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(54) Title: FREE-FLOWING BASIC CASTABLE AND CASTINGS PRODUCED THEREFROM

(57) Abrégé/Abstract:
The invention relates to free-flowing castable and castings produced therefrom. Refractory nonbasic and basic castables have been known for a long time. The traditional refractory castables have thixotropic properties and must be lined using vibration technology. In the past, free-flowing castables were solely based on alumina raw materials. Attempts to produce an aqueous, highly concentrated basic suspension which would form the basis of free-flowing castables failed to meet the requirements in terms of rheological properties and a low degree of hydration of the MgO-based materials. It is the aim of the invention to provide the above-mentioned castable for the monolithic lining or repair of high-temperature equipment and for the production of refractory castings. This is achieved by providing a fine-grained and a mixed fine and coarse-grained alternative. For the fine-grained alternative a refractory, dilatancy-promoting material on MgO basis with a grain size between 0.1 and 45 μm and at least one dilatancy-promoting dispersing and wetting agent is employed with the addition of predetermined amounts of mixing water. For the mixed fine and coarse-grained alternative, again on MgO basis, in addition a refractory material with a grain size of up to 15 mm as well as binding agents are employed. In both alternatives, refractory and other additives improving the quality of the final products can also be employed.

Abstract

The invention relates to free-flowing castable and castings produced therefrom. Refractory nonbasic and basic castables have been known for a long time. The traditional refractory castables have thixotropic properties and must be lined using vibration technology. In the past, free-flowing castables were solely based on alumina raw materials. Attempts to produce an aqueous, highly concentrated basic suspension which would form the basis of free-flowing castables failed to meet the requirements in terms of rheological properties and a low degree of hydration of the MgO-based materials. It is the aim of the invention to provide the above-mentioned castable for the monolithic lining or repair of high-temperature equipment and for the production of refractory castings. This is achieved by providing a fine-grained and a mixed fine and coarse-grained alternative. For the fine-grained alternative a refractory, dilatancy-promoting material on MgO basis with a grain size between 0.1 and 45 μm and at least one dilatancy-promoting dispersing and wetting agent is employed with the addition of predetermined amounts of mixing water. For the mixed fine and coarse-grained alternative, again on MgO basis, in addition a refractory material with a grain size of up to 15 mm as well as binding agents are employed. In both alternatives, refractory and other additives improving the quality of the final products can also be employed.

Free-flowing basic castable and castings produced therefrom

The invention concerns a basic dilatant refractory, free-flowing castable and castings produced therefrom, such as bricks, precast shapes, low-weight refractory products and/or functional products such as perforated bricks, porous plugs, and casings.

Castables are defined as refractory materials introduced or shaped by casting. The appropriate consistency of the slips is achieved by mixing dry components with mixing water or mixing solution.

The castable can solidify by hydraulic setting of the calcium aluminate cements without heating, by chemical bonding or micropowder bonding without and with heating, and by sinter processes at operating temperatures. Examples for chemical bonding are a phosphate bonding, water glass bonding, microsilica bonding, or bonding arising when metal powders are used. Micropowder bonding is chiefly a result of the operation of London-van der Waals attraction forces. Refractory castables exhibiting more than one bonding type at once are advantageous for numerous applications, as they show the desired strength over a wide temperature range.

Refractory castables have been known for a long time. Depending on their chemical composition and on the raw materials used, one distinguishes nonbasic and basic castables. Alumina castables and zircon-containing castables are among the nonbasic ones. Basic raw materials for basic castables are magnesia, magnesiochromite, chromium ore, chromium oxide and spinel, for instance $MgCr_2O_4$. Different metal oxides, metal carbides, metal powders or carbon supports are used as refractory additives.

Traditional refractory castables lined with the aid of vibration technology are thixotropic. Thixotropy implies a decrease in apparent viscosity with the time of load at constant shear velocity or increase in apparent viscosity (thixotropic rigidification) with decreasing shear velocity. Compaction aids such as pneumatic or electrical vibrators must be used for fluidification and compaction of a thixotropic slip, since this slip is half-dry and stiff after mixing with water. An inhomogeneous distribution of coarse and fine grains, or demixing, is obtained when a thixotropic castable is fluidified by an overdose of mixing water, which may be necessary for a lining of narrow cracks and/or complex shapes. An overdose of water will moreover produce a decrease in physical test parameters, such as open porosity and strength. Such monolithic refractory linings have a lower resistance against infiltration and corrosion when used in metallurgical equipment.

Using mechanical compaction aids such as vibrators and/or bottle vibrators has the following disadvantages:

- The compacted castable does not always possess optimum homogeneity, that is, shrinkage cavities may be present;
- Problems when lining narrow cracks and complex shapes, since bottle vibrators have a reduced radius of action;
- physical stress for operators.

A thixotropic castable on the basis of magnesite preferred for the lining of steel foundry ladles is know from EP 0,248,171 B1. The bonding of this slip consists of boric acid, alkali polyphosphates and calcium hydroxide. Vibrators are used in order to achieve sufficient density during lining.

A hydrous, refractory castable on the basis of MgO and having a carbon content between 3 and 10 % by weight, a dispersing agent in an amount between 0.1 and 2.0 % by weight, and a reactive silicic acid in an amount between 1 and 10 % by weight is described in DE 195,18,468 A1. According to this document (see column 2, lines 4 to 7) the silicic acid is decisive for preventing a hydration of the sintered magnesia. This slip, too, which is used for a monolithic lining of metallurgical melting vessels, and preferably of the slag region of foundry ladles, is compacted by vibration technology.

The use of an oxide-type micropowder dispersed in a nonaqueous dispersion medium is known from EP 0,573,029 B1. This fine-grained suspension on the basis of MgO, Al_2O_3, Cr_2O_3 and/or TiO_2 can be used to produce refractory ceramic materials and castings of high density and strength. The risk of hydration of MgO is reduced since nonaqueous solvents are used to prepare the suspension. Tests have shown that the castings can be made by dry pressing from a slip containaing 85 % by weight of coarse-grained matrix material in the grain fraction between 1.0 µm and 3 mm as well as 15 % by weight of a finely divided, previously dispersed MgO micropowder. The raw density and strength of the green compact and of fired castings is distinctly higher than that known in the art. The use of nonaqueous MgO suspensions for the preparation of castables is little appropriate on account of the environmental impacts and of safety risks during the drying and heating of lined equipment.

The use of basic aqueous suspensions having a high concentration of MgO micro-powder could be advantageous for the production of castings, for instance by dry pressing or ramming, if it was possible to prepare such suspensions. However, it would be necessary not to have an excessive degree of hydration of the MgO-based materials in the suspension.

A process for the preparation of magnesia of low hydration is further known from the document EP 0,448,156 A1. However, it is not possible to produce a castable with free-flowing properties by this process, even when hydration is low and a large amount of mixing water is used. In this context the reader is referred to the reference examples cited at the end of the description.

Free-flowing alumina castables are a relatively new development. In contrast to the thixotropic castables, mechanical compaction aids are not needed in order to achieve an appropriate consistency and physical test parameters comparable with those of the thixotropic slips. Free flow is promoted by dilatant properties of the slip. Dilatancy is defined as a decrease in viscosity occurring with decreasing shear velocity, here in the sense of so-called rheological dilatancy.

A nonbasic refractory, hydraulically bonded castable is described in EP 0,525,394 B1. This castable on the basis of alumina raw materials is composed as follows, and exhibits free flow when 3.5 to 7.0 parts by weight of mixing water are added for each 100 parts by weight of solids:

- 65 to 87 % by weight of a refractory matrix material on the basis of Al_2O_3, ZrO_2 and/or Cr_2O_3 with a grain size between 0.1 and 10 mm;
- 7.0 to 22.0 % by weight of a reactive refractory component on the basis of Al_2O_3, ZrO_2 and/or Cr_2O_3 with a grain size between 0.1 and 10 μm:
- 0.5 to 10.0 % by weight of a hydraulic binder with an Al_2O_3 content above 68 % by weight;
- 0.2 to 6.5 % by weight of one or several stabilizing additives and/or additives promoting the water retention of the castable.

Decisive for the desired flow properties of the free-flowing alumina castable are the adjustment of the grain size ranges in the refractory matrix material and the reactive refractory component as well as the adjustment of the mixing water with the additives named.

The fluidity of a free-flowing castable is rated according to the flow value. The flow value Fo is determined immediately after mixing with the mixing water with a vibration-free consistency test, and using the formula:

$$Fo = [(dm,mm - 100mm)/100mm] \times 100, \%$$

where dm is the mean diameter of the sample after a certain time of flow, and 100 mm is the lower diameter of the truncated cone.

The consistency test of the free-flowing castables is performed at present, most often using a truncated cone of ø100 x ø70 x 50 mm and a flow time of 60 sec in accordance with ASTM C-860. The castable is considered free-flowing when the flow value Fo is at least 80 % when determined with the vibration-free consistency test using above truncated cone. A European standard for the consistency testing procedure and evaluation of the flow value for free-flowing castables is still in preparation. It has been proposed that the truncated cone should measure ø100 x ø70 x 80 mm and the flow time should be 120 sec. One must expect that the flow value will be correspondingly larger when using this truncated cone.

A high market acceptability and good practical results are recorded at present with free-flowing, hydraulically bonded castables on the basis of alumina raw materials in several industries. They have found applications, both in all those cases where thixotropic nonbasic castables had already been used in the past, and in the new applications involving high-temperature equipment which are difficult to open up.

