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54 Titre : Inorganic polymers and use thereof in composite materials.

57 Abrégé :

The invention relates to a new inorganic polymer which is based on modified water glass, is characterized by numerous unusual properties and can be used as a substitute for, for example, concrete, cement and ceramics.

Fig. 12

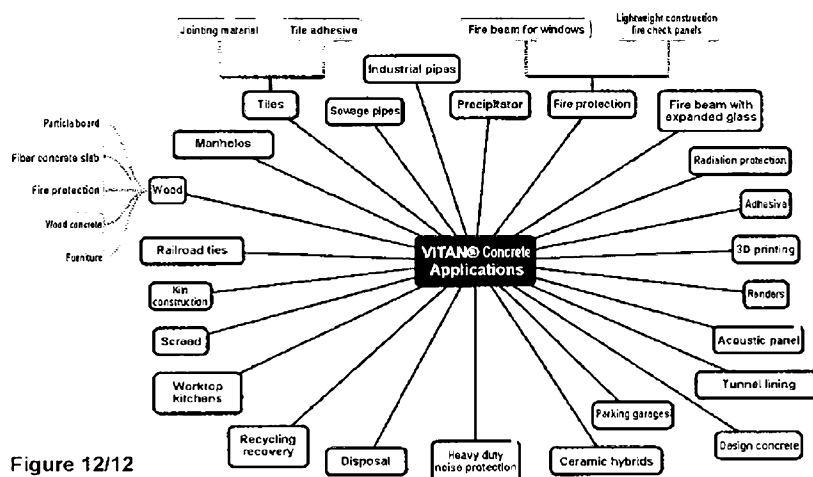


Figure 12/12

Inorganic polymers and use thereof in composite materials

PRIORITY CLAIM

- 5 The present international patent application claims the priority of the German patent application

DE 10 2019 005 107.6

of 23.07.2019.

FIELD OF THE INVENTION

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[0001] The invention is situated in the field of inorganic chemistry and relates to an inorganic polymeric material based on a modified waterglass that can be used, for example, as a concrete substitute or ceramic substitute, to a method for producing it, and to composite materials which can be produced from it.

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TECHNOLOGICAL BACKGROUND

[0002] Concrete is a very widespread building material which has for a long time been used for a whole swath of different applications. The concrete and its properties vary here in accordance with the applications. It may be necessary, for instance, to use particularly
20 chemically stable varieties of concrete for the building, for instance, of harbor installations exposed to salt water; concrete can be used in applications where dynamic cyclical stresses are particularly severe, such as heavy-load traffic sections, railroad ties, airport taxiways, etc.; severe flexural and/or compressive stresses have to be countered in the construction of span bridges and high-rise buildings, etc. There may be applications which call for particularly high
25 temperature resistance, as in the case, for instance, of so-called magmatic or volcanic concrete, designed for storing the heat of hot fluids, or for which it is necessary to ensure temperature resistance in the event of fire. Other applications require concrete of very low density, for instance foamed concrete. There is concrete intended to harden more quickly or more slowly, to flow further or less far prior to hardening, and so on.

[0003] These requirements are met by varieties of concrete, it having been possible, by dint of very long experience, to adapt concrete formulas by altering the constituents, selecting suitable additives such as plasticizers, surfactants, and so on. A feature which unites conventional concrete, however, is the regular processing of cement. The English word cement goes back to the Latin term *opus caementitium*. The starting material for cement is
35 nowadays ground from predominantly natural raw materials in a dry process and mixed, then fired in rotary kilns in a continuous operation, cooled and ground again.

[0004] More recently, however, the use of such cement has encountered considerable concerns. As reported by Horst-Michael Ludwig in "Neuartige Bindemittel – Die Zeit nach dem Portlandzement, in: Betone der Zukunft, Herausforderungen und Chancen, 14. Symposium Baustoffe und Bauwerkserhaltung Karlsruher Institut für Technologie (KIT), 21. März 2018" [Innovative binders – the post-Portland cement era, in: Concretes of the future, challenges and opportunities, 14th Karlsruhe Institute of Technology (KIT) symposium on building materials and preservation of buildings, March 21, 2018], around 0.80 metric ton of CO₂ is released per metric ton of clinker; this, in combination with the massive quantities of cement consumed worldwide (2016: around 4 billion metric tons), makes the cement industry responsible for 5% to 8% of the anthropogenically emitted carbon dioxide, in spite of the fact that nowadays the traditional Portland cement is barely still used at all in pure form. The magnitude of the problem becomes clear on comparison with air travel, which so often features in the headlines. Whereas the entirety of air travel leads to annual CO₂ emissions of around 700 million metric tons, the emissions arising from the cement industry are well above 2 billion metric tons of CO₂ per annum.

[0005] For more than 20 years, the worldwide emissions of CO₂ due to cement have been reduced through the use of so-called Portland composite cements of group CEM II (cements containing granulated slag and finely ground limestone). CEM II cements containing fly ash have so far barely been employed in Germany. Conversely, a major role is played by blast furnace cements of class CEM III; over the last 10 years they have doubled their market share, from around 10% to more than 20%.

[0006] For further CO₂ savings, there are already discussions among cement experts of alternative binders to classic Portland cement; the respective potential CO₂ savings are indicated in brackets:

- (A) reactive belite-rich Portland cement clinker (9%)
- (B) belite-ye'elimite-ferrite clinker (26%)
- (C) highly heated calcium silicate clinker (CCSC) (37%)
- (D) magnesium oxide, produced from magnesium silicates (possibly up to 100%)

[0001] However, the savings potentials of options A – C are unconvincing, and option D has not yet reached a sufficient state of technical development; see Ellis Gartner, Tongbo Sui, "Alternative cement clinkers", Cement and Concrete Research 114 (2018) 27–39.

[0002] CO₂ neutrality by 2050 is unachievable with Portland cement, and with the alternative variants thereof that are currently under discussion by the experts.

[0003] Identified more and more frequently as future cement alternatives, therefore, are alkali-activated cements, referred to as geopolymers, which can be formed from fly ash or granulated slag in conjunction with waterglass Portland cement-like binders. In a geopolymerization reaction, new, negatively charged Al(IV) centers (tetrahedrally coordinated) are formed endothermically, and have covalent bonding via oxygen atoms to Si

centers. Geopolymers therefore are not formed automatically at room temperature. It is instead necessary to supply heat for the formation of the negative Al centers. Issues frequently raised, moreover, are that the requisite amounts of waterglass are unavailable (at least at present) for cement substitution, and that fly ash and granulated slag have long been used as aggregates for current Portland cement. The production of waterglass could be scaled up in a CO₂-neutral way if the power was obtained on a solar basis. Conversely, fly ash, granulated slag and blast furnace slag will no longer be available in a CO₂-free world. It is therefore desirable to be able to specify cement-free concrete alternatives for at least some, preferably many, and especially preferably all concrete variants.

- 10 **[0004]** As well as the CO₂ problem, the resources in terms of aggregates used in concrete production are likewise not infinite and this as well is not unimportant, since one metric ton of concrete contains on average only about 150 kg of the albeit particularly climate-unfriendly cement, whereas the remainder consists of sand and gravel. These aggregates as well are now becoming more scarce worldwide, as reported by Matthias Achternbosch in
- 15 "Technikfolgenabschätzung zum Thema Betone der Zukunft – Herausforderungen und Chancen, in: Betone der Zukunft, Herausforderungen und Chancen, 14. Symposium Baustoffe und Bauwerkserhaltung Karlsruher Institut für Technologie (KIT), 21. März 2018" [Technical impact assessment on the topic of concretes of the future – challenges and opportunities, in: Concretes of the future, challenges and opportunities, 14th Karlsruhe Institute of Technology
- 20 (KIT) symposium on building materials and preservation of buildings, March 21, 2018]. Owing to the high viscosity, only particles having a size of more than 2000 µm in diameter can be readily admixed to conventional varieties of concrete. Desert sand and fine sand with grain diameters of less than 150 µm are unsuitable for concrete, as reported by P. Albers, H. Offermanns, M. Reisinger, in "*Sand als Rohstoff, Kristallin und amorph*" [Sand as raw material, crystalline and amorphous], Chemie in unserer Zeit, 30 (2016), 162-171. In instances
- 25 where smaller particles are admixed, the energy requirement involved in dispersing the particles with sufficient homogeneity in an as yet unhardened material, in particular, is very high from the standpoints both of machinery and of energy.

- [0005]** Furthermore, even in instances where concrete is still to be used in spite of the climate problems, there are still problems associated with its use, in spite of the many years of development of increasingly improved varieties of concrete, for the reason that its temperature stability is relatively low. Concrete undergoes decomposition starting at about 600°C, and this causes problems in fire prevention or in tunnel construction (in the event of a fire in the tunnel, the temperatures reached are well above 600°C); in this regard, see also
- 30 Ulrich Schneider, "*Verhalten von Beton bei hohen Temperaturen*" [Behavior of concrete at high temperatures], Issue 337 (1982), Deutscher Ausschuss für Stahlbeton.

[0006] The problems with conventional materials available to the market are not, however, confined to the concrete sector. With ceramics as well it is desirable to be able to bring about improvements.

[0007] There are a range of different applications for ceramics or ceramic materials. As well as the "classic" use of the term for sanitary ceramics such as washbasins and toilet bowls, tiles, and so on, there are nowadays also technical ceramics known, such as ceramics with particular stability toward abrasion, high temperatures, chemical attack, and so on. It is therefore no surprise that while ceramic materials are indeed in part defined as "inorganic, nonmetallic, of low solubility in water, and at least 30% crystalline", this definition is nevertheless not universally accepted and is also not used in this form in all areas of the industry. Generally speaking, however, ceramics are commonly understood to be shaped from an unfired material at room temperature and to acquire their desired, typical materials properties thereafter, as a result of a temperature treatment at usually above 800°C. Shaping occasionally takes place at an elevated temperature as well, or even by way of melt flow with subsequent crystallization.

[0008] The production of ceramics as well, therefore, again requires a high level of energy, which, as mentioned, is already undesirable and critical for reasons of climate. Here as well, an alternative would be desirable, at least for certain applications, especially those involving a particularly high energy requirement for manufacturing, owing for instance to the large mass of ceramics to be replaced, as in the case of toilet bowls, or owing to the widespread use, or owing to the required properties.

