SURFACE -TREATED CALCIUM CARBONATE AND ITS USE IN WATER PURIFICATION AND FOR THE DEWATERING OF SLUDGES AND SEDIMENTS

The invention relates to a process for the purification of water and/or dewatering of sludges and/or sediments~~, to the use of a surface-treated calcium carbonate for water purification and/or dewatering of sludges and/or sediments, as well as to the use of a surface-treated calcium carbonate for reducing the amount of polymeric flocculation aids in water and/or sludges and/or sediments and to a composite material comprising a surface-treated calcium carbonate and impurities originated from different sources obtainable by said process~~.

Water pollution has posed a serious problem all over the world. In this regard, water pollution is suggested as being the leading cause of death and diseases in developing countries but also industrialized countries continue struggling with such pollution problems. In general, water, sludges and sediments are referred to as being polluted when impaired by anthropogenic contaminants and either does not support a human use, such as serving as drinking water, and/or has negative impacts on aquatic and/or land based flora and fauna.

The specific contaminants or impurities leading to pollution in water, sludges and sediments, include a wide variety of chemical substances, pathogens and physical or sensory changes such as elevated temperature and discoloration. In this regard, the chemical contaminants may include organic substances as well as inorganic substances. In particular, many of the inorganic components may also be naturally occurring (calcium salts, sodium salts, manganese salts etc.) so that their concentration is often the key in determining what is a natural water, sludge, or sediment component and what is a contaminant. Sources of such water, sludge or sediment pollutions typically originate from urban waste waters, i.e. domestic waste water or a mixture of domestic waste water with industrial waste water and/or run-off rain water, as well industrial waste waters, i.e. any waste water which is discharged from premises used for carrying on any trade or industry.

particles. Thus, the presence of anionic monomer units is not excluded as long as there are still sufficient cationic monomer units providing a positive overall charge. The same applies for amphotheric polymers which provide for an overall positive charge when bound to the calcium carbonate particles.

The term "accessible surface area" in the meaning of the present invention refers to the surface of the calcium carbonate particle that is accessible or exposed to the cationic polymer applied by mixing and/or coating techniques known to the skilled person and thereby forming a monolayer of cationic polymer on the surface of the calcium carbonate particle. In this regard, it should be noted that the amount of cationic polymer required for full saturation of the accessible surface area is defined as a monolayer concentration. Higher concentrations thus can be chosen thereby forming bilayered or multi-layered structures on the surface of the calcium carbonate particle. Such monolayer concentrations can be readily calculated by the skilled person, based on the publication of Papirer, Schultz and Turchi (Eur. Polym. J., Vol. 20, No. 12, pp. 1155-1158, 1984).

~~Another aspect of the present invention is directed to the use of a surface-treated calcium carbonate for water purification and/or dewatering of sludges and/or sediments, wherein at least 1 % of the accessible surface area of the calcium carbonate is covered by a coating comprising at least one cationic polymer. A further aspect of the present invention is directed to the use of a surface-treated calcium carbonate for reducing the amount of polymeric flocculation aids in water and/or sludges and/or sediments, wherein at least 1 % of the accessible surface area of the calcium carbonate is covered by a coating comprising at least one cationic polymer.~~

It is preferred that the surface-treated calcium carbonate comprises ground calcium carbonate and/or precipitated calcium carbonate ~~and/or surface-modified calcium carbonate, preferably surface-modified calcium carbonate~~. It is also preferred that the source of ground calcium carbonate (GCC) is selected from marble, chalk, calcite,