From a knowledge of rheological properties of the Al_2O_3 suspensions and from experience with free-flowing alumina castables, so far it had not been possible to provide free-flowing basic castables. Experts evidently have believed up to now that the properties of materials on the basis of magnesia and the rheological requirements constitute essential obstacles for the development of a free-flowing basic castable. This refers to a relatively high demand of mixing water and the hydrating tendency of magnesia-based raw materials. Free flow of a basic castable requires above all an optimum dispersion and distinct dilatancy of the highly concentrated aqueous MgO suspension. The flow behavior of a refractory castable mainly depends on the rheological properties of the suspension developing from the fine-grained components of the slip.

The present invention has the aim of providing a dilatant refractory basic, free-flowing castable on the basis of magnesia and/or chromium ore. Both an exclusively fine-grained and a mixed fine and coarse-grained alternative are to be provided.

According to a first aspect, the invention provides for a refractory free-flowing basic castable composition or highly concentrated aqueous suspension, on the basis of MgO and/or chromium ore, the castable composition or highly concentrated suspension comprising: a) 76.0 to 99.9 wt.% of a refractory dilatancy-promoting material on the basis of MgO and/or chromium ore with a grain size between 0.1 and 45.0 μm; and b) 0.1 to 4.0 wt.% of one or several dilatancy-promoting dispersing and wetting agents, having 20 to 30 parts by weight of mixing water, based on the amount of the solid fraction of the castable composition or suspension. The dispersing agents have distinct MgO hydration retarding properties, the dispersing and wetting agents are selected from the group consisting of polyfunctional polyelectrolytes and salts of polybasic carboxylic acids, and the castable composition or suspension has a flow value of at least 80 %. The castable according to this aspect of the invention can be used to seal very narrow cracks, for instance <10 mm, or as a highly concentrated aqueous suspension, to produce compact bricks, for instance dry-pressed or rammed. It has further been found to be advantageous when binders, refractory or other additives are used as an option. Dilatant properties can only be attained with an excellent dispersion, i.e., comminution of large, hard particle agglomerates in the suspension. This finding is used when an aqueous, highly concentrated suspension is used to produce bricks. A very good dispersion of the suspension is needed in this case in order to attain a dense, homogeneous matrix of the bricks.

According to a second aspect, the invention provides for a refractory free-flowing basic castable composition on the basis of MgO and/or chromium ore, comprising: a) 35.0 to 84.8 wt.% of a refractory material on the basis of MgO and/or chromium ore with a grain size between 0.045 and 15.0 mm; b) 15.0 to 50.0 wt.% of a refractory dilatancy-promoting material on the basis of MgO and/or chromium ore with a grain size between 0.1 and 45.0 μm; c) 0.1 to 4.0 wt.% of one or several dilatancy-promoting dispersing and wetting agents, having 5 to 10 parts by weight of mixing water, based on the solid fraction of the castable composition; and d) 0.1 to 15.0 wt.% of one or several binding agents. The dispersing agents have distinct MgO hydration retarding properties, the dispersing and wetting agents are selected from the group consisting of polyfunctional polyelectrolytes and salts of polybasic carboxylic acids, and the castable composition has a flow value of at least 80 %. Here again the elements mentioned in connection with the first aspect, are needed in order to attain free flow of the basic castable according to the invention, but now the use of binders is compulsory. The introduction or shaping of the castable can in this alternative occur by pouring or pumping. This alternative is applicable primarily for a monolithic lining or repair of high-temperature equipment and/or the production of precast shapes, functional products or low-weight refractory products.

The basic castable according to the first and second aspects of the invention, has the effect of flowing freely and homogeneously after addition of the mixing water and mixing, but without the vibratory compaction needed for the thixotropic castables, i.e., without the input of external energy. The fluidity is rated in terms of the consistency test following ASTM C-860 described earlier, where the flow value should be at least 80 %.

It is a condition for practical applications of a free-flowing basic castable that the hydration of the MgO-based materials used to prepare the slip is markedly retarded. This is achieved with the dispersion agents and binders used, the latter being utilized optionally, i.e., when needed in the case of the first aspect, and definitely in the case of the second aspect. The degree of hydration of the caustic-calcined MgO after contact with the dispersing solution used here was five times smaller than after contact with water. The test was performed over a period of 30 min at 25 °C followed by rapid drying at 160 °C. The degree of hydration was determined gravimetrically, a degree of hydration of 100 % corresponding to complete transformation of the MgO to $Mg(OH)_2$. The dried or fired test bodies produced from the free-flowing basic castable revealed no hydration damage. The use of MgO powders pretreated e.g. with carboxylic acids is a further possibility for reducing the hydration of the free-flowing, basic castables.

The document EP 0,525,394 B1 discloses a free-flowing nonbasic castable, while with the process described in the document EP 0,448,156 A1 a castable having free-flowing properties cannot be achieved, hence even a pooling of these two documents will not suggest the solution offered in the first and second aspects of the invention.

The advantages of the free-flowing basic castable according to the invention over the free-flowing alumina castable can become apparent in numerous applications, such as a better corrosion and erosion resistance toward aggressive slags, molten metals, and furnace atmospheres and/or a favorable price/performance ratio.

