P*, %, was determined by the formula

$$P = \frac{d_2 - d_1}{d_1} \times 100,$$

where d_1 and d_2 is the bottom diameter of the cone before and after slumping.

The shaking table method was used to test vibration-molded ceramic castables in the $Al_2O_3 - SiO_2 - SiC - C$ system [1, 2]. Foreign manufacturers use a cone with dimensions of ∅ 100 × ∅ 70 × 80 mm to test self-flow low- and ultralow-cement refractory castables [11]. The capacity of such a cone is typically 1.5 kg of concrete mix. A mix with a spreading diameter of 200 – 250 mm is recognized as fabricable. A phase-rheological method for evaluating the degree of thinning and stabilization of ceramic suspensions has been described [11, 23] by which the rheological properties and porosity of a preform before and after thinning of the suspension are compared.

Now we propose a method for evaluating the efficiency of a thinning agent. By this method, the rheological properties of a suspension [at several specified values of moisture content *W* (or C_V)] are compared in the original state (before a thinning agent was added) and in the deflocculated state (with the thinning agent added). The reological properties are determined using a rotary viscosimeter (to measure an effective viscosity η, Pa · sec) or an efflux viscosimeter (to measure a conventional viscosity VC, °E). Based on results obtained, relationships $\eta = f(W)$ or $VC = f(W)$ are plotted as shown in Fig. 6.

An essential condition here is that moisture content and viscosity for suspensions under study must correlate within a definite range of their respective values. As is known, all concentrated suspensions are non-Newtonian (quasi-viscous) fluids. Their viscosity is controlled by the shear velocity $\dot{\varepsilon}$ or

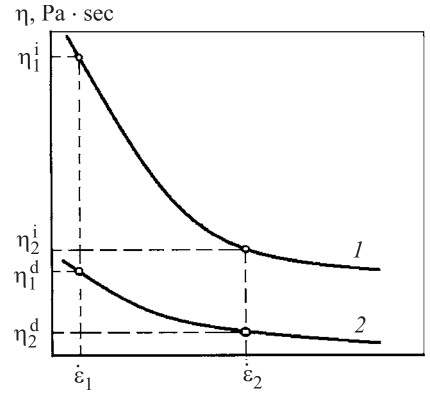

Fig. 7. Schematic diagram illustrating the η versus $\dot{\varepsilon}$ relationship for intact (*1*) and deflocculated suspensions (*2*): η_1^i and η_1^d refer to the viscosity of intact and deflocculated suspensions at $\dot{\varepsilon}_1$; η_2^i and η_2^d — the same for $\dot{\varepsilon}_1 = \dot{\varepsilon}_2$.

shear stress σ; therefore to plot the relationship $\eta = f(W)$, one may take values of η corresponding either to low ($\leq 10\ \text{sec}^{-1}$) or to medium (or even high) values of $\dot{\varepsilon}$. The horizontal dashed lines in Fig. 6*a* and *b* correspond to an isoviscous state of the suspensions in question, and the vertical dashed lines connect the isoviscosity points to the corresponding values of *W*. The efficiency of a thinning agent (deflocculant) is evaluated by the difference ΔW_{rel} of the suspension with the thinner added (curves *2*) and its original state (curves *1*). Thus,

$$\Delta W_{\text{rel}} = \frac{W_1 - W_2}{W_1} \times 100,$$

where W_1 and W_2 is the moisture content of the original and deflocculated suspension at the same viscosity. Obviously, the higher the value of ΔW_{rel}, the higher the efficiency of the thinning agent.

In some cases, the thinning efficiency is better evaluated using the method illustrated in Fig. 7, especially in application to suspensions with a thixotropic flow behavior. By this method, the viscosities of intact (curve *1*) and deflocculated (curve *2*) suspensions are compared at a constant concentration. The degree of thinning can be evaluated using viscosities either for the intact thixotropic structure (η_1 at $\dot{\varepsilon} = \dot{\varepsilon}_1$) or for the disturbed thixotropic structure (η_2 at $\dot{\varepsilon} = \dot{\varepsilon}_2$). A shortcoming of this method is that the required concentration of suspensions is, as a rule, appreciably higher than the concentration of intact suspensions. Therefore if in the former case (see Fig. 6) the concentration increment is evaluated under the conditions of correlated viscosity, in the latter case (see Fig. 7) the viscosity decrement is evaluated at a constant suspension concentration.