dolomite, limestone and mixtures thereof and/or the precipitated calcium carbonate (PCC) is selected from one or more of the aragonitic, vateritic and calcitic mineralogical crystal forms. It is further preferred that the calcium carbonate particles of the surface-treated calcium carbonate have a weight median particle diameter d_{50} value of between 0.04 μm and 250 μm, preferably between 0.06 μm and 225 μm, more preferably between 1 μm and 200 μm, even more preferably between 1 μm and 150 μm, and most preferably between 1 μm and 100 μm and/or the calcium carbonate particles of the surface-treated calcium carbonate have a specific surface area of from 1 to 250 m^2/g, more preferably from 20 to 200 m^2/g, even more preferably from 30 to 150 m^2/g and most preferably from 30 to 100 m^2/g. It is still further preferred that the coating of the surface-treated calcium carbonate comprises at least one cationic polymer having a positive charge density in the range of 1 mEq/g and 15 mEq/g, more preferably in the range of 2.5 mEq/g and 12.5 mEq/g and most preferably in the range of 5 mEq/g and 10 mEq/g and/or the coating of the surface-treated calcium carbonate comprises at least one cationic polymer in which at least 60 % of the monomer units have a cationic charge, preferably at least 70 %, more preferably at least 80 %, even more preferably at least 90 % and most preferably equal to 100 %. It is even further preferred that the coating of the surface-treated calcium carbonate comprises at least one cationic polymer having a weight average molecular weight M_w of below 1,000,000 g/mole, more preferably from 50,000 to 750,000 g/mole, even more preferably from 50,000 to 650,000 g/mole and most preferably from 100,000 to 300,000 g/mole. It is also preferred that the coating of the surface-treated calcium carbonate comprises at least one cationic polymer being a homopolymer based on monomer units selected from the group consisting of diallyldialkyl ammonium salts; tertiary and quaternized amines; quaternized imines; ~~acrylamide; methacrylamide; N,N-dimethyl-acrylamide; acrylic acid; methacrylic acid; vinylsulfonic acid; vinyl-pyrrolidone; hydroxyl-ethyl-acrylate; styrene; methyl-methacrylate and vinyl-acetate;~~ preferably diallyldialkyl ammonium salts ~~and acrylic acid~~ and most preferably diallyldimethyl ammonium chloride ~~and acrylic acid~~. It is also preferred that the coating of the surface-treated calcium carbonate comprises at

least one cationic polymer being a copolymer based on monomer units selected from diallyldialkyl ammonium salts ~~and methacrylic acid~~ and comonomer units selected from the group consisting of acrylamide; methacrylamide; N,N-dimethyl acrylamide; acrylic acid; methacrylic acid; vinylsulfonic acid; vinyl pyrrolidone; hydroxyl ethyl acrylate; styrene; methyl methacrylate; vinyl acetate and mixtures thereof~~, preferably the monomer units are selected from diallyldialkyl ammonium salts and methacrylic acid and comonomer units selected from acrylamide and acrylic acid~~. It is further preferred that at least 10 % of the accessible surface area of the calcium carbonate is covered by a coating comprising a cationic polymer, preferably at least 20 % of the accessible surface area, more preferably at least 30 %, even more preferably at least 40 % and most preferably at least 50 % of the accessible surface area. It is still further preferred that the surface-treated calcium carbonate is in powder form and/or in the form of granules or in the form of slurry. In a further embodiment the surface-treated calcium carbonate is used in combination with at least one polymeric flocculation aid. The polymeric flocculation aid has a weight average molecular weight M_w in the range from 100,000 to 10,000,000 g/mole, preferably in the range from 300,000 to 5,000,000 g/mole, more preferably in the range from 300,000 to 1,000,000 g/mole and most preferably in the range from 300,000 to 800,000 g/mole and/or the polymeric flocculation aid is non-ionic or ionic, preferbly a cationic or anionic polymer selected from polyacrylamides, polyacrylates, poly(diallyldimethylammonium chloride), polyethyleneimines, polyamines, starches and mixtures thereof.

~~A still further aspect of the present invention is directed to a composite material comprising a surface-treated calcium carbonate and impurities obtainable by the process.~~

~~When in the following reference is made to preferred embodiments or technical details of the inventive process for the purification of water and/or dewatering of sludges and/or sediments, it is to be understood that these preferred embodiments or~~

~~technical details also refer to the inventive use of the surface-treated calcium carbonate for water purification and/or dewatering of sludges and/or sediments, to the inventive use of the surface-treated calcium carbonate for reducing the amount of polymeric flocