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Description

The invention relates to a method for improving the strength and impermeability of soils and engineering structures, particularly ducts and pipelines. In the specification and claims the terms "soil" and "engineering structure" are interpreted in the broadest sense; these terms also covering various storage tanks, tunnels, natural and artificial cavities, rocks, etc., and soils surrounding them.

It is well known that most of the engineering structures, such as underground ducts, pipelines and storage tanks, do not possess the required impermeability characteristics, owing, in part, to the inappropriate quality of the construction materials and, in part, to defects in the impermeability of pipe connections, or because of damages in the engineering structures upon the effect of ageing, traffic, etc. It is also well known that the repair of engineering structures, particularly underground ducts and pipelines, requires enormously high investments and labour, and in most cases the result is insufficient.

US-A-4 056 837 describes a method of consolidating soils by a hardener being a mixture of an aqueous solution of water glass and an acidic reactant. This mixture is injected into the soil. Acids, aldehydes, esters, such as glycerin diacetate, and amides, such as formamide, are used as an acidic reactant. The mixture can contain a gel control agent, too. Suitable gel control agents include inorganic salts, organic salts and mono- or polyhydric alcohols.

FR-A-2 533 579 discloses a method for improving the impermeability of soils by contacting a solution of water glass with fluorosilicic acid in the presence of a water soluble, organic polymer forming a hydrogel and in the presence of a crosslinking agent, such as salts of iron.

Hungarian patent No. 153,975 describes a simple and rapid method for improving the strength and impermeability of soils and engineering structures. According to this method, water glass or a water glass-containing medium is applied into or onto the article to be treated, and then the water glass is exposed to the effect of hydrogen fluoride, silicon tetrafluoride and/or hydrogen silicofluoride. Water glass, when contacted with a gaseous fluoride, rapidly gellifies and completely plugs the leakages, cracks and cavities. When this method is utilized to render underground engineering structures (such as ducts or storage tanks) water-tight, it is an additional advantage that water glass which enters the soil through the cracks solidifies as well, improving thereby the embedding of the structure and strengthening the surrounding soil. Fluoride gases have the additional advantage that they improve the corrosion resistance of concrete and reinforced concrete elements.

Despite of its numerous advantages, this method has had only a very narrow application in practice. The widespread application of this method is considerably restricted by the fact that hydrogen fluoride and silicon tetrafluoride are strongly poisonous, thus their use is prohibited in most of the countries due to environmental protection reasons. It is a further disadvantage that the resulting silicic acid gel is not elastic, thus it cannot follow the movements of the article or soil treated. Since the swellability of silicic acid gels is inappropriate, they cannot plug the new cracks formed in the gel upon movement.

In order to avoid the above disadvantages methods have been elaborated in which aqueous acids are utilized to gellify water glass instead of the poisonous acidic fluoride gases, and, to ensure the required elasticity and swellability of the gel, synthetic organic polymers are formed in the gel structure in parallel with the gel formation. Such methods are disclosed in Hungarian patents Nos. 186,586 and 189,250, in the published Hungarian patent application No. 1095/84, as well as in the published international patent application No. PCT/HU-85/00027. A common feature of the techniques disclosed therein is that the gel is formed by admixing two liquids with one another: one of the liquids comprises water glass and organic polymer-forming components, such as polymerizable monomers or a linear polymer to be cross-linked, which are compatible with water glass, whereas the other liquid is an aqueous solution of the acid required to gellify water glass and of the substances required to perform polymerization or cross-linking, such as catalyst, initiator, cross-linking agent, etc.

When the appropriate mixing of the two liquids is provided for, hydrogels of good quality, possessing appropriate strength, elasticity and swellability can be formed. However, with the so-called "filling-up" techniques generally applied in soil strengthening and in the water-tight plugging of the defects of engineering structures (particularly underground ducts, pipelines and tunnels) the appropriate mixing of the two liquids generally cannot be ensured throughout the whole section of the soil or engineering structure to be treated. The essence of filling-up technique is that first one of the two liquids, generally the water glass-containing solution, is applied onto the area to be treated e.g. in such a way that the liquid is filled into the duct section to be repaired, and then, after an appropriate waiting time, the excess of the first liquid is optionally removed, and the second liquid, generally the aqueous solution comprising the acid and the substance required for polymerization, is introduced. Through the defect sites of uneven dimensions the liquids enter the soil at an uneven rate, and, as a consequence of the uneven pore and cavity structure of

the soil, their movement rate in the soil is uneven, too. This involves that there are considerable local variations between the mixing ratios of the two liquids. This means that at certain sites gel cannot be formed at all in the first filling-up cycle, whereas at other sites, depending on the actual mixing ratio, considerable local variations in gel quality can be observed. Thus e.g. when a water glass solution is introduced first and then an aqueous solution which cannot form gel per se upon neutralization (such as an aqueous solution comprising an acid other than hydrogen silicofluoride and additional non-gelling components, e.g. cross-linking agents, polymerization catalysts, etc.) is applied onto the water glass solution, no gel is formed from the portions of the acidic solution which are in excess or which cannot be mixed with the water glass solution. These portions of the acidic solution flow through the soil section, more or less impregnated with water glass, without utilization, cutting channel-like passages through the soil. These channel-like passages render the gel structure more or less open to water exfiltration, thus the water tightness of the gel formed in the first filling-up cycle is inappropriate. A gel with the required water tightness can be obtained only by repeating the filling-up cycle two or more times, which decreases the efficiency of the process and involves a considerable increase in operation costs.

When each of the two liquids comprises a component which gellifies upon neutralization (such as one of the liquids comprises water glass and the other comprises a monomer or oligomer which polymerizes when contacting it with an alkali), uneven mixing of the two liquids has the consequence that, instead of obtaining a gel with homogeneous microstructure in which the organic and mineral parts are amalgamated, a gel consisting of easily distinguishable discrete mineral (silicate) and organic (polymer) blocks, i.e. a gel with inhomogeneous microstructure is formed. The strength and swelling characteristics of the organic and mineral blocks greatly differ from one another. These gels with inhomogeneous microstructure combine essentially all the disadvantages of the completely mineral and completely organic gels: at the mineral blocks the gel is non-elastic, rigid, and cracks upon soil movements, whereas at the organic blocks the gel is too soft and cannot withstand the damaging effects of higher strains.

Uneven mixing outlined above is a necessary concomitant of all filling-up techniques which apply two liquids. In order to avoid the disadvantageous consequences of uneven mixing a pair of gel-forming liquids is required, in which

- gel can be formed from both liquids upon a chemical reaction, and
- the properties of the gels formed separately from the two liquids are highly similar.

Furthermore, in order to decrease the rigidity of the gel and to ensure an appropriate swellability, a substance is required which does not polymerize and gellify per se, but is able to be built into the gel structure wherein it exerts a plasticizing effect. In order to decrease the disadvantageous consequences of uneven mixing it is desirable that this substance should be able to reach by diffusion even those liquid portions which do not mix with one another.

Now it has been found that the above requirements can be fulfilled by using a pair of liquids in which one of the liquids is an aqueous solution of water glass optionally also comprising one or more natural or synthetic oligomer or polymer, and the other liquid is a silicic acid sol in which the dispersion medium consists, at least in part, of a water-miscible organic liquid which is able to react with the alkali content of the water glass solution, gellifying thereby the water glass.

The gels formed from the water glass solution upon neutralizing its alkali content and from the silicic acid sol upon reacting the organic dispersion medium are equally silicate gels with very close physical properties. Both the alkali present in the water glass solution and the reactive organic dispersion medium present in the silicic acid sol are able to move by diffusion, thus, after a certain period of time, the reaction proceeds even in those liquid portions which have not been mixed with one another or in which mixing has been inappropriate. It has also been found that the organic dispersion medium of the silicic acid sol immediately builds into the gel structure in parallel with gel formation and exerts there a plasticizing effect, i.e. leads to the formation of a more swelling and more deformable gel. As a net result, upon the reaction of the alkali present in the water glass solution and the organic dispersion medium present in the silicic acid sol, which proceeds immediately in the well-mixed liquid portions and within a diffusion-controlled period in the less or non-mixed liquid portions, a silicate gel is formed from both liquids which contains the organic dispersion medium or its reaction product entrapped into the gel structure. Gel formation proceeds even at those sites where the mixing of the two liquids is inappropriate or the mixing ratio differs from the pre-adjusted value, and the properties of the gel blocks formed at the sites of inhomogeneous mixing well approach to those of the gel blocks formed from homogeneous mixtures.

Based on the above, the invention relates to a method for improving the strength and impermeability of soils and engineering structures by forming a silicate gel. According to the invention one proceeds in such a way that in one step

- an alkaline water glass solution comprising water glass in an amount of 15-40 % by weight calculated as dry substance optionally together with one or more natural or synthetic oligomer and/or polymer in an amount not exceeding the dry substance content of the water glass solution, and in another step
- a silicic acid sol comprising SiO_2 in an amount of 5-50 % by weight, preferably 10-45 % by weight, calculated as dry substance in which 10-100 % by volume of the dispersion medium consists of a water-miscible organic liquid capable of reacting with an alkali while separation of silicic acid, the organic liquid being diethylene glycol diacetate, glycerol diacetate, ethylene carbonate, ethyl urethane or formamide,

are applied onto or into the soil or engineering structure to be treated, and the liquids applied are allowed to gellify.

The term "water glass" as used in the specification and claims covers alkali metal (Na, K) and ammonium water glasses and mixtures thereof.

The aqueous solution of water glass may comprise natural and/or synthetic oligomers and/or polymers. Of the natural oligomers and polymers hydrolysed proteins and natural latex, whereas of the synthetic oligomers and polymers polyvinyl alcohol and butadiene latex are mentioned. Obviously, the oligomers or polymers applied should be alkali-resistant and compatible with the aqueous water glass solution. These polymers are entrapped into the gel structure either physically or chemically upon gel formation, and increase the deformation and swelling ability of the gel.

The silicic acid sols (so-called "organosols") applied in the method of the invention are known or can be prepared by known methods [R.K. Iler: Colloid Chemistry of Silica and Silicates; Cornell University Press, Ithaca, N.Y., pp. 90-95 (1955) and R.K. Iler: The Chemistry of Silica; John Wiley and Sons, N.Y., pp. 331-343 and 415-419 (1979)]. These sols comprise disperse silicic acid particles with a particle size of 3-200 nm, preferably 10-50 nm. The disperse silicic acid particles may be optionally pre-treated on their surface; mono- or polyvalent alcohols, alkylene oxide oligomers or polymers or Al^{3+} or Fe^{3+} ions can be attached, through the surface hydroxy groups, to the surface of these pre-treated silicic acid particles. The silicic acid sols comprising silicic acid particles pre-treated on their surface are known or can be prepared by known methods, e.g. as disclosed in the above text-books. According to our experiences silicic acid sols comprising silicic acid particles pre-treated on their surface provide better results than those comprising untreated silicic acid particles. The term "silicic acid sol" as used in the specification and claims covers sols comprising such pre-treated silicic acid particles as well.

At least 10 % by volume of the dispersion medium of the silicic acid sol should consist of a water-miscible organic liquid capable of reacting with alkaline agents. The term "water-miscible" refers to liquids with unrestricted water miscibility, i.e. which form stable mixtures with water at any ratio. Such organic liquids are, diethylene glycol diacetate, glycerol diacetate, ethylene carbonate, ethyl urethane and formamide. The remainder of the dispersion medium, if any, may consist of any organic liquid unrestrictedly miscible with both water and the organic liquids mentioned above and being indifferent towards alkaline agents; of them alcohols and ketones are to be mentioned. The dispersion medium may also contain water in an amount not exceeding 80 % by volume.

The invention is elucidated in detail by the aid of the following non-limiting Example.

Example

A defective duct section with a diameter of 300 mm, bordered by two shafts, is filled up first with 10 m³ of a concentrated aqueous water glass solution (Component A). The losses in water glass solution are supplemented in such a way that the height of the liquid does not drop below 1.5 m. After 30 minutes the liquid is pumped from the duct with a high performance pump within 5 seconds, and then 10 m³ of Component B with the composition given below are filled into the duct section:

Glucose diacetate	2 m ³
Ludox CL-X (a silicic acid sol comprising 46 % by weight of SiO_2 ; pH = 9.1, sold by E.I. DuPont de Nemours and Co., Wilmington, Delaware, USA)	3 m ³
Diethylene glycol monomethyl ether	1 m ³
Water	4 m ³

The liquid height is maintained at 1.5 m in the duct by supplementing Component B until exfiltration stops (for about 60 minutes). Thereafter the excess of Component B is pumped from the duct.