[0009] It should also be mentioned that certain known materials such as concrete or ceramic do result in product properties that are particularly desirable for certain products, yet have other properties which are disadvantageous, or are affected by a lack of opportunity or by insufficient opportunity to use the known materials for the desired purposes, owing, for instance, to no suitable processing options being available. Accordingly it may be desirable, for example, to generate built structures with concrete by new methods such as 3D printing; however, the cure times, viscosities, and so on do not allow simple processing. Here it would be desirable to open up new fields of application to the new material through better processing options, these fields being inaccessible to the old, original material such as concrete or ceramic. There are also, incidentally, applications in which neither ceramic nor concrete is presently used, and where, for example, a lighter, more precise, quicker and/or less energy-intensive processing might offer advantages, as in the replacement, for instance, of the presently commonplace enclosing of radioactive substances in glass for final or interim storage.

RELEVANT PRIOR ART

[0010] **WO 1997 006120 A1** (ALPHA BREVET) discloses a method for rapid curing of lightweight concrete containing aggregates, e.g., EPS, Styropor, expanded clay, pumice or the like, where a curing fluid, consisting of waterglass or of mixtures of waterglass and water, is applied to or introduced into the layer of lightweight concrete.

[0011] WO 2003078349 A1 (CHEMICKO) discloses a fly ash-based, geopolymeric binder for the production of slurries, mortars and concretes or for fixation of waste, said binder containing 70 to 94 percent by weight of power station fly ash with a measured surface area of 150-600 m²/kg and 5 to 15 percent by weight of an alkaline activator, the activator consisting of a mixture of alkaline hydroxide and alkaline silicate, waterglass for example, with this activator containing 5 to 15 percent by weight of Me₂O and having an SiO₂/Me₂O ratio in the range from 0.6 to 1.5, where Me is Na or K.

[0012] EP 0641748 B1 (SCHANZE) relates to a waterglass-based material for securing wall plugs, threaded rods and the like in cavities, especially drilled holes, in concrete, stone and brick masonry, with at least one finely particulate, high-activity coreactant, such as SiO₂ and/or Al₂O₃, for example, more particularly from waste materials, and also with fillers, such as finely ground quartz and/or silica sand, for example, the material being characterized in that the waterglass, more particularly potassium waterglass, has a molar ratio of SiO₂ to alkali metal oxide of greater than 1.4, preferably 1.45 – 1.60, but in any case less than 2, and in that the material additionally contains, per 100 parts by weight of waterglass, 10 to 40, preferably 20 to 30 parts by weight of a curing agent in the form of a compound which neutralizes the alkali metal of the waterglass with elimination of an acid which is stronger than silicic acid.

PROBLEM ADDRESSED BY THE INVENTION

[0007] Against this background it is desirable to be able to specify alternatives to conventional concrete that can be classed as climate-friendly, which are able to achieve at least some of the desired positive properties of conventional varieties of concrete, and/or which even possess better properties.

[0008] One of the desired qualities, therefore, though not the only one, is for the provision of a material which can be used as a substitute for concrete, having at least the strength of concrete, while being superior to concrete in terms of temperature stability and CO₂ balance, and enabling the use of desert sand and fine sand as aggregate material.

[0009] It is likewise desirable, furthermore, to provide a substitute for at least some ceramic applications as well, such as for sanitary ceramics, and so on, but also for industrial ceramics.

[0010] The problem addressed by the present invention was therefore critically that of providing substitute materials for the above-stated applications and also for further fields of use such as 3D printing, the eco-friendly binding of dusts, salts and pollutants, the production of coating materials for renovation purposes, for example, or building materials for interior finishing.

[0011] These substitute or replacement materials ought at the same time to have a multiplicity of properties, for example:

- curing within minutes – particularly when poured – within a broad temperature range from -25 to +60°C;

- low CO₂ burdening in production and use;
- low shrinkage with high compressive and flexural strengths;
- reduction in fire load, i.e., temperature-stable even at temperatures above up to 2400°C;
- 5 • resistant to corrosion due to water, acid, and salt;
- suitable for imparting water repellence;
- fully recyclable.

DESCRIPTION OF THE INVENTION

10 **[0012]** A first subject of the invention relates to an inorganic polymer containing Si, Al, Ca, alkali metal and O, which is distinguished by the fact that in a ²⁷Al MAS-NMR spectrum of the solid, compared with the ²⁷Al MAS-NMR spectrum of calcium aluminate, there is an additional signal whose chemical shift lies between that of the main peak of calcium aluminate and the calcium aluminate peak next upfield to the main peak. The inorganic polymer is distinguished more particularly by the additional fact that in a solid-state IR
15 spectrum it has a band at about 950 – 910 cm⁻¹.

[0013] Surprisingly it has been found that the inorganic polymers of the present invention entirely meet the complex profile of requirements described above.

Characterization of the inorganic polymers

20 **[0014]** The concrete substitute of the invention is produced from waterglass, calcium aluminate, water and alkali metal hydroxide (preferably NaOH and/or KOH); the material therefore contains Si, Al, Ca, an alkali metal (preferably Na and/or K) and O. In the reaction, negatively charged aluminum tetrahedra – activated by OH⁻ groups – react with charge-neutral silicon tetrahedra, with the negative charge of the Al tetrahedra compensated by Ca²⁺
25 ions from the calcium aluminate.

The inorganic polymer of the invention can be identified via ²⁷Al MAS-NMR spectroscopy and so distinguished from the starting materials and from conventional geopolymers, etc. In the literature there are numerous indications regarding the interpretation of such ²⁷Al spectra, from, for example, C. Gervais, K. J. D. MacKenzie, M. E. Smith, "Multiple magnetic field ²⁷Al solid state NMR study of the calcium aluminates CaAl₄O₇ and CaAl₂₂O₁₉" in Magn. Reson. Chem. 2001, 39, 23-28; from K. J. D. MacKenzie, I. W. M. Brown, R. H. Meinhold, "Outstanding Problems in the Kaolinite-Mullite Reaction Sequence Investigated by ²⁹Si and ²⁷Al Solid-state Nuclear Magnetic Resonance: I, Metakaolinite", J. Am.Ceram. Soc. 68, (1985), 293-297, and from P. S. Singh, M. Trigg, I. Bugar, T. Bastow, "Geopolymer formation processes at room
30 temperature studied by ²⁹Si and ²⁷Al MAS-NMR", Materials Science and Engineering **A 396** (2005) 392–402.

[0015] It should be emphasized again that the present reaction is a covalent bond formation between Al and Si tetrahedra and not a hydration reaction. In the ^{27}Al MAS-NMR spectrum, pure calcium aluminate gives a sharp signal at 78 ppm, which is assigned to the negatively charged Al tetrahedra, and a broader signal at 12 ppm, which is assigned to hexa coordinated Al atoms. If calcined calcium aluminate is mixed with water, it cures in the course of a hydration reaction. The tetrahedron signal of the aluminum at 78 ppm disappears completely in this case, since tetra coordinated aluminum is converted completely into hexa coordinated aluminum. The signal at 12 ppm therefore rises by the same degree as the signal at 78 ppm falls. As stated, with an excess of water, the signal at 78 ppm disappears entirely.

[0016] In the case of the new reaction described here, the situation is different. Although water is added (in the form of waterglass and additional water), almost the entire aluminum remains tetra coordinated. It is not consumed by reaction in the form of a hydration to give hexa coordinated aluminum. The reaction is therefore identifiable not only from the remaining of a part of the 78 ppm signal, but also by the new formation of defined Al-O-Si bonds, which are evident in the ^{27}Al MAS-NMR at 65 ppm (to be more exact: between 59 and 65 ppm, depending on the number of Al atoms involved). The new bonding is also apparent in the IR spectrum at around 950 cm^{-1} . The ^{27}Al MAS-NMR signal of the aluminum tetrahedra used at 78 ppm (to be precise: 77.7 ppm) in conjunction with the signal between 59 and 65 ppm is characteristic. The spectral ratio provides unambiguous characterization of the new bonding species. The ratio of the area values of the signal around 65 ppm (the actual bonding signal from -O-Si-O-Al-O bonds) to the signal at 78 ppm (the signal of the -O-Al-O-bonds) runs from 0 (only -O-Al-O bonds in the calcium aluminate) to more than 10. The figure is bounded in the upper range by the recognition of the signal at 78 ppm for Si/Al ratios close to 1. Here the signal at 78 ppm becomes very small, possibly close to zero, since almost all of the entire calcium aluminate i/Al ratio will have been consumed by reaction. It is possible here to specify a signal-to-noise ratio of the baseline to a signal at 78 ppm of about 3 as a recognition limit.

[0017] Applying this knowledge from the prior art, the signals in the region from 0 to 100 ppm in **Figure 6** can be assigned as follows:

- Al(VI) at 11.77 ppm
- Al(V) at 47.19 ppm
- Al(IV) at 77.68 ppm (main peak)

[0018] The main peak at about 78 ppm is characteristic for calcium aluminate and is not found, for example, either in the spectrum of tobermorite or in the spectrum of Roman concrete (see "*Unlocking the secrets of Al-tobermorite in Roman seawater concrete*" by Marie D. Jackson, Sejung R. Chae, Sean R. Mulcahy, Cagla Meral, Rae Taylor, Penghui Li, Abdul-Hamid Emwas, Juhyuk Moon, Seyoon Yoon, Gabriele Vola, Hans-Rudolf Wenk, and Paulo J.M. Monteiro, Cement and Concrete Research, Volume 36, Issue 1, January 2006, pages 18-29).

[0019] The material of the invention is therefore characterized in that in a ^{27}Al MAS-NMR spectrum in the range of 0 – 100 ppm (when using $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ as external standard) it has the three peaks of calcium aluminate and additionally a signal between the main peak and the next peak upfield, it being possible for this signal to be present as a shoulder. The formation of new bonds of course changes the relative peak heights as compared with those in the spectrum of calcium aluminate.

[0020] The IR spectrum of the solid material of the invention preferably displays a characteristic band around $950 - 910\text{ cm}^{-1}$. Conventional geopolymers vibrate here at somewhat higher wavenumbers, between $950 - 1000\text{ cm}^{-1}$. Also observable in the IR spectrum are two characteristic shifts of the water bands at about 1390 cm^{-1} and at a signal between 2800 and 3000 cm^{-1} (see **Figure 10**).