The ranges of application of the fine-grained and the mixed fine and coarse-grained castable will be clarified later by the elements cited in the embodiments of the first and second aspects of the invention and underpinned by the examples.

The following elements are decisive for the distinct dilatant properties - as shown by the shape of the flow curves in Fig. 1 - and for free flow of the basic castable according to the invention:

- adjusted grain composition,
- the chemical and physical properties of the grain fraction <45 μm,
- the type and amount of dispersing agent. According to a preferred embodiment the mixing solution is added in amounts accurate to 0.2 percent by weight.

Further advantageous embodiments of the invention become apparent from the embodiments.

In an embodiment, the dispersing agents and binders used will substantially retard the MgO hydration of the castable according to the invention.

The refractory MgO-based materials used in the grain fraction <45 μm according to the first aspect, are preferably the synthetic magnesia types such as caustic-calcined magnesia, sintered magnesia and fused magnesia. The MgO powders obtained by spray-calcining are also designated as caustic-calcined magnesia. Such dilatancy-promoting refractory materials can be used advantageously, both according to the first and second aspects of the invention. The refractory material, again on MgO basis, in the grain size fraction up to 15 mm consists of sintered magnesia, fused magnesia, magnesiochromite co-clinker, and/or magnesiochromite fused grains, according to further elements of embodiments.

It is one of the advantages of the free-flowing castable according to the invention that it can be provided with one or several types of binders. According to the elements of embodiments, both different chemical, hydraulic but also temporary binders can be used, and in its hardened state the castable has physical test parameters comparable to those of a basic thixotropic castable.

The refractory additives according to embodiments have a grain fraction between 0.1 μm and 3 mm and can influence both the properties and the applications of the castable, depending on the type of additive. The refractory additives can substantially raise the thermomechanical resistance, the infiltration resistance and/or the thermal shock resistance of the castable.

Investigations of surface-chemical and rheological properties of aqueous MgO suspensions <45 μm have substantially contributed to finding a solution to the aims set for the invention. A knowledge of the dispersion mechanism is advantageous when selecting refractory additives and, if necessary, the type and amount of binder. An interaction of these components with the fine-grained fraction of the refractory material on the basis of MgO and/or chromium ore can suppress or reinforce dilatant properties and free flow. In the group of phosphates known as chemical binders, for instance, only few are suitable to prepare free-flowing basic castable, if - as indicated in a modification of the elements of embodiments - a particular type of polyelectrolyte is used as the dispersing agent.

A positive effect on dispersing action and dilatant properties of a free-flowing basic castable has been attained according to the elements of embodiments of the invention by using particular amines. This effect can be attributed to the adsorption of amines and change in zeta potential of the MgO particles in suspension.

The additives employed according to the elements of embodiments have diverse effects. Thus, organic fibers can prevent cracks due to drying during heating. Steel fibers can improve the thermal shock resistance of a free-flowing basic castable. A lower degree of infiltration of molten metal and slag by capillary action can be attained when for instance adding, according to the invention, spherical materials having diameters of 5 to 80 μm which will evaporate or burn away.

According to the elements of embodiments, the free-flowing basic castable according to the invention can be employed on account of its properties in all those applications where up to now the thixotropic basic castables are used, i.e., for the refractory monolithic lining or repair of high-temperature equipment, as well as for vibration-free production of refractory castings such as precast shapes, functional products, low-weight refractory products, and above that for the production of dry-pressed or rammed, compact bricks. High-temperature equipment which according to experience is lined with refractory basic products includes, according to the elements of embodiments, ladles, reactors, vessels for treatments, vessels for transport, storage tanks, tundishes, furnaces, converters, regenerators, and runners in the steel, metal, cement, lime and gypsum, chemical and other industries.

In the following the invention will be explained in the instance of embodiments. Examples 1 to 3 refer to the free-flowing castables of different compositions according to the elements of embodiments of the invention, examples 4 and 5 refer to the dilatant castables according to the elements of the first aspect.

Example 1

A free-flowing dilatant castable according to the invention on the basis of magnesia with phosphate/microsilica bonding has the following composition:

Sintered magnesia 98.5 % MgO	0.045 to 5 mm	66.0 % by weight
Fused magnesia 98.3 % MgO	<0.045 mm	15.0 % by weight
Caustic-calcined magnesia >97.0 % MgO	<0.045 mm	15.0 % by weight
Phosphate binder		1.0 % by weight
Binder on microsilica basis		2.0 % by weight
Silicon powder		1.0 % by weight
Dry mass		100.0 % by weight
Polyfunctional polyelectrolyte		0.7 % by weight
Water		7.8 % by weight
Mixing solution, relative to solids fraction of dry mass		8.5 % by weight

Example 2

A free-flowing dilatant castable according to the invention on the basis of magnesia hydraulically bonded has the following composition:

Sintered magnesia 98.5 % MgO	0.045 to 5 mm	65.0 % by weight
Fused magnesia 98.3 % MgO	<0.045 mm	15.0 % by weight
Caustic-calcined magnesia >97.0 % MgO	<0.045 mm	12.0 % by weight
Calcined alumina	0.2 to 6.0 μm	3.0 % by weight
Alumina cement > 69 wt.% Al_2O_3		5.0 % by weight
Dry mass		100.0 % by weight
Polyfunctional polyelectrolyte		0.4 % by weight
Amine		0.2 % by weight
Water		6.9 % by weight
Mixing solution, relative to solids fraction of dry mass		7.5 % by weight

Example 3

A free-flowing dilatant castable according to the invention on the basis of magnesia and chromium ore with phosphate/microsilica bonding has the following composition:

Sintered magnesia 98.5 % MgO	0.045 to 5 mm	31.0 % by weight
Chromium ore Transvaal	0 to 1.5 mm	35.0 % by weight

Fused magnesia 98.3 % MgO	<0.045 mm	15.0 % by weight
Caustic-calcined magnesia >97.0 % MgO	<0.045 mm	15.0 % by weight
Phosphate binder		2.0 % by weight
Binder on microsilica basis		2.0 % by weight
Dry mass		100.0 % by weight
Sodium salt of polybasic carboxylic acids		0.4 % by weight
Amine		0.3 % by weight
Water		7.8 % by weight
Mixing solution, relative to solids fraction of dry mass		8.5 % by weight

Example 4

A fine-grained dilatant castable according to the invention on the basis of magnesia with microsilica bonding has the following composition:

Fused magnesia 98.3 % MgO	<0.045 mm	49.8 % by weight
Caustic-calcined magnesia >97.0 % MgO	<0.045 mm	47.0 % by weight
Natural organic polymer		0.2 % by weight
Binder on microsilica basis		3.0 % by weight
Dry mass		100.0 % by weight
Polyfunctional polyelectrolyte		1.8 % by weight
Amine		0.3 % by weight
Water		23.4 % by weight
Mixing solution, relative to solids fraction of dry mass		25.5 % by weight

The dry components of the slip in examples 1 to 4 were mixed in a forced-action mixer for 6 to 15 minutes, first dry and then with the amount of mixing solution indicated. The fluidity after mixing and the physical test parameters of castable hardened and dried at 160 °C, calcined at 900 °C, and calcined at 1500 °C can be seen from Table 1.

Table 1

The flow value Fo and the physical test parameters of the free-flowing basic castable of examples 1 to 4 (RD: raw density; OP: open porosity; CCS: cold crushing strength)

	Example 1	Example 2	Example 3	Example 4
Mixing water, wt.%	7.8	6.9	7.8	23.4
Fo, %	105	90	120	130
After drying at 160 °C:				
RD, g/cm^3	2.71	2.78	2.84	2.17
OP, vol.%	17.7	16.8	14.0	28.3
CCS, N/mm^2	34	39	44	32
After calcining at 900 °C:				
RD, g/cm^3	2.68	2.75	2.78	2.06
OP, vol.%	22.1	19.5	23.1	36.8
CCS, N/mm^2	17	23	12	8
After calcining at 1500 °C:				
RD, g/cm^3	2.82	2.92	2.94	2.23
OP, vol.%	18.7	14.3	20.6	27.4
CCS, N/mm^2	45	41	27	28

The physical test parameters of the free-flowing dilatant basic castable of examples 1 to 3 listed in Table 1 show that the level of the values for thixotropic, MgO-based castables with comparable bonding was attained. A higher strength of the castable according to the invention can be attained when using larger amounts of binders. However, in some cases this may affect the chemical resistance and refractoriness under load.

For the basic aqueous dilatant castable in example 4, a basic thixotropic castable with comparably fine grain composition is not available as a reference from prior art.

The degree of hydration of the castable of example 4 was determined in a hydration test of 24 h at 60 °C and a relative humidity of 100 %, and found to be 21 %.

Example 5 and the reference examples to examples 4 and 5 were introduced in order to describe even better the hydration resistance of the MgO materials and the fluidity of the castables produced or not produced according to the elements of this invention.

Reference example to example 4

A fine-grained castable on magnesia basis with microsilica bonding:

Fused magnesia 98.3 % MgO	<0.045 mm	49.8 % by weight
Caustic-calcined magnesia >97.0 % MgO	<0.045 mm	47.0 % by weight
Sodium hexametaphosphate		0.2 % by weight
Binder on microsilica basis		3.0 % by weight
Dry mass		100.0 % by weight
Boron oxide		0.9 % by weight
Water		34.1 % by weight
Mixing solution (saturated boric acid solution), relative to solids fraction of dry mass		35.0 % by weight

Flow value Fo = 0, castable not free-flowing

Degree of hydration 0.1 %, test at 60 °C, 24 h, relative humidity 100 %

Despite a very low degree of hydration this castable lacks free-flowing properties.