The quality of repair was checked by water pressure test. No reduction in water level could be observed, which means that the repair was perfect.

Claims

1. A method for improving the strength and impermeability of soils and engineering structure by forming a silicate gel, characterized in that
 - in one step an alkaline water glass solution comprising water glass in an amount of 15-40 % by weight, calculated as dry substance, optionally together with one or more natural or synthetic oligomer and/or polymer in an amount not exceeding the dry substance content of the water glass solution, and
 - in another step a silicic acid sol comprising SiO_2 in an amount of 5-50% by weight, preferably 10-45 % by weight, calculated as dry substance, in which 10-100% by volume of the dispersion medium consists of a water-miscible organic liquid capable of reacting with an alkali while separation of silicic acid, the organic liquid being diethylene glycol diacetate, glycerol diacetate, ethylene carbonate, ethyl urethane or formamide,
 are applied onto or into the soil or engineering structure to be treated, and the liquids applied are allowed to gellify.
2. A method as claimed in claim 1, characterized in that the silicic acid sol comprises silicic acid particles with mono- or polyvalent alcohols, alkylene oxide oligomers or polymers or Al^{3+} or Fe^{3+} ions bound to their surface.

Patentansprüche

1. Verfahren zur Verbesserung der Festigkeit und Wasserundurchlässigkeit von Böden und Baukörpern durch Bildung eines Silikatgels, dadurch gekennzeichnet, daß
 - in einer Stufe eine alkalische Wasserglaslösung, welche Wasserglas in einer Menge von 15-40 Gew.-%, berechnet als Trockensubstanz, umfaßt, wahlweise zusammen mit einem oder mehreren natürlichen oder synthetischen Oligomeren und oder Polymeren in einer den Trockensubstanzgehalt der Wasserglaslösung nicht übersteigenden Menge, und
 - in einer anderen Stufe ein Kieselsäuresol, welches SiO_2 in einer Menge von 5-50 Gew.-%, vorzugsweise 10-45 Gew.-%, berechnet als Trockensubstanz, umfaßt, in welchem 10-100 Vol.-% des Dispersionsmediums aus einer wassermischbaren organischen Flüssigkeit, die zu einer Reaktion mit einem Alkali unter Abtrennung von Kieselsäure fähig ist, bestehen, wobei die organische Flüssigkeit Diethylenglykoldiacetat, Glycerindiacetat, Ethylencarbonat, Ethylurethan oder Formamid ist,
 auf oder in den zu behandelnden Boden oder Baukörper auf/eingebracht werden, und das Gelieren der auf/eingebrachten Flüssigkeiten ermöglicht wird.
2. Verfahren nach Anspruch 1, dadurch gekennzeichnet, daß das Kieselsäuresol Kieselsäureteilchen mit an ihre Oberfläche gebundenen mono- oder polyvalenten Alkoholen, Alkylenoxidoligomeren oder -polymeren oder Al^{3+} - oder Fe^{3+} -Ionen umfaßt.

Revendications

1. Procédé pour améliorer la résistance mécanique et l'imperméabilité de sols et de structures d'édifices par formation d'un gel de silicate, caractérisé en ce qu'on applique
 - dans une étape, une solution alcaline d'un verre soluble, contenant un verre soluble en une quantité de 15 à 40 % en poids, le calcul étant effectué sur la base de la substance sèche, facultativement en association avec un ou plusieurs oligomères et/ou polymères naturels ou synthétiques en une quantité n'excédant pas la quantité de substance sèche présente dans la solution de verre soluble, et
 - dans une autre étape, un sol d'acide silicique comprenant du SiO_2 en une quantité de 5 à 50 % en poids, de préférence de 10 à 45 % en poids, le calcul étant effectué sur la base de la substance sèche, dans lequel 10 à 100 % en volume du milieu de dispersion consiste en un liquide organique miscible à l'eau capable de réagir avec une substance alcaline avec séparation simultanée d'acide silicique, le liquide organique étant le diacétate de diéthylèneglycol, le



The quality of repair was checked by water pressure test. No reduction in water level could be observed, which means that the repair was perfect.