[0021] The inorganic polymers of the invention have the following preferred composition:

- (a) waterglass: about 2.5 to about 12.5 wt%, preferably about 5.0 to about 10.0 wt% (calculated as solid)
- (b) alkali metal hydroxide: about 0.7 to about 7.0 wt%, preferably about 1.0 to about 5.0 wt%
- (c) water: about 6.8 to about 20 wt%, preferably about 10.0 to about 15 wt%
- (d) calcium aluminate: about 10 to about 70 wt%, preferably about 20 to about 50 wt%, and more particularly from about 30 to about 40 wt%, and optionally
- (e) aggregates: 0 to about 80 wt%, preferably 20 to about 60 wt%, and more particularly about 30 to about 50 wt%, and/or
- (f) additives: 0 to about 10 wt% and preferably 2 to about 5 wt%,

[0022] with the proviso that the figures for amounts add up to 100 wt%. The solid material formed exhibits unusually high compressive and flexural tensile strengths and also temperature stability. For the sake of good order it may be noted that preparations which add up to less than or more than 100.0 wt% are not embraced by the invention and its claims, and that a skilled person is able at any time, using the present technical teaching, to select preparations in accordance with the invention.

[0023] In comparison to conventional concrete, which contains no alkali metal ions but has a high fraction of calcium and silicon, the material of the invention has a molar ratio of alkali metal cations (generally Na^+ and/or K^+) to calcium of about 1:1 to about 1:5 and more particularly about 1:2.

Production method

[0024] A further subject of the invention relates to a method for producing the inorganic polymer, comprising or consisting of the following steps:

- (a) providing waterglass, alkali metal hydroxide, water, calcium aluminate
- (b) mixing or contacting the substances from step (a), and optionally
- (c) curing the mixture from step (b).

[0025] In the course of the reaction, the compensating charge of the negatively charged Al tetrahedra changes from Ca^{2+} to the added alkali metal ions (e.g., K^+ or Na^+). The exchanged calcium ions are released completely in the form of $\text{Ca}(\text{OH})_2$. The precipitation of the $\text{Ca}(\text{OH})_2$ is the driving force of the reaction, and calcium aluminate is therefore essential for the reaction. It is possible to use more calcium aluminate than is needed for the stoichiometric bonding of the Na^+ ions by the negatively charged Al tetrahedra. If less calcium aluminate is used, the blocks which are formed no longer remain water-stable.

[0026] The ratio of Si tetrahedra and Al⁻ tetrahedra is freely adjustable in an Si/Al range from 1/12 to 1/1. The preselected Si/Al⁻ ratio determines the amount of Ca aluminate to be used (as source of Al⁻ tetrahedra) and the amount of waterglass to be used (as the source of Si tetrahedra). Via this Si/Al⁻ ratio, the desired compressive and flexural tensile strengths (and also, indirectly, the cure time) are adjusted. The highest compressive strength is achieved at an Si/Al⁻ ratio of 1/8. Figure 1 shows the compressive strengths attained for various Si/Al⁻ ratios (reaction with sodium waterglass, NaOH, calcium aluminate, and various amounts of finely ground quartz for establishing identical initial viscosities in the reaction mixture).

[0027] The upper limit of the possible mixtures is calculated for a commercial sodium waterglass having a modulus value of $s = 4$ (and hence having an Si/ Na^+ ratio of 2:1) as being an Si/Al ratio of 2:1. A mixture of this kind, consisting of pure waterglass and calcium aluminate, will not react, since the free base for the activation (e.g., NaOH) is missing. Mixtures are therefore reactive only from an Si/Al ratio ≈ 1 . The upper limit for the proportion of alkali is imposed by the viscosity of the alkali (in the form of an aqueous solution). Solutions of the alkali in waterglass with an alkali metal ion fraction of more than 1.5, based on the alkali metal ion fraction of the waterglass, can no longer be mixed with solid calcium aluminate, owing to their high viscosity. The lower limit on the mixtures which are realizable is situated at a ratio of about Si/Al $\approx 1:8$. Larger amounts of calcium aluminate (for ratios between 1/8 and 1/12) can be mixed homogeneously with the (undiluted) waterglass only if water is added. The result, however, is that the unwanted competing reaction of hydration of the calcium aluminate occurs, leading to less stable products. Ratios therefore make sense only from a ratio of Si/Al ≈ 0.125 (i.e. 1/8).

[0028] For the purposes of the present invention, what are called silicon nanoparticles are among the species suitable as waterglasses or Si tetrahedron sources. SiO_2 nanoparticles (such as Köstrosol 1540) likewise react with calcium aluminate, instead of waterglass. 10 g of Köstrosol, mixed with 3 g of NaOH and 20 g of calcium aluminate, become solid within 3 min.

[0029] From the experimental trials and the mandated stoichiometry, the following three preferred mixtures (in %) are derived, marking out the range limits of possible reaction mixtures:

Si/Al ratio	1/12	8/12	12/12
Calcium aluminate	70.2	35.0	26.3
Waterglass (solid)	5.10	19.9	22.0
NaOH (solid)	2.34	9.10	4.70
Water	22.4	36.0	47.0

5

[0030] For KOH and potassium waterglass, the values for alkali and waterglass are situated above those of sodium hydroxide and sodium waterglass by a maximum factor of $54/40 = 1.35$. The proportion of inert materials can be increased up to 80%. The percentage ratios listed above therefore fall at most to $1/5$ of the above values. Accordingly, the value for the calcium aluminate content does not fall below 5.26% for any mixture.

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[0031] The amount of OH^- ions used determines the reaction rate, as does the amount of Al tetrahedra. If a high concentration of OH^- ions is used, the mixture reacts more quickly than when using a lower OH^- ion concentration. A high concentration of Al tetrahedra has the same effect as a high OH^- ion concentration. Generally speaking, the greater the amount of aluminum tetrahedra and the greater the amount of NaOH in the mixture, the faster the binder cures. The cure times can be set freely between a few minutes (for an Si/Al ratio of 1:12) and several hours (for an Si/Al ≈ 1).

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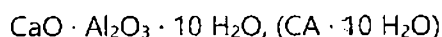
[0032] It has proven advantageous to observe the following two conditions, individually or jointly:

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- the ratio of calcium ions (from the calcium aluminate) to alkali metal ions (from waterglass and from the activation by NaOH) ought to be 1:2 (or greater);
- the ratio Al^-/Na^+ ought to be at least 1:1, but may also be greater than 1 (thus permitting a calcium aluminate excess).

[0033] The calcium aluminates used consist generally of 29 wt% CaO and 71 wt% Al_2O_3 , corresponding approximately to a 3:1 mixture of CA and CA_2 , for which the corresponding empirical formula is $(\text{CaO})_4(\text{Al}_2\text{O}_3)_5$ (C_4A_5) with a molar mass of 734. The reactive aluminates take up the following maximum amounts of water:

25



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[0034] Purely theoretically, therefore, one mole of $(\text{CaO})_4(\text{Al}_2\text{O}_3)_5$ is able thus to take up 38 mol of water, but only $8 + 7 = 15$ water molecules are stably bound per mole of C_4A_5 .

With the new binder, it is found experimentally that, with a fair degree of accuracy, 10 mol of water are incorporated per mole of calcium aluminate (C_4A_5). This suggests that exactly one molecule of water per Al center is required in the end product for charge stabilization. This is less incorporation of water than in the case of simple hydration of C_4A_5 .

- 5 **[0035]** It must be emphasized that the present reaction here is a covalent bond formation between Al and Si tetrahedra and not a hydration reaction, in which a solid microstructure with crystal formation is formed. Accordingly, the calcium aluminate need not necessarily have been calcined; it is necessary only for Al tetrahedra to be present with calcium as the counterion! Accordingly, the calcium aluminate to be consumed by reaction may also be
10 prepared wet-chemically at room temperature from sodium aluminate and $CaCl_2$ or $CaSO_4$.

[0036] For the production of the inorganic polymer of the present invention, one or more waterglasses are used. Waterglasses are usually produced from sand and Na and/or K carbonate. They consist of readily water-soluble silicates with a negative charge which is compensated by monovalent counteranions (M^+).

- 15 **[0037]** As well as purely inorganic waterglasses, it is also possible to use waterglasses which have an organic radical, such as a propyl radical (e.g., Protectosil WS808 from Evonik); they may be used alone or in a mixture with purely inorganic waterglasses. Where waterglasses of these kinds with an organic radical are used, it is possible to produce water-repellent surfaces.

- 20 **[0038]** It is possible to use one sodium waterglass (sometimes also referred to as sodium silicate) or a mixture of different sodium waterglasses. It is also possible to use one potassium waterglass (sometimes also referred to as potassium silicate) or a mixture of different potassium waterglasses. One embodiment comprises a mixture of sodium and potassium waterglass, such as a 90:10 to 10:90 mixture, for example.

- 25 **[0039]** Waterglasses are characterized by their s number, which indicates the mass ratio SiO_2/M_2O (M = alkali metal); the smaller the value of s , the greater the amount of alkali metals present. Waterglasses with various s values are available commercially. The s value of a waterglass determines the chemical constitution of the silicate. For an s value of $s = 1$, the silicate has on average a negative charge. Theoretically, the s value may go down to 0.25.

- 30 **[0040]** Waterglasses with s values up to around 8 are known. For the present invention, for example, waterglasses having an s value of 0.4-5 are used. Aqueous solutions of waterglasses are viscous. For a given SiO_2 fraction (s value), sodium waterglasses lead generally to a higher viscosity than potassium waterglasses. For the production of the inorganic polymer of the invention it is possible to start, for example, from commercial waterglass solutions having a
35 solids content of about 22 to about 52 wt%.

[0041] The second essential component for producing the material of the invention is an alkali metal hydroxide, preferably NaOH and/or KOH. Commercially available alkali metal hydroxides can be used without purification.

[0042] A further essential starting material is calcium aluminate; it is possible, for example, to use a commercially available calcium aluminate such as Secar[®] 71 from Kerneos Inc. or one from Almatix GmbH such as CA-14 or CA-270.

5 **[0043]** Additionally required is water; here, there is no need for distilled or deionized water (though it can be used) – instead, mains water or even salt water can be used, since the reaction for production is alkali-tolerant.

10 **[0044]** With preference, first waterglass (or waterglass solution), alkali metal hydroxide and water are brought into contact and then the calcium aluminate is mixed in. It is optionally also possible to mix in one or more aggregates. The aggregates are selected preferably from finely ground rock, coarse broken stone, and sand (e.g., sea sand, river sand, fine sand and desert sand); in the case of conventional cement/concrete, only sharp-edge sand with a mean particle size of $> 2000\ \mu\text{m}$ can be used, whereas in the present invention it is also possible to use fine sand and desert sand composed of particles rounded by grinding, with a mean particle size $\leq 150\ \mu\text{m}$ (particle size determined by sieving; weight average).