The efficiency of deflocculants for concrete mixes can be evaluated using the principle that has been considered above for suspensions (Fig. 8). Here the selected rheological parameter (or consistency index) is flowability which is determined either by the shaking table test method (for vibration-molded castables) or by the standard slump cone test method (for self-flow castables or cast concretes). According to data from [2], optimum molding conditions are reached at a flowability of 80 – 100% (Fig. 8, hatched area). By analogy with suspensions, the value of ΔW_{rel} is determined as the difference $W_1 - W_2$ of the moisture contents at which the required flowability is reached (see Fig. 8). The flowability of vibration-molded concrete mixes can also be studied using the layer leveling method described in [1, p. 345].

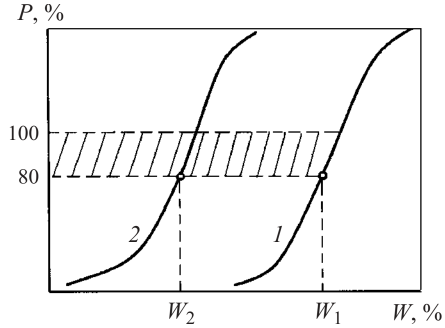

Fig. 8. Schematic diagram showing the flowability *P* of concrete mixes in relation to the moisture content *W* in the intact (*1*) and deflocculated state (*2*): W_1 and W_2 refer to the lower limit of technological flowability for the intact and deflocculated mixes.

Dispersing alumina efficiency. In this work, we used two synthetic materials — CTC-30-grade alumina and Ca-270-grade high-alumina cement (both available from Alcoa Co.) — to study the effect of dispersing alumina on the rheological properties of suspensions.

Deflocculation (thinning) of ceramic suspensions and, correspondingly, concrete mixes is controlled by surface effects that take place at the interface [19]. Under these conditions, the consumption rate of deflocculants (dispersants) is determined by the specific surface of particulate matter [1, 2, 4]. For concrete mixes, the optimum concentration of dispersants is about 1%; for suspensions of high-disperse raw materials (from Alcoa Co.), it is 2 – 3%. This is due to the fact that the specific surface of these materials in concrete mixes accounts for more than 95%, whereas the mass fraction of matrix components does not exceed 35%. It is known [20] that as the volume concentration of a matrix system in a concrete mix varies from 31 to 45%, its specific solid-phase surface S_{sp} changes from 5.81 to 7.36 m^2/cm^3. In particular, for CTC-30 reactive alumina, the specific surface S_{sp} is 15 m^2/cm^3 (3.8 m^2/g). With 3% dispersant added, the actual consumption rate of the thinning agent (its concentration in the dispersing aluminas being 18 – 20%) is 0.54 – 0.6% or, 0.14 – 0.16%, corrected for S_{sp} (m^2/g), or 0.03 – 0.042%, corrected for S_{sp} (m^2/cm^3). These specific concentrations for thinning additives are comparable with, or larger by a factor of 1.52 – 2, than those reported in [1, 2, 4, 11, 20 – 23].