A castable according to the invention or a highly concentrated MgO suspension can be formulated in such a way that MgO hydration is particularly effectively retarded by the action of dispersing and binding agents used according to embodiments of the invention. This was shown in the instance of example 5, where a caustic-calcined magnesia that was very fine-grained and hence prone to undergo hydration was employed.

Example 5

A dilatant, fine-grained castable on magnesia basis according to the invention:

Caustic-calcined magnesia >97.0 % MgO	<0.045 mm	94.0 % by weight
Hydraulic binder		6.0 % by weight

Dry mass	100.0 % by weight
Polyfunctional polyelectrolyte	2.0 % by weight
Dispersing agent	1.0 % by weight
Water	35.0 % by weight
Mixing solution, relative to solids fraction of dry mass	38.0 % by weight

Flow value Fo = 120 %

Degree of hydration 5 %, Test at 60 °C, 24 h, relative humidity 100 %.

Reference example to example 5

A fine-grained castable on magnesia basis:

Caustic-calcined magnesia >97.0 % MgO	<0.045 mm	94.0 % by weight
Hydraulic binder		6.0 % by weight
Dry mass		100.0 % by weight
Sodium hexametaphosphate		0.2 % by weight
Boron oxide		1.3 % by weight
Water		50.0 % by weight
Mixing solution (saturated boric acid solution with sodium hexametaphosphate), relative to solids fraction of dry mass		51.5 % by weight

Flow value Fo = 0, slip not free-flowing

Degree of hydration 31 %, test at 60 °C, 24 h, relative humidity 100 %

It can be seen from reference examples 4 and 5 that MgO hydration is reduced when employing known prior-art hydration retardants for MgO, viz., a saturated boric acid solution, as well as sodium hexametaphosphate as a dispersing agent, but free flow of the basic castable cannot be achieved despite a very large amount of mixing water. In the above reference examples, MgO materials promoting dilatancy and hence free flow were used but a dispersing agent according to the invention was not used.

From the reference example 5 it can be seen that a very fine-grained caustic-calcined magnesia could not be protected from hydration as efficiently as in example 5 with saturated boric acid solution. Moreover, it is known that boric acid, already from a concentration of 0.05 %, when used as hydration retardant for magnesia has a negative effect on refractoriness.

For comparison: the degree of hydration of a very fine-grained caustic-calcined magnesia was 85 % in water without dispersing and binding agents, when determined at 60 °C, 24 h, relative humidity 100 %.

Figure 1 shows the flow curves (arrows indicate the curves for increasing and decreasing shear velocity) of dilatant aqueous suspensions on the basis of MgO <45 μm prepared with two different MgO concentrations (75 % and 78 %). The composition of the mixing solution corresponds to that of Example 4. The flow curves were determined with the cone-plate system.

Claims

1. Refractory free-flowing basic castable composition or highly concentrated aqueous suspension on the basis of MgO and/or chromium ore, comprising:

   76.0 to 99.9 wt.% of a refractory dilatancy-promoting material on the basis of MgO and/or chromium ore with a grain size between 0.1 and 45.0 μm; and
   0.1 to 4.0 wt.% of one or several dilatancy-promoting dispersing and wetting agents, having 20 to 30 parts by weight of mixing water, based on the amount of the solid fraction of the castable composition or suspension,

   wherein the dispersing agents have distinct MgO hydration retarding properties, the dispersing and wetting agents are selected from the group consisting of polyfunctional polyelectrolytes and salts of polybasic carboxylic acids, and the castable composition or suspension has a flow value of at least 80 %.

2. Castable composition or suspension according to claim 1, comprising:
   80.0 to 98.5 wt.% of a refractory dilatancy-promoting material on the basis of MgO and/or chromium ore with a grain size below 25.0 μm; and
   0.1 to 4.0 wt.% of one or several dilatancy-promoting dispersing and wetting agents, having 21 to 26 parts by weight of mixing water, based on the solid fraction of the castable composition.

3. Castable composition or suspension according to claim 1, further comprising 0.1 to 15.0 wt.% of one or several binding agents that have distinct MgO hydration retarding properties.

4. Castable composition or suspension according to claim 3, comprising 0.5 to 12.0 wt.% of said binding agents.

5. Castable composition or suspension according to claim 3, wherein the binding agents are selected from the group consisting of phosphates, sulfates, microsilica, water glasses, alumina cements, clays, boron compounds and temporary binding agents.

6. Castable composition or suspension according to claim 1, further comprising up to 6.5 wt.% of one or several refractory additives on the basis of Al_2O_3, Cr_2O_3, ZrO_2, TiO_2, SiC, metal powder, or carbon support, with a grain size below 3 mm.

7. Castable composition or suspension according to claim 6, wherein the refractory additives are selected from the group consisting of calcined alumina, fused corundum, MA spinel, chrome oxide green, baddeleyite, titanium oxide, silicon carbide, magnesium powder, silicon powder, aluminum powder, iron powder,

ferrochrome powder, soot, and graphite, the refractory additives having a grain size between 0.1 μm and 3 mm.