15 **[0045]** It is also possible, optionally, for additives to be mixed in as well, selected for example from iron phosphate, calcium phosphate, magnesium phosphate, iron oxides, lead oxides, BaSO_4 , MgSO_4 , CaSO_4 , Al_2O_3 , metakaolin, kaolin, inorganic pigments, wollastonite, rockwool, and mixtures thereof.

20 **[0046]** The supply of heat is not necessary for the reaction, but may – if necessary – be considered for the purpose of accelerating curing. It has been found that curing takes place at between about -24°C and $+50^\circ\text{C}$ and even that curing under water is possible. Curing takes place preferably at temperatures in the range from about 25 to about 40°C .

25 **[0047]** The viscosity of the reaction solutions can be adjusted by varying the amounts of the starting materials in a range from 25 to 700 mPa (at 20°C). The reaction solutions in the lower viscosity range are also suitable for 3D printing. The cure time may be adjusted between 50 sec and 40 min. The cure time may be adjusted, for example, via the amount of water and the calcium aluminate fraction.

30 **[0048]** The anionic polymer of the invention may both be produced from a medium-viscosity liquid (consisting of waterglass solution and alkali metal hydroxide) and a powder (calcium aluminate and optionally aggregates), mixed for example in a ratio of about 1:1 (the liquid component in this case is stable for at least 5 months), and be produced from a liquid phase (aqueous alkali metal hydroxide; long stability) and a high-viscosity suspension which contains waterglass solution, calcium aluminate and, where appropriate, aggregates (similar to mortar, stable for 1 week) in a ratio, for example, of 1:20 to 1:50, where the method with
35 liquid phase and high viscosity suspension would be suitable for 3D printing. Ultimate hardness is achieved after about 21 days. Where fine sands having a particle diameter of $< 500\ \mu\text{m}$ are used as aggregate, it has proven advantageous first to mix the fine sand with waterglass and alkali and then to add the calcium aluminate.

INDUSTRIAL APPLICABILITY

Concrete and cement substitution

5 [0049] The CO₂ emissions released in the production of concrete cannot be forced below a fixed limiting value, since about 2/3 of these emissions are due to the release of CO₂ when the CaCO₃ is converted to CaO. Calculating the emission at 0.75 metric ton of CO₂ for each metric ton of cement produced, or 0.354 metric ton of CO₂ for one m³ of concrete with a compressive strength of 40 N/mm², it is possible by comparison to achieve a considerable reduction in the CO₂ emissions of waterglass, NaOH and, to a limited extent, calcium
10 aluminate as well when using solar power. The figure reported for the proportional CO₂ emissions in the example formulas, based on (present-day) concrete, relates to the CO₂ emissions of waterglass, NaOH and calcium aluminate when they are produced 100% from solar power. The production of the composite materials of the invention as a concrete substitute, conversely, may be produced with up to 70% lower CO₂ emission, relative to an
15 equivalent standard concrete.

[0050] By virtue of the lower viscosities as compared with concrete, aggregates such as fine sand and desert sand (with < 150 µm, e.g., 120 µm, particle diameter) can be mixed in by hand. Because the product is not susceptible to salt corrosion and cures even under water, marine sand can also be used as an aggregate. In this way, underwater constructions as well
20 can be erected without problems. **Figure 12** shows an overview of possible applications of the VITAN® composite material of the invention in the concrete substitutes segment.

Ceramic substitution

25 [0051] Where no aggregates such as sand are used, it is possible to obtain smooth surfaces, which enable use as a ceramic substitute. The advantage here in particular is that ceramics, tiles for example, are obtained by pouring the mixture into a mold, with no need for baking. In this way, even bespoke productions in short runs can be realized inexpensively. Before curing takes place, all possible shapes can be produced, such as pipes, plant tubs and the like, for example.

30 [0052] The mixtures, moreover, are foamable and are therefore very generally suitable for upgrading and renovating work around the house, both for professionals and for home improvers. In home improvement stores, such preparations, preferably in the form of 2-component systems, may be offered and sold in a cartridge, for example, in the form of spray mortar, troweling compound or fillers, for example.

35 [0053] The solid material, with or without aggregates, features temperature stability of well above 1000°C, so making the material suitable, for example, for high-temperature applications (e.g., as a thermal solar store) or as a protective casing for lithium-ion batteries,

for example. By this route it is also possible to produce hybrid materials such as, for example, composites with plastics or metals (e.g., aluminum).

[0054] As well as the high temperature stability, the material is notable for compressive strength of up to 180 N/mm² and hence achieves levels twice as high as conventional concrete. Furthermore, the flexural tensile strength is up to 17 N/mm² (measured according to DIN 1048) and hence achieves approximately three times the level of conventional concrete. Moreover, the material of the invention can be heated to glowing red in the flame from a Bunsen burner (around 1200°C) and subjected to shock cooling in water without breaking or fracturing. This is true even when the temperature change is frequent and repeated. The material, accordingly, can be regarded as stable to temperature change with temperature changes by more than 100°C, preferably more than 200°C, especially preferably more than 500°C and very preferably more than 1000°C, both for heating and for cooling, and the heating and/or cooling by the temperature differences stated may be operated in particular with a rate of temperature change of greater than 100°C/min, preferably greater than 200°C/min, more particularly greater than 500°C/min, very preferably greater than 1000°C/min; the rate of temperature change here is preferably, indeed, greater than 1000°C/30 sec, preferably 1000°C/15 sec.

Aggregates

[0055] As well as the aforesaid aggregates, it is also possible to admix fibers, fabrics, wood, wood chips and disintegrated metals, especially steel, and also pellets from recycled concrete or recycled brick, comminuted weathered sandstone, and also comminuted perlite, powdered pumice or granulated pumice. Fibers contemplated include inorganic fibers such as CNTs, glass fibers, metal fibers and mixtures thereof, and also organic materials such as coir, bamboo or sisal. The length of the fibers may be greater than 0.3 mm, preferably more than 1 mm, and preferably less than 5 cm, preferably less than 1 cm. The stated fibers may be embedded in the form of fabrics, in which case the fibers within a fabric may be longer than the stated upper limits, since here there is a small risk of the blocking of pumps, mixers, etc. by excessively long fibers. It may be mentioned that the properties may be improved by the fibers in a manner known per se. The material is also suitable for lightweight construction and dry construction, since high flexural tensile strengths are achieved even with little filling material, and this is conducive to the use of thin structures. For particularly exacting fire protection requirements, there are of course limits on the aggregates. One particular embodiment is obtained with wood or fibers as aggregate, in the form of pressboard panels.

Binding of pollutants

[0056] In the production of the material of the invention, depending on the amount of aggregate, little to no contraction is observed. At the production stage, the mixture is

virtually liquid for a short time and is therefore also suitable for impregnating fabrics and fleeces – as a result it would be possible, for example, to produce a composite material with carbon fiber mats. With barium sulfate and lead oxide, the mixture for producing the material of the invention (i.e., the reaction mixture prior to hardening) forms stable mixtures and is therefore also suitable for the bound enclosure of pollutants and radioactive wastes.

Lyophilization

[0057] Lyophilic compounds of the silane type, such as octyl triethoxysilane, for example, are capable of lyophilizing the surfaces if they are admixed in amounts of about 0.5 to 3 wt% to the binder. This makes not only the surface but also the entire substance water-repellent. In this way it is possible to carry out sanding without the lyophilized product losing its water-repellent character. In addition, the admixing of the waterglasses Rhodarsil R51T (tripotassium methylsilanetriolate, a methyl siliconate) and Protektosil WS 808 (tripotassium propylsilanetriolate, a propyl siliconate) at between a few % to 100% (as a waterglass replacement) enables comprehensive lipophilization of the surfaces.

Composite materials

[0058] A further subject of the present invention relates to a composite material comprising or consisting of

- (a) the inorganic polymer of the present invention and
- (b) at least one aggregate and/or additive.

[0059] For the purposes of the present invention, the term "composite material" is used synonymously with the terms "solid composition" or "molding". The aggregates in this case may be selected from the group consisting of sand, coarse broken stone, finely ground quartz, rubber, organic polymers, wood, fibers, salts or pollutants and mixtures thereof. Particularly preferred composite materials are those for which the aggregate is marine sand, desert sand or fine sand having a mean particle diameter of $\leq 150 \mu\text{m}$.

[0060] The composite materials are typically notable in that they comprise or consist of

- (a) about 20 to about 80 wt%, preferably about 30 to about 70 wt% and more particularly about 40 to about 60 wt% of inorganic polymers and
- (b) about 80 to about 20 wt%, preferably about 70 to about 30 wt% and more particularly about 60 to about 40 wt% of aggregates and/or additives.

[0061] In further preferred embodiments, the composite material may be an adhesive bonding agent, a coating material, a binder, a material for 3D printing, a ceramic, a concrete substitute or a cement substitute. A further example are fiber composite materials, i.e., composite materials of the inorganic polymers with fibers such as sisal, bamboo, hemp and

the like. The fiber composite materials are suitable, for example, for producing components, such as water tanks, which are otherwise commonly produced from plastics. The composite material may also be a wood composite material, as a substitute for pressboard panels, for example. Wood composite materials according to the invention are notable for diverse
5 positive properties; in particular, they are formaldehyde-free, nonflammable, stable to water, and have a fungicidal effect deriving from their alkalinity.

[0062] A further subject of the invention relates to a method for producing a composite material, comprising or consisting of the following steps:

- (a) providing waterglass, alkali metal hydroxide, water, calcium aluminate
- 10 (b) providing at least one aggregate and/or additive,
- (c) mixing or contacting the substances from steps (a) and (b), and
- (d) curing the mixture from step (c).

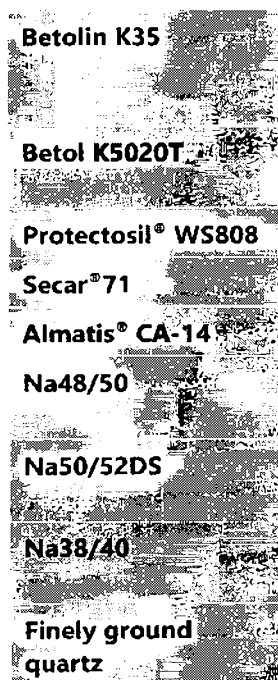
[0063] A further subject of the invention relates to the use of the inorganic polymers as described above for producing adhesive bonding agents, coating materials, binders,
15 materials for 3D printing, fiber composites, wood composites, ceramics, concrete substitutes or cement substitutes, preferably in amounts of about 5 to about 80 wt%, preferably about 15 to about 65 wt% and more particularly about 25 to about 50 wt%.