Claims

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1. A method for improving the strength and impermeability of soils and engineering structure by forming a silicate gel, characterized in that

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- in one step an alkaline water glass solution comprising water glass in an amount of 15-40 % by weight, calculated as dry substance, optionally together with one or more natural or synthetic oligomer and/or polymer in an amount not exceeding the dry substance content of the water glass solution, and

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- in another step a silicic acid sol comprising SiO_2 in an amount of 5-50% by weight, preferably 10-45 % by weight, calculated as dry substance, in which 10-100% by volume of the dispersion medium consists of a water-miscible organic liquid capable of reacting with an alkali while separation of silicic acid, the organic liquid being diethylene glycol diacetate, glycerol diacetate, ethylene carbonate, ethyl urethane or formamide,

are applied onto or into the soil or engineering structure to be treated, and the liquids applied are allowed to gellify.

20 2. A method as claimed in claim 1, characterized in that the silicic acid sol comprises silicic acid particles with mono- or polyvalent alcohols, alkylene oxide oligomers or polymers or Al^{3+} or Fe^{3+} ions bound to their surface.

Patentansprüche

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1. Verfahren zur Verbesserung der Festigkeit und Wasserundurchlässigkeit von Böden und Baukörpern durch Bildung eines Silikatgels, dadurch gekennzeichnet, daß

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- in einer Stufe eine alkalische Wasserglaslösung, welche Wasserglas in einer Menge von 15-40 Gew.-%, berechnet als Trockensubstanz, umfaßt, wahlweise zusammen mit einem oder mehreren natürlichen oder synthetischen Oligomeren und oder Polymeren in einer den Trockensubstanzgehalt der Wasserglaslösung nicht übersteigenden Menge, und

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- in einer anderen Stufe ein Kieselsäuresol, welches SiO_2 in einer Menge von 5-50 Gew.-%, vorzugsweise 10-45 Gew.-%, berechnet als Trockensubstanz, umfaßt, in welchem 10-100 Vol.-% des Dispersionsmediums aus einer wassermischbaren organischen Flüssigkeit, die zu einer Reaktion mit einem Alkali unter Abtrennung von Kieselsäure fähig ist, bestehen, wobei die organische Flüssigkeit Diethylenglykoldiacetat, Glycerindiacetat, Ethylencarbonat, Ethylurethan oder Formamid ist,

auf oder in den zu behandelnden Boden oder Baukörper auf/eingebracht werden, und das Gelieren der auf/eingebrachten Flüssigkeiten ermöglicht wird.

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2. Verfahren nach Anspruch 1, dadurch gekennzeichnet, daß das Kieselsäuresol Kieselsäureteilchen mit an ihre Oberfläche gebundenen mono- oder polyvalenten Alkoholen, Alkylendioxdilomeren oder -polymeren oder Al^{3+} - oder Fe^{3+} -Ionen umfaßt.

45 Revendications

1. Procédé pour améliorer la résistance mécanique et l'imperméabilité de sols et de structures d'édifices par formation d'un gel de silicate, caractérisé en ce qu'on applique

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- dans une étape, une solution alcaline d'un verre soluble, contenant un verre soluble en une quantité de 15 à 40 % en poids, le calcul étant effectué sur la base de la substance sèche, facultativement en association avec un ou plusieurs oligomères et/ou polymères naturels ou synthétiques en une quantité n'excédant pas la quantité de substance sèche présente dans la solution de verre soluble, et

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- dans une autre étape, un sol d'acide silicique comprenant du SiO_2 en une quantité de 5 à 50 % en poids, de préférence de 10 à 45 % en poids, le calcul étant effectué sur la base de la substance sèche, dans lequel 10 à 100 % en volume du milieu de dispersion consiste en un liquide organique miscible à l'eau capable de réagir avec une substance alcaline avec séparation simultanée d'acide silicique, le liquide organique étant le diacétate de diéthylèneglycol, le



diacétate de glycérol, le carbonate d'éthylène, l'éthyluréthane ou le formamide, sur ou dans le sol ou la structure d'édifice à traiter, et on laisse la gélification des liquides appliqués s'effectuer.

- 5 2. Procédé suivant la revendication 1, caractérisé en ce que le sol d'acide silicique comprend des particules d'acide silicique avec des alcools mono- ou polyvalents, des oligomères ou polymères d'oxyde d'alkylène ou des ions Al^{3+} ou Fe^{3+} liés à leur surface.

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