8. Castable composition or suspension according to claim 1, further comprising 0.05 to 2.5 wt.% of one or several additives for preventing cracks arising during drying when heating, for raising thermal shock resistance, or for preventing the infiltration of molten metal and/or slag.

9. Castable composition or suspension according to claim 8, wherein said additives are selected from the group consisting of organic fibers, steel fibers, and spherical vaporizable or combustible materials having a diameter of 5 to 80μm.

10. Castable composition or suspension according to claim 1, further comprising a dispersing agent that is an amine which contains one or several nitrogen substituents selected from the group consisting of $-C_2H_4OR$, -H, $-CH_3$, $-C_2H_5$, and $-C(CH_3)_2CH_2OH$, wherein R = H or C_2H_4.

11. Castable composition or suspension according to claim 1, wherein the refractory dilatancy-promoting material on the basis of MgO is selected from the group consisting of sintered magnesia, fused magnesia, caustic-calcined magnesia, and combinations thereof.

12. Refractory free-flowing basic castable composition on the basis of MgO and/or chromium ore, comprising:

35.0 to 84.8 wt.% of a refractory material on the basis of MgO and/or chromium ore with a grain size between 0.045 and 15.0 mm;
15.0 to 50.0 wt.% of a refractory dilatancy-promoting material on the basis of MgO and/or chromium ore with a grain size between 0.1 and 45.0 μm;
0.1 to 4.0 wt.% of one or several dilatancy-promoting dispersing and wetting agents, having 5 to 10 parts by weight of mixing water based on the solid fraction of the castable composition; and
0.1 to 15.0 wt.% of one or several binding agents,

wherein the dispersing agents have distinct MgO hydration retarding properties, the dispersing and wetting agents are selected from the group consisting of polyfunctional polyelectrolytes and salts of polybasic carboxylic acids, and the castable composition has a flow value of at least 80 %.

13. Castable composition according to claim 12, comprising:

    55.0 to 75.0 wt.% of a refractory material on the basis of MgO and/or chromium ore with a grain size between 0.045 and 15.0 mm;
    25.0 to 42.0 wt.% of a refractory dilatancy-promoting material on the basis of MgO and/or chromium ore with a grain size below 25.0 µm;
    0.1 to 4.0 wt.% of one or several dilatancy-promoting dispersing and wetting agents, having 5 to 10 parts by weight of mixing water based on the solid fraction of the castable composition; and
    1.0 to 10.0 wt.% of one or several binding agents.

14. Castable composition according to claim 12, wherein the binding agents have distinct MgO hydration retarding properties and are selected from the group of phosphates, sulfates, microsilica, water glasses, alumina cements, clays, boron compounds, and temporary binding agents.

15. Castable composition according to claim 12, further comprising up to 6.5 wt.% of one or several refractory additives on the basis of Al_2O_3, Cr_2O_3, ZrO_2, TiO_2, SiC, metal powder, or carbon support, with a grain size below 3 mm.

16. Castable composition according to claim 15, wherein the refractory additives are selected from the group consisting of calcined alumina, fused corundum, MA spinel, chrome oxide green, baddeleyite, titanium oxide, silicon carbide, magnesium powder, silicon powder, aluminum powder, iron powder, ferrochrome powder, soot, and graphite, the refractory additives having a grain size between 0.1 µm and 3 mm.

17. Castable composition according to claim 12, further comprising 0.05 to 2.5 wt.% of one or several additives for preventing cracks arising during drying when heating, or for raising thermal shock resistance, or for preventing the infiltration of molten metal and/or slag.

18. Castable composition according to claim 17, wherein said additives are selected from the group consisting of organic fibers, steel fibers, and spherical vaporizable or combustible materials having a diameter of 5 to 80µm.

19. Castable composition according to claim 12, further comprising a dispersing agent that is an amine which contains one or several nitrogen substituents selected from the group consisting of $-C_2H_4OR$, -H, $-CH_3$, $-C_2H_5$, and $-C(CH_3)_2CH_2OH$, wherein R = H or C_2H_4.

20. Castable composition according to claim 12, wherein the refractory material having a grain size between 0.045 and 15.0 mm is selected from the group consisting of

sintered magnesia, fused magnesia, magnesiochromite coclinker, magnesiochromite fused grain, and combinations thereof, and the refractory dilatancy-promoting material having a grain size between 0.1 and 45.0 μm is selected from the group consisting of sintered magnesia, fused magnesia, caustic-calcined magnesia, and combinations thereof.

21. Castable composition or suspension according to claim 1, for use in the refractory monolithic lining, the repair of high-temperature equipment, or the production of refractory castings.

22. Castable composition or suspension according to claim 21, for use in the production of refractory castings selected from the group consisting of precast shapes, functional products, low-weight refractory products, dry-pressed or rammed compact bricks, and combinations thereof.