EXAMPLES

General information for the examples

5

Examples 1 to 9 used the following materials:



Potassium waterglass, $s = 2.6$; Wöllner GmbH, aqueous solution with 35% solids content

Potassium waterglass, $s = 1.49$; Wöllner GmbH, aqueous solution with 48% solids content

Waterglass with propyl radical, $s = 0.4$; Evonik; 55% solids content

Calcium aluminate ($\text{Al}_2\text{O}_3 \geq 68.5\%$, $\text{CaO} \geq 31.0\%$), Kerneos Inc.

Calcium aluminate ($\text{Al}_2\text{O}_3 = 71\%$, $\text{CaO} = 28\%$), Almatiss GmbH, Frankfurt

Sodium waterglass, $s = 2.6$, Wöllner GmbH, aqueous solution with 44.5% solids content

Sodium waterglass, $s = 1.54$, Wöllner GmbH, aqueous solution with 48% solids content

Sodium waterglass, $s = 3.4$, Wöllner GmbH, aqueous solution with 35.8% solids content

1205-SIKRON-Quartz SF800

The density was determined by determining the volume and the weight of a rectangular specimen and calculating the density as weight/volume.

10 The compressive strength of the samples was measured using a Z250 universal testing machine from Zwick/Roell. The compressive forces (in N) were plotted as a graph against the deformation distance. The maximum pressure reached was placed in relation to the surface area (mm^2) of the sample.

Example 1

15 100 g of K35, 100 g of K5020T, 36 g of WS808, 50 g KOH and 64 g of water) were mixed with 600 g of Secar® 71 and 60 g of finely ground quartz. The mixture could be stirred for five minutes and was solid after 20 min. The density of the cured material was 2.13 g/cm^3 , the compressive strength 179 N/mm^2 .

Example 2

100 g of K35, 100 g of K5020T, 36 g of WS808, 50 g KOH and 64 g of water were mixed with 600 g of Almatiss[®] CA-14 and 60 g of finely ground quartz. The mixture could be stirred for five minutes and was solid after 20 min. The density and compressive strength of the cured material were comparable with those of Example 1.

Example 3

80 g of Na 48/50, 20 g of Na50/52DS, 21 g of NaOH and 29 g of water were mixed with 350 g of Secar[®] 71 and 4.3 g of KH₂PO₄. The density of the cured material was 2.11 g/cm³, the compressive strength 132 N/mm².

Example 4

80 g of Na 48/50, 20 g of Na50/52DS, 21 g of NaOH and 29 g of water were mixed with 350 g of Almatiss[®] CA-14 and 4.3 g of KH₂PO₄. The density and compressive strength of the cured material were comparable with those of Example 3.

Examples 5-7 used the following waterglass-water mixtures:

WG1: 9.92 g of NaOH, dissolved in 20 g of water, mixed with 100.2 g of Na38/40

WG2: 19.98 g of NaOH, dissolved in 10 g of water, mixed with 100.6 g of Na38/40

Example 5

The concrete substitute was produced from 40 g of Almatiss[®] CA-14 and 19.4 g of WG1; the mixture was solid after 32 min and had a gray color. The density was found to be 2.21 g/cm³ and the compressive strength 101.3 N/mm². (Sample B1)

Example 6

The concrete substitute was produced from 40 g of Almatiss[®] CA-14 and 9.48 g of WG1; the mixture was solid after 3-4 min and had a white color. (Sample C1)

Example 7

The concrete substitute was produced from 40 g of Almatiss[®] CA-14 and 28.86 g of WG2; the mixture was solid after 20 min and had a gray color. The density was found to be 1.97 g/cm³.
5 (Sample D1)

The ²⁷Al MAS-NMR spectra of Examples 5-7 are shown in Figs. 2 – 4. Fig. 1 (Sample A) shows, for comparison, the ²⁷Al MAS-NMR spectrum of Almatiss[®] CA-14.

Example 8A and B

10 102 g of Na38/40, 10 g of NaOH, 50 g of water and 925 g of coarse broken stone were mixed with 165 g of Secar[®] 71 (A) or 165 g of Almatiss[®] CA14 (B). Density: 2.27 g/cm³ (A), compressive strength: 40.9 N/mm² (A); density and compressive strength for (B) were comparable.

Example 9A and B

15 102 g of Na38/40, 10 g of NaOH and 18 g of water were mixed with 325 g of desert sand (120 µm particle size) and 180 g Secar[®] 71 (A) or 180 g of Almatiss[®] CA14 (B). Density: 2.01 g/cm³ (A), compressive strength: 37.5 N/mm² (A), flexural tensile strength: 7.8 N/mm² (A);
20 density, compressive strength and flexural strength of (B) were comparable.

Example 10

Tables 1A to 1C below give peak areas, peak heights and also cure times and compressive strengths for inorganic polymers of the invention having different Si/Al ratios:

Table 1A

Peak areas (in percent) of the individual ^{27}Al signals

Si/Al ratio	78 ppm	65 ppm	47.2 ppm*	11 ppm	65/78 ppm
0	80.8	0.0	6.7	12.5	0
0.125	40.1	17.6	3.1	39.2	0.44
0.156	25.1	30.6	3.1	34.5	1.2
0.231	21.6	38.8	3.1	36.5	1.8
0.375	7.40	49.5	3.1	40.0	6.7
0.625	7.58	56.2	3.1	33.1	7.4
0.875	11.7	62.0	3.1	23.2	5.3

* The signal at 47.2 ppm can be assigned to a penta coordinated aluminum, and plays no part in the reaction.

Table 1B

Peak heights (in percent) of the individual ^{27}Al signals

Si/Al ratio	78 ppm	65 ppm	47.2 ppm*	11 ppm	65/78 ppm
0	80.8	0.0	6.7	12.5	0
0.125	40.0	12.5	3.5	44.0	0.31
0.156	33.9	25.5	3.5	37.1	0.75
0.231	40.6	19.8	3.5	36.1	0.49
0.375	15.5	26.8	3.5	54.2	1.7
0.625	16.8	40.4	3.5	39.3	2.4
0.875	35.3	38.6	3.5	22.6	1.1

Table 1C

Data for various mixtures: cure times and compressive strengths

Si/Al ratio	NaOH [g]	Na38/40 [g]	Ca aluminate [g]	Cure time [min]	Compressive strength [N/mm ²]
0.125	14.2	86	286	5	57 (5d)
0.156	20.0	100 + 10 g H ₂ O	268	17	77 (21d)
0.231	10.0	100 + 10 h H ₂ O	180	20	60 (21d)
0.375	14.2	86	96	100	75 (5d)
0.625	14.2	86	58	140	32 (5d)
0.875	9.1	91	44	50	47 (5d)

5

Examples 11a to 11c*Rapid curing*

100 g of K42 (Betolin K42 from Woellner), 20 g of KOH, 50 g of water with 55 g of water and 420 g of calcium aluminate. The mixture is solid after 90 sec, with a compressive strength of 123 N/mm².

100 g of K35 (Betolin K35 from Woellner), 20 g of KOH, 50 g water with 55 g of water and 425 g of calcium aluminate, solid after 8 min, with a compressive strength of 169 N/mm².

Si/Al ratio 0.33: 100 g of Na38/40 (Betol 38/40 from Woellner), 10 g of NaOH, 10 g of water, 250 g of calcium aluminate, 125 g of desert sand, solid after 12 min, with a compressive strength of 162 N/mm².

Mixtures in accordance with the examples above with rapid curing are ideally suitable for 3D printing.

Example 12

20 6.4 g of NaOH + 86 g of waterglass Na38/40 with 36 g of calcium aluminate (and 330 g of building sand) is solid after 90 min (ultimate hardness: 41 N/mm²). The Si/Al⁺ ratio is 1/1. (Proportional CO₂ emissions, based on concrete: 20%)

Example 13

25 14 g of NaOH + 86 g of waterglass Na38/40 with 50 g of calcium aluminate (and 370 g of building sand) is solid after 180 min (ultimate hardness: 30 N/mm²). The Si/Al⁺ ratio is about 3/4 (5.7/8). (Proportional CO₂ emissions, based on concrete: 24%)

Example 14

14 g of NaOH + 86 g of waterglass Na38/40 with 50 g of water and 35 g of calcium aluminate (and 680 g of building sand) is solid after 24 h (ultimate hardness: 11 N/mm²). The Si/Al⁺ ratio is 1/1. (Proportional CO₂ emissions, based on concrete: 11%)

5

Example 15

30 g of NaOH + 32 g of waterglass Na38/40 and 68 g of waterglass Na48/50 with 70 g of water and 370 g of calcium aluminate (and 31 g of finely ground quartz) is solid after 12 min (ultimate hardness: 155 N/mm²). The Si/Al⁺ ratio is 1/8. (Proportional CO₂ emissions, based on concrete: 100%)

10

DESCRIPTION OF THE FIGURES

The invention is elucidated in more detail by means of the following figures, without being limited to them. The significations of the figures are set out below.

- | | | |
|----|----------------|--|
| 5 | Figure 1 | Compressive strengths attained for different Si/Al ⁺ ratios (reaction with sodium waterglass, NaOH, calcium aluminate and different amounts of finely ground quartz for setting identical initial viscosities for the reaction mixture). |
| | Figure 2 | ²⁷ Al MAS-NMR spectrum (Si-Al ratio 0.875) with the binding peak maximum at 59.3 ppm and at 943 cm ⁻¹ in the IR. |
| 10 | Figure 3 | ²⁷ Al MAS-NMR spectrum (Si-Al ratio 0.625) with the binding peak maximum at 59.1 ppm and at 940 cm ⁻¹ in the IR. |
| | Figure 4 | ²⁷ Al MAS-NMR spectrum (Si-Al ratio 0.375) with the binding peak maximum at 63.4 ppm and at 943 cm ⁻¹ in the IR. |
| 15 | Figure 5 | ²⁷ Al MAS-NMR spectrum (Si-Al ratio 0.125) with the binding peak maximum at 65.0 ppm and at 952 cm ⁻¹ in the IR. |
| | Figure 6 | ²⁷ Al MAS-NMR spectrum of calcium aluminate (Almatis® CA-14) |
| | Figure 7 | ²⁷ Al MAS-NMR spectrum of the solid obtained in example 5 |
| | Figure 8 | ²⁷ Al MAS-NMR spectrum of the solid obtained in example 6 |
| | Figure 9 | ²⁷ Al MAS-NMR spectrum of the solid obtained in example 7 |
| 20 | Figure 10 | IR spectrum of calcium aluminate, waterglass + NaOH and end product (after 8 min reaction time and after 80 min reaction time) |
| 25 | Figure 11a + b | Kinetics of polymerization. The figure shows the change over time in the IR absorption spectrum of a mixture of waterglass and calcium aluminate after activation with NaOH. Shown at the top is the change in the IR spectra in transmission between 650 and 2000 cm ⁻¹ , at the bottom in absorption between 650 and 1200 cm ⁻¹ . Absorptions above 1300 cm ⁻¹ come from water. Particularly evident is the transformation of an Si-O-Si bonding into an Al-O-Si bonding with a shift from 995 to 930-960 cm ⁻¹ as the dominant bonding. |
| 30 | Figure 12 | Overview of concrete applications. |