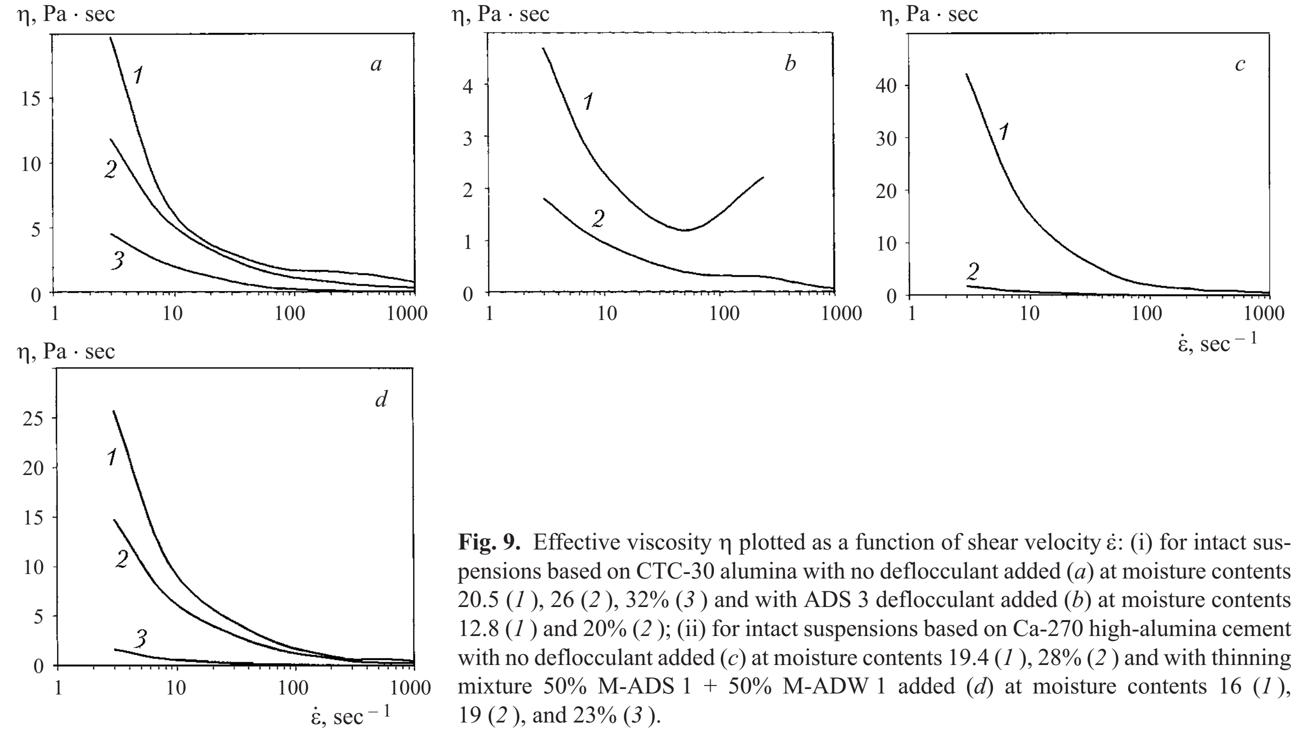

Fig. 9. Effective viscosity η plotted as a function of shear velocity $\dot{\varepsilon}$: (i) for intact suspensions based on CTC-30 alumina with no deflocculant added (*a*) at moisture contents 20.5 (*1*), 26 (*2*), 32% (*3*) and with ADS 3 deflocculant added (*b*) at moisture contents 12.8 (*1*) and 20% (*2*); (ii) for intact suspensions based on Ca-270 high-alumina cement with no deflocculant added (*c*) at moisture contents 19.4 (*1*), 28% (*2*) and with thinning mixture 50% M-ADS 1 + 50% M-ADW 1 added (*d*) at moisture contents 16 (*1*), 19 (*2*), and 23% (*3*).

The rheological behavior of suspensions based on CTC-30 alumina is demonstrated in Fig. 9*a* and *b*. For intact suspensions (with no additives present) with a moisture content of 20.5 – 32%, a thixotropic flow behavior is characteristic; with the optimum amount of ADS 3 dispersant added at a decreased moisture content, thixotropic-dilatant features become apparent (Fig. 9*b*, curve *1*). With $\dot{\varepsilon}$ increasing from 3 to 50 $\sec^{-1}$, the viscosity η tends to decrease (roughly by a factor of 4), a behavior typical of normal thixotropic systems; however, a tendency to increase was noted in the sequel. Under conditions of increased moisture content (Fig. 9*b*, curve *2*), the thixotropic flow behavior was less conspicuous in comparison with the intact suspension (Fig. 9*a*, curve *1*). The viscosity η of deflocculated suspension at low values of $\dot{\varepsilon}$ is smaller by a factor of 8 – 10 as compared to that of the intact suspension. Adding the dispersant causes an increase in C_V from 0.50 to 0.65 (Fig. 9*a* and *b*, curve *1*). It should be noted that for suspensions with high-disperse grain composition the value $C_V = 0.65$ is rather high.