23. Castable composition or suspension according to claim 21, for use in the production of high-temperature equipment selected from the group consisting of a ladle, a reactor, a furnace, a vessel for treatment, transport or storage, a tundish, a converter, a regenerator and a runner.

24. Castable composition or suspension according to claim 23, wherein said high-temperature equipment is for use in the steel, metal, cement, lime, gypsum, or chemical industry.

25. Castable composition according to claim 12, for use in the refractory monolithic lining, the repair of high-temperature equipment, or the production of refractory castings.

26. Castable composition according to claim 25, for use in the production of refractory castings selected from the group consisting of precast shapes, functional products, low-weight refractory products, dry-pressed or rammed compact bricks, and combinations thereof.

27. Castable composition according to claim 25, for use in the production of high-temperature equipment selected from the group consisting of a ladle, a reactor, a furnace, a vessel for treatment, transport or storage, a tundish, a converter, a regenerator and a runner.

28. Castable composition according to claim 27, wherein said high-temperature equipment is for use in the steel, metal, cement, lime, gypsum, or chemical industry.

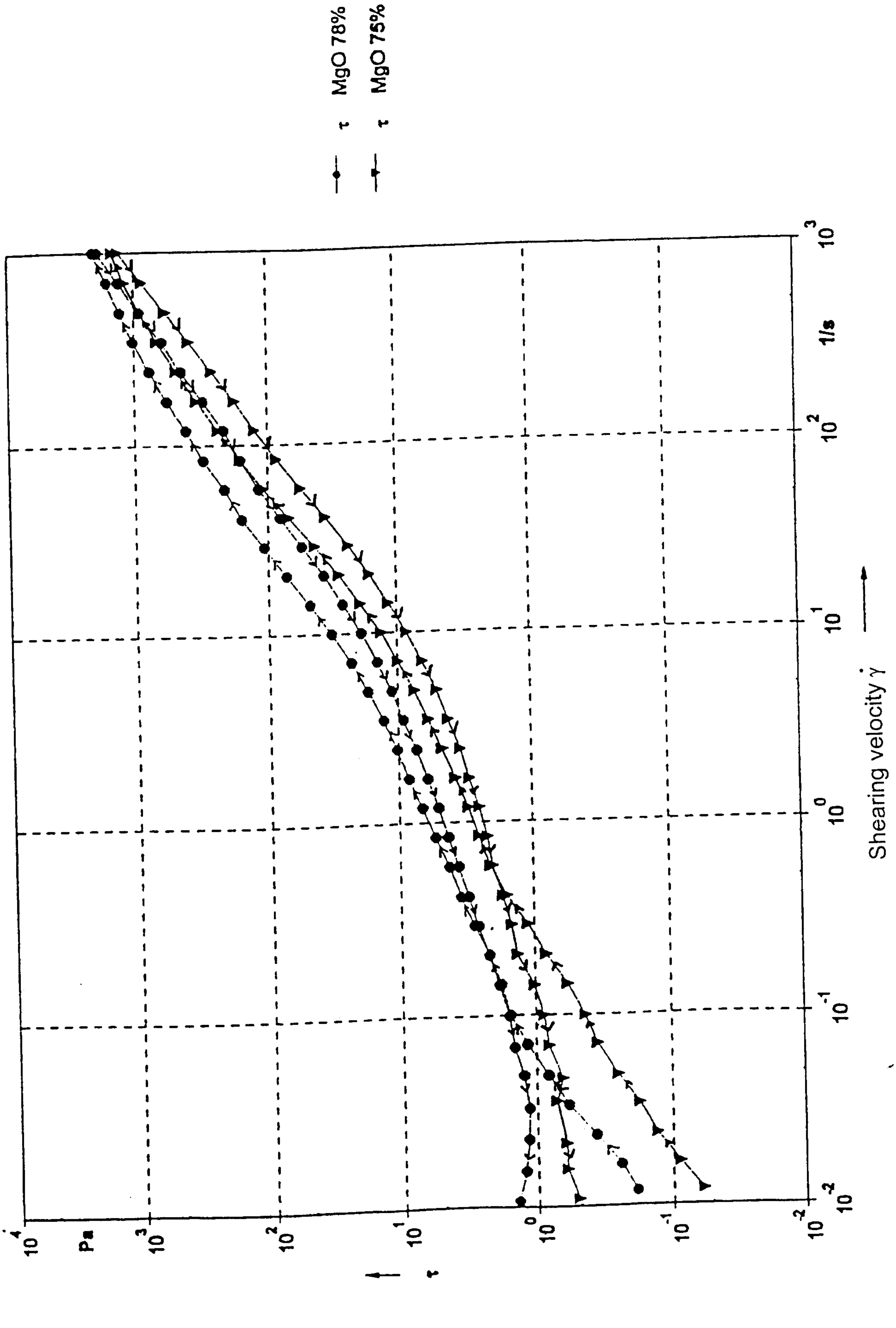

Fig. 1