CLAIMS

-
1. **An inorganic polymer** containing Si, Al, Ca, alkali metal and O, characterized in that in
5 a ^{27}Al MAS-NMR spectrum of the solid, compared with the ^{27}Al MAS-NMR spectrum of
calcium aluminate, there is an additional signal whose chemical shift lies between that
of the main peak of calcium aluminate and the calcium aluminate peak next upfield to
the main peak.
2. The inorganic polymer of claim 1, characterized in that in a solid-state IR spectrum it
has a band at about $950 - 910\text{ cm}^{-1}$.
- 10 3. The inorganic polymer of claims 1 and/or 2, characterized in that it has the following
composition:
- (a) waterglass: about 2.5 to about 12.5 wt%, (calculated as solid);
 - (b) alkali metal hydroxide: about 0.7 to about 7.0 wt%;
 - (c) water: about 6.8 to about 20 wt%;
 - 15 (d) calcium aluminate: about 10 to about 70 wt%; and optionally
 - (e) aggregates: 0 to about 80 wt%, and/or
 - (f) additives: 0 to about 10 wt%,
- with the proviso that the amounts add up to 100 wt%.
4. The inorganic polymer of at least one of claims 1 to 3, characterized in that it has a
20 molar ratio of alkali metal cations to calcium of about 1:1 to about 1:5.
5. **A method for producing the inorganic polymer** of claim 1 or 2, comprising or
consisting of the following steps:
- (a) providing waterglass, alkali metal hydroxide, water, calcium aluminate
 - (b) mixing or contacting the substances from step (a), and optionally
 - 25 (c) curing the mixture from step (b).
6. The method of claim 5, characterized in that the curing is carried out at temperatures in
the range from about 25 to about 40°C .
7. **A composite material** comprising or consisting of
- (a) the inorganic polymer of claim 1 or 2 and
 - 30 (b) at least one aggregate and/or additive.
8. The composite material of claim 7, characterized in that the aggregates are selected
from the group consisting of sand, coarse broken stone, finely ground quartz, rubber,
organic polymers, wood, fibers, fabrics, salts, pollutants, radioactive wastes, and

mixtures thereof.

9. The composite material of claim 8, characterized in that the aggregate comprises marine sand, desert sand or fine sand having a mean particle diameter of $\leq 150 \mu\text{m}$.
10. The composite material of claim 7, characterized in that the additives are selected from the group consisting of iron phosphate, calcium phosphate, magnesium phosphate, iron oxides, lead oxides, BaSO_4 , MgSO_4 , CaSO_4 , Al_2O_3 , metakaolin, kaolin, inorganic pigments, wollastonite, rockwool, and mixtures thereof.
11. The composite material of at least one of claims 6 to 10, characterized in that it comprises or consists of
 - (a) about 20 to about 80 wt% of inorganic polymers and
 - (b) about 80 to about 20 wt% of aggregates and/or additives.
12. The composite material of at least one of claims 6 to 11, characterized in that it is an adhesive bonding agent, a coating material, a binder, a material for 3D printing, a fiber composite, a wood composite, a ceramic, a concrete substitute or a cement substitute.
13. **A method for producing a composite material**, comprising or consisting of the following steps:
 - (a) providing waterglass, alkali metal hydroxide, water, calcium aluminate,
 - (b) providing at least one aggregate and/or additive,
 - (c) mixing or contacting the substances from steps (a) and (b), and
 - (d) curing the mixture from step (c).
14. **The use of the inorganic polymers** as claimed in at least one of claims 1 to 4 for producing adhesive bonding agents, coating materials, binders, materials for 3D printing, fiber composites, wood composites, ceramics, concrete substitutes or cement substitutes.
15. The use of claim 14, characterized in that the inorganic polymers are used in amounts of about 5 to about 80 wt%.

Figures (12)