Data for Ca-270 high-alumina cement suspensions are shown in Fig. 9*c* and *d*. Adding a complex thinner causes a sharp decrease in viscosity, and the moisture content from 19.4% (intact suspension) goes down to 16% (deflocculated suspension). All suspensions retain a thixotropic flow regime — a behavior that was observed in HCBS to which actually the systems in question belong [2, 23].

The experimental curves in Fig. 9 were analyzed to reveal effects associated with the addition of dispersing (deflocculating) agents. The effective viscosity η for intact and deflocculated suspensions plotted as a function of the shear velocity $\dot{\varepsilon}$ are shown in Fig. 10. Relevant characteristics are summarized in Table 2. The effect due to the ADS 3 dispersant is extremely high in CTC-30 alumina suspensions. For viscosities of < 10 $\sec^{-1}$ in the thixotropic flow regime, the difference ΔW_{rel} reaches 56 – 60%. The decrease in ΔW_{rel} to 29% at $\dot{\varepsilon} = 243 \sec^{-1}$ (Fig. 10*d*) reveals a dilatancy in the deflocculated suspension. Still, as regards the self-flow vibration-molded castables, of greater importance are characteristics at low (< 10 $\sec^{-1}$) and medium (< 50 $\sec^{-1}$) values of $\dot{\varepsilon}$.

Data for the Ca-270-based suspension (Fig. 10*e* – *h*) show that, with the complex dispersant added, the value of ΔW_{rel} is found in a rather narrow range of 24 – 27% over the

TABLE 2. Characterization of the Efficiency of Dispersing Aluminas

$\dot{\varepsilon}$, $\sec^{-1}$	η, Pa · sec	Suspension W, %		ΔW, %	ΔW_{rel}, %
		intact	deflocculated		
CTC-30 – ADS 3 (Fig. 10a – d)					
3	5	32	12.9	19.1	60
9	2	32	14	18	56
48	1	26	14	12	46
243	1	22.5	16	6.5	29
Ca-270 – (M-ADW 1 + M-ADS 1) (Fig. 10e – h)					
3	20	23	16.8	6.2	27
9	10	22.3	16.2	6.1	27
48	2	23	17.4	5.6	24
243	0.6	22.9	16.6	6.3	27