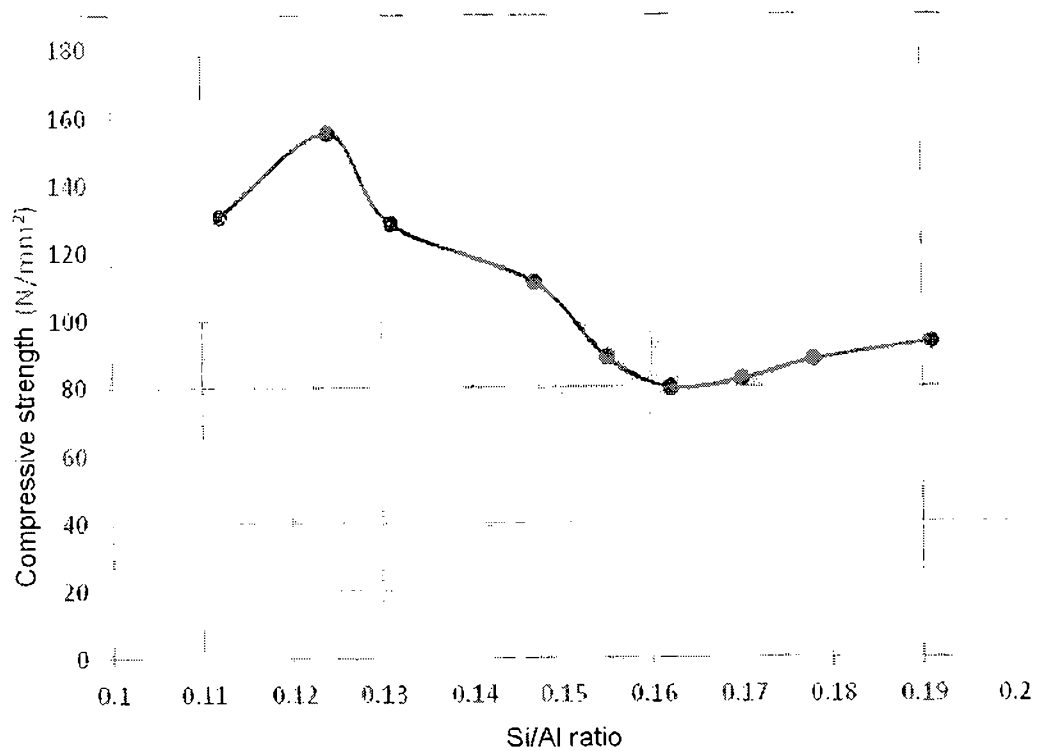


Figure 1/12

2/12

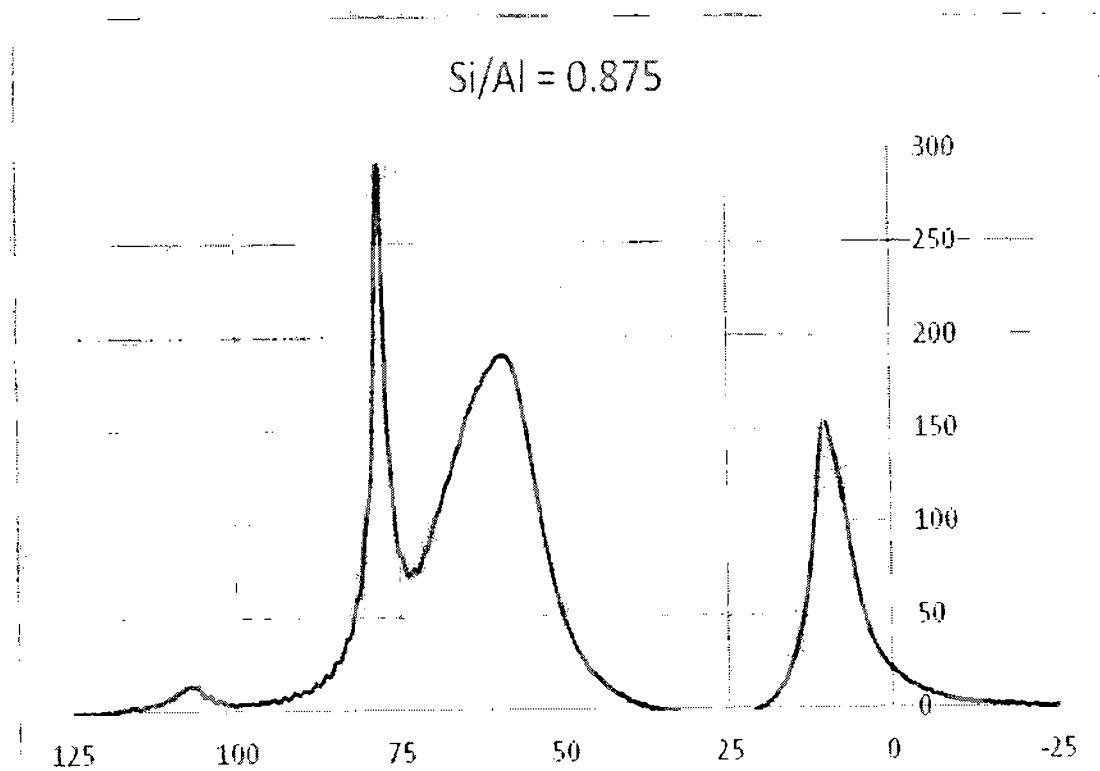


Figure 2/12

3/12

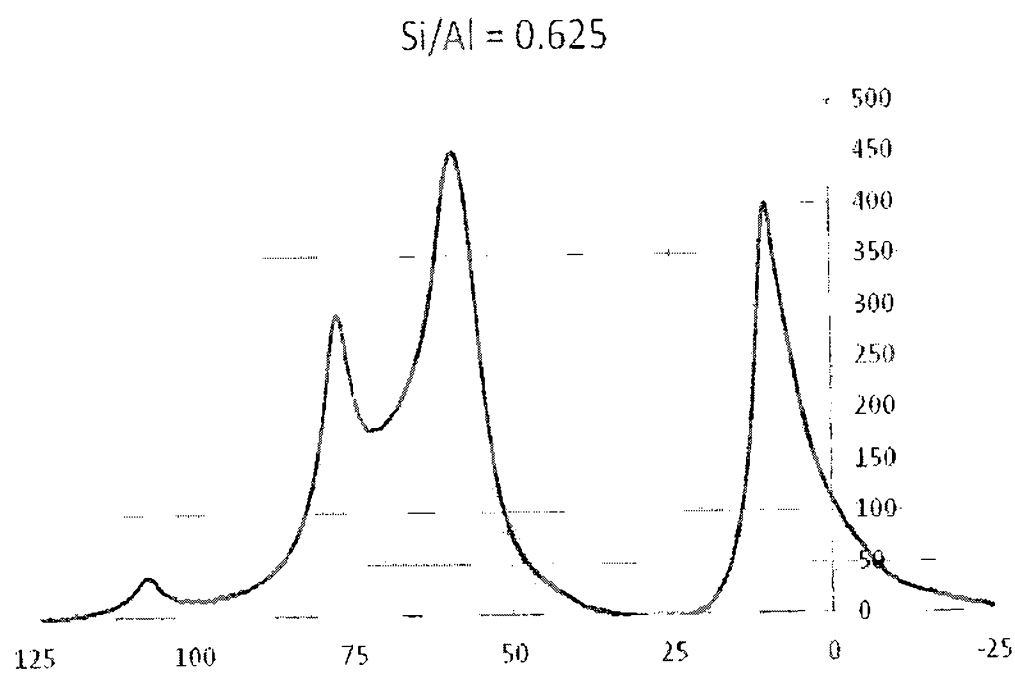


Figure 3/12

4/12

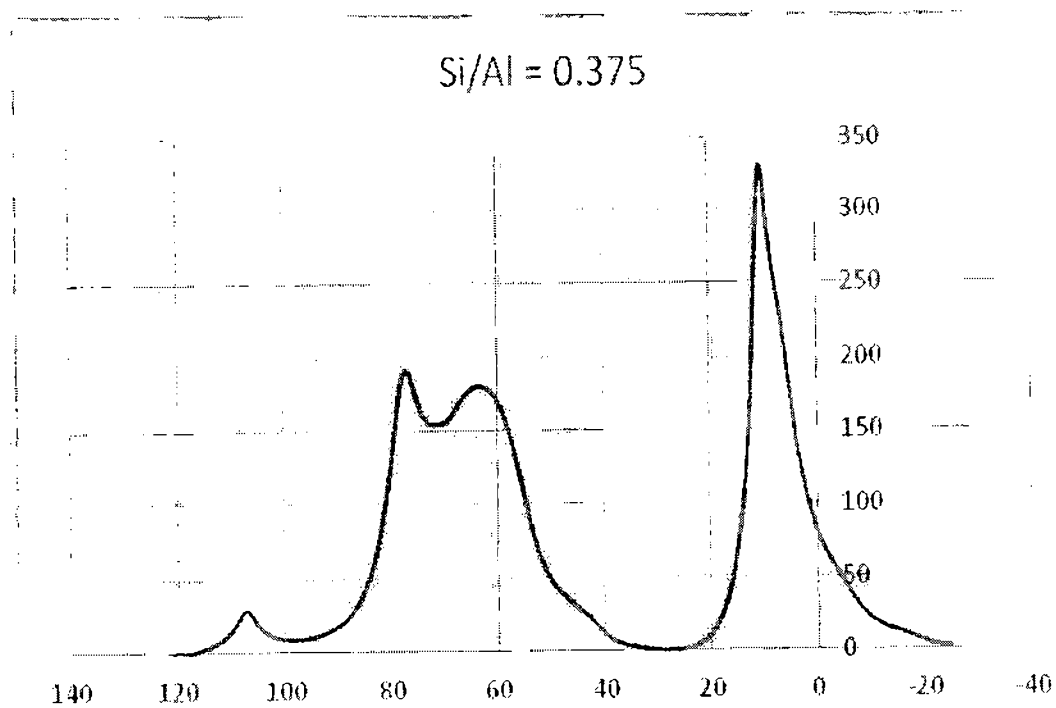


Figure 4/12

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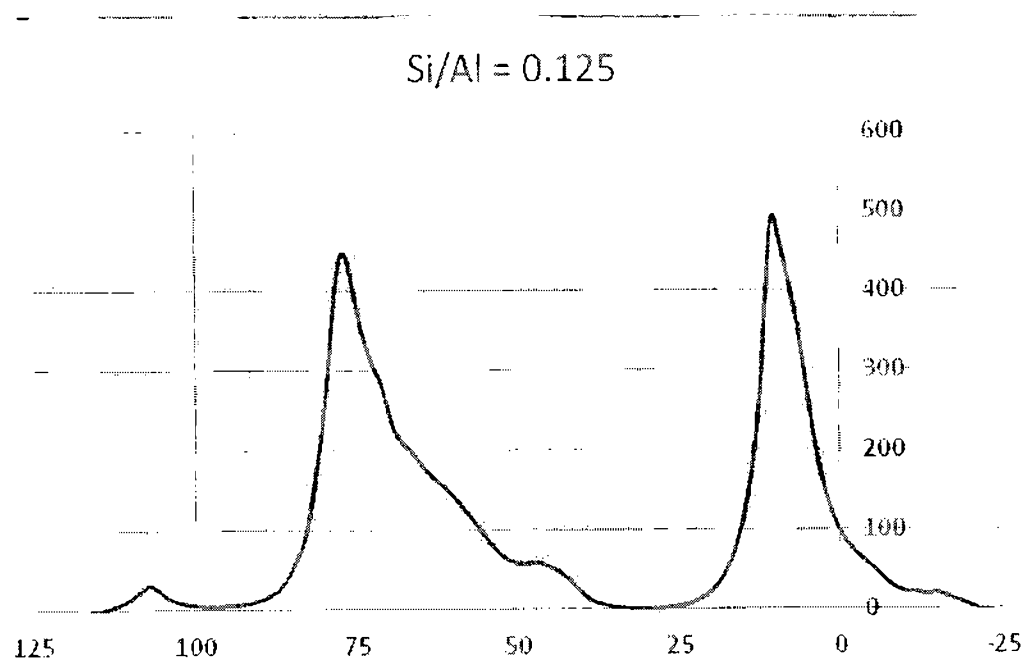


Figure 5/12

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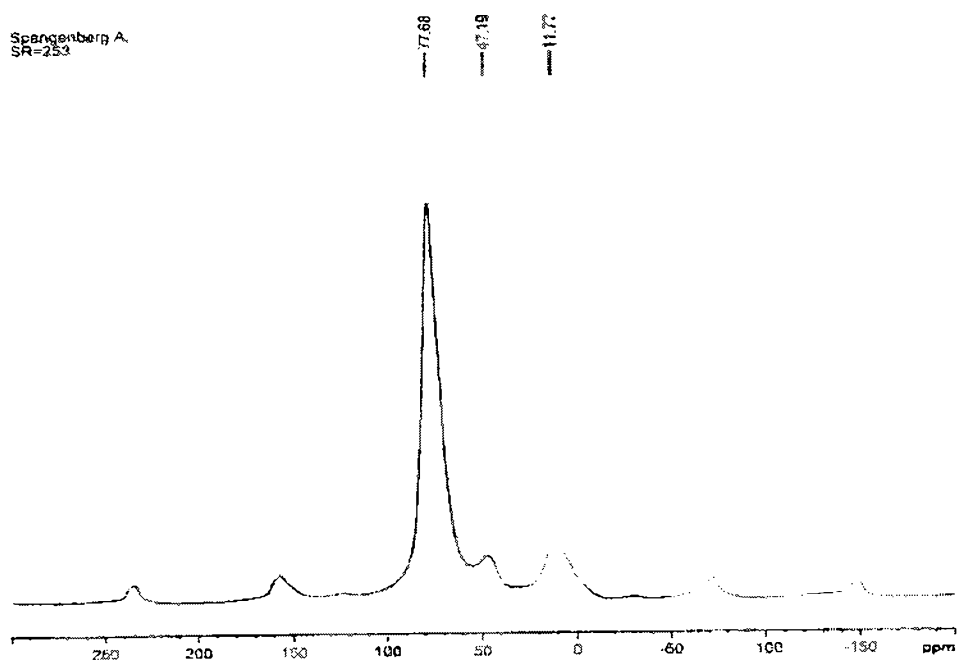


Figure 6/12

7/12

Spangenberg B1.
SR#253

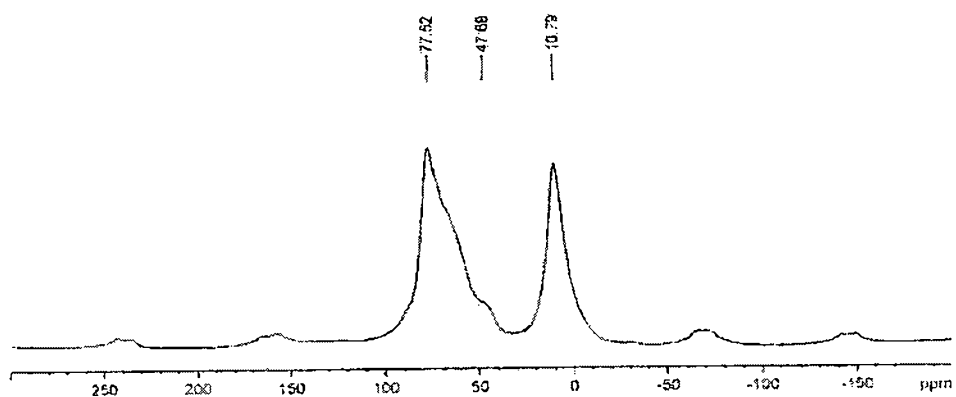


Figure 7/12

8/12

Spangenberg C1 MAS: 8 kHz
SP-253

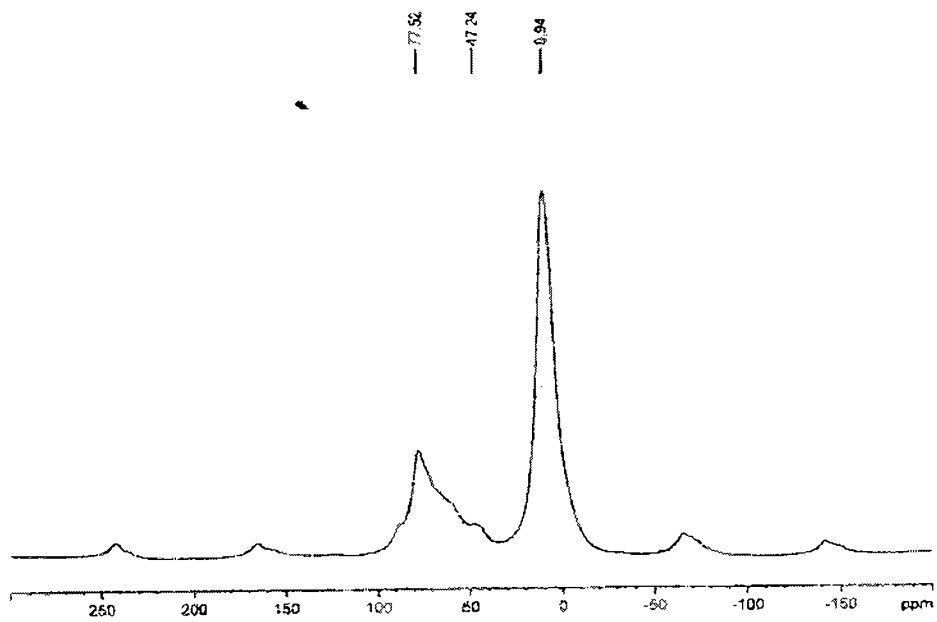


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Spangenberg D1.
SR-253

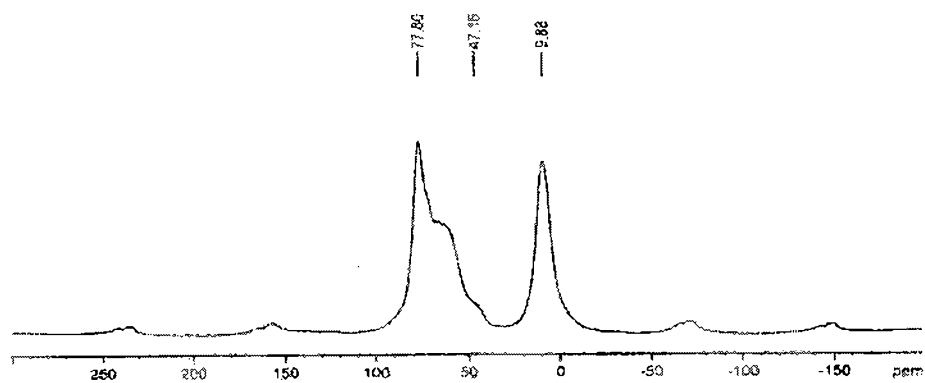


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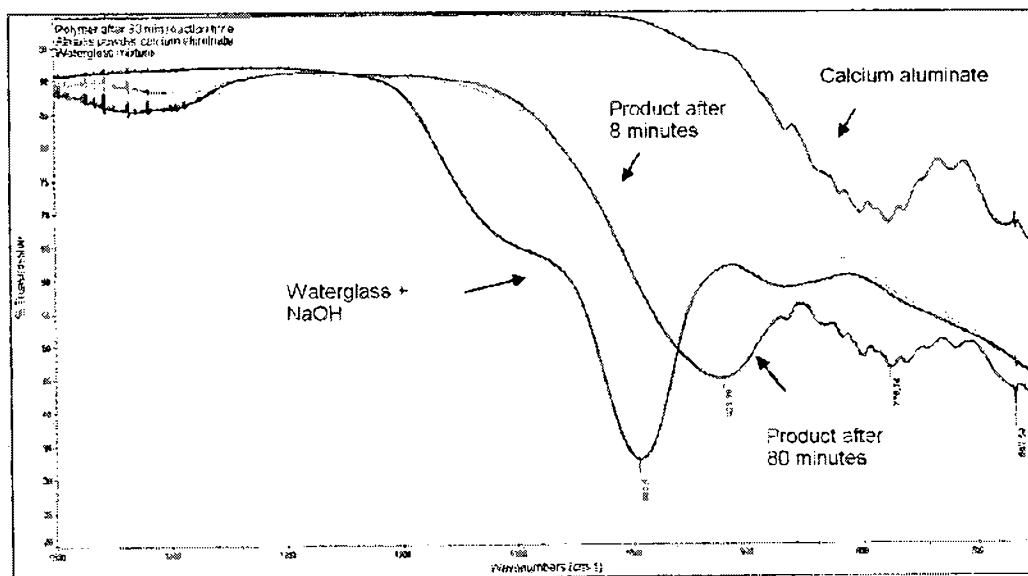


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Figure 11A

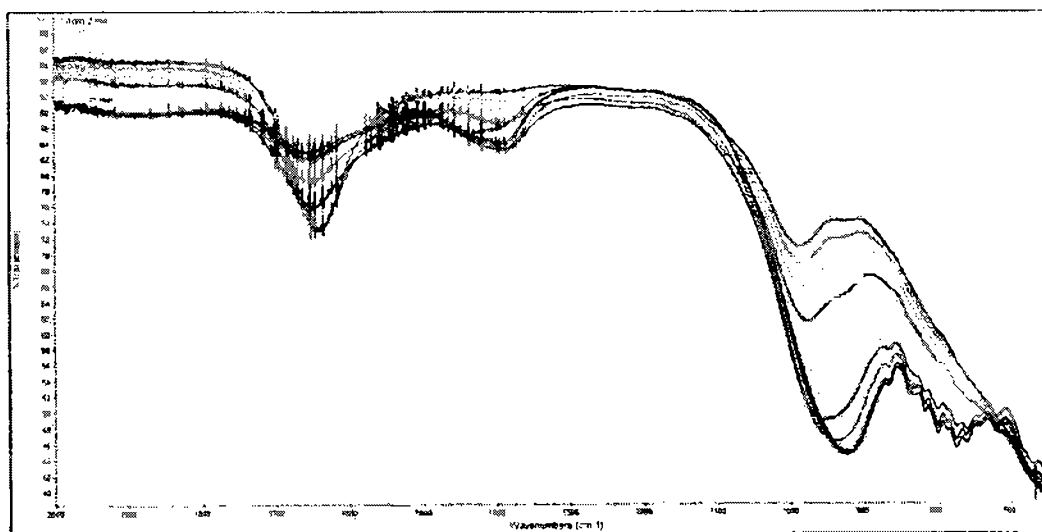


Figure 11B

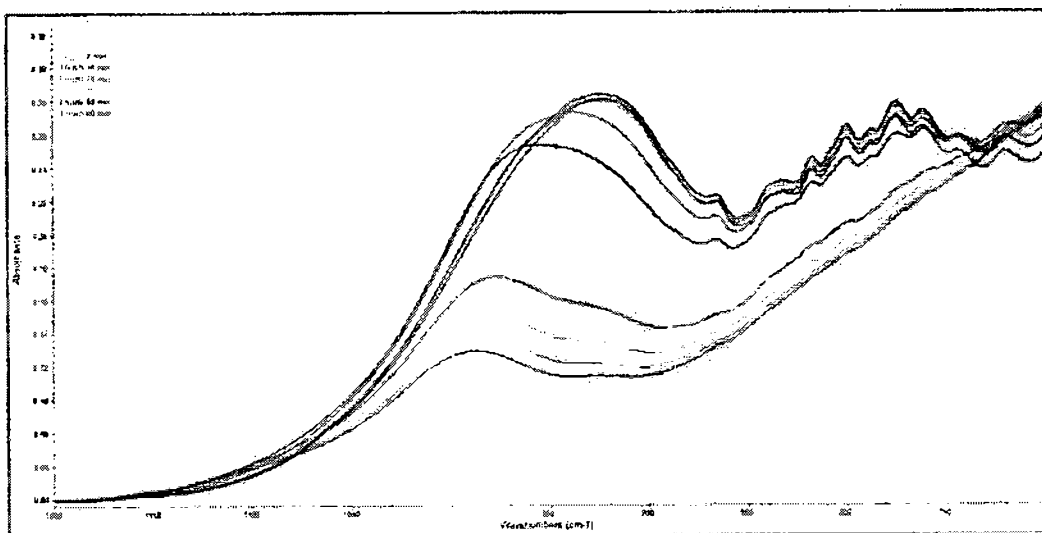


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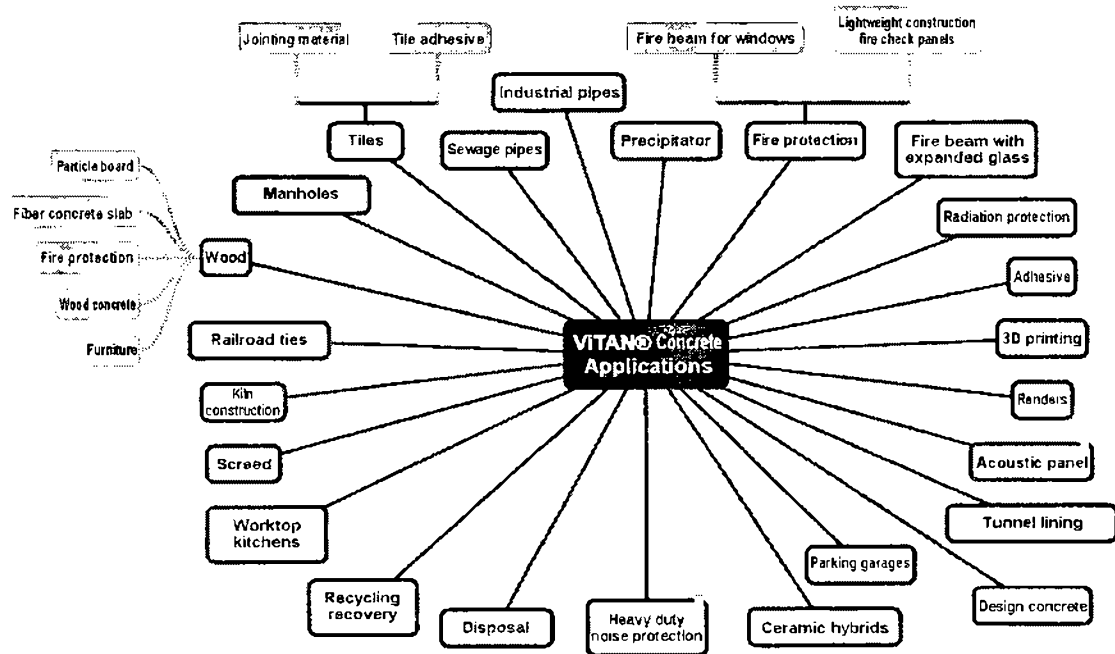


Figure 12/12



Abstract

The invention relates to a new inorganic polymer which is based on modified water glass, is characterized by numerous unusual properties and can be used as a substitute for, for
5 example, concrete, cement and ceramics.