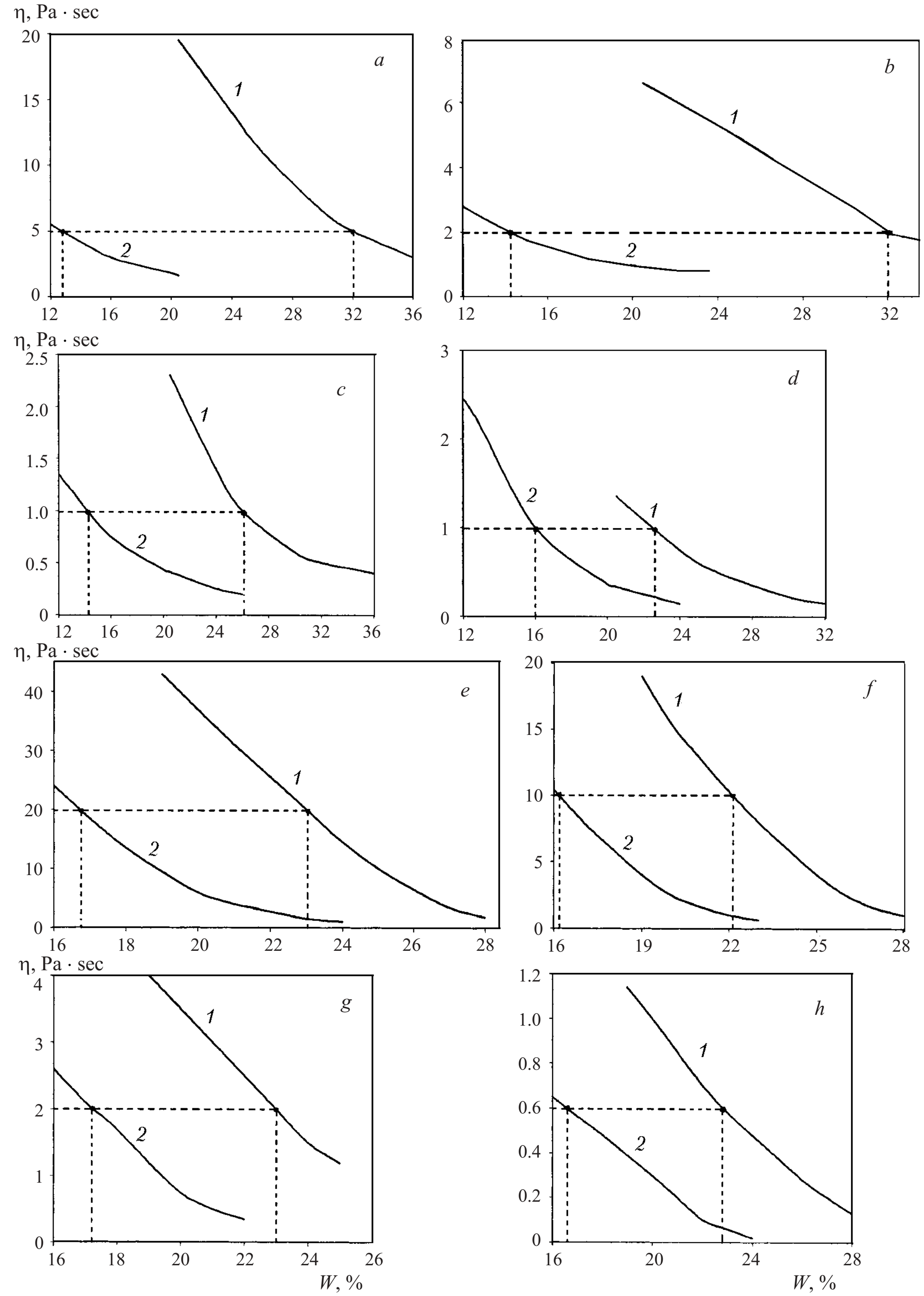

Fig. 10. Effective viscosity η plotted as a function of moisture content *W* for intact (*1*) and deflocculated suspensions (*2*) of CTC-30 reactive alumina (*a* – *d*) and Ca-270 high-alumina cement (*e* – *h*) at $\dot{\varepsilon}$ = 3 (*a*, *e*), 9 (*b*, *f*), 48 (*c*, *g*), and 243 sec^{-1} (*d*, *h*).

entire interval of $\dot{\varepsilon}$ — an effect less conspicuous in comparison to CTC-30 alumina.

Classification of thinning additives (deflocculants). In analogy with the classification of plasticizers in the technology of structural concretes (see Fig. 4), it was thought expedient to work out a classification for thinning agents that are used in the technology of ceramics and refractories. The parameter ΔW_{rel} can be used as the evaluation criterion both for intact and deflocculated systems. In terms of ΔW_{rel}, four classes are proposed for thinning agents:

Class	I	II	III	IV
ΔW_{rel}, %	> 40	20 – 40	10 – 20	< 10

This classification implies that, in terms of ΔW_{rel}, thinners of class II correspond to superplasticizers of category *I* for castables with $\Delta W_{\text{rel}} > 20\%$. No superplasticizers with $\Delta W_{\text{rel}} > 40\%$ have been reported. It may be hypothesized that some additives (of alumina dispersant type) are capable of producing in ceramic suspensions a larger effect than in castables.

It should be noted that thinning agents behave with respect to ceramics and refractories (unlike to castables) in a selective manner, which requires an individual classificatory approach. Because of the different chemical nature of the suspension's solid phase, situations may be envisioned where the same dispersant in some cases is assigned to class I, and in other cases — to class III or IV.

Thus, aqueous suspensions based on dispersing alumina have been characterized and their rheological properties studied. The suspensions with various dispersants added display, in successive stages of their disturbed thixotropic structure, substantially different viscosities at comparable moisture contents. Methods for evaluating the effect due to thinning agents used for the deflocculation of ceramic casting systems have been proposed. A four-rank classification for thinning agents has been proposed. The thinning effect due to alumina dispersants has been tested on suspensions of reactive alumina and high-purity high-alumina cements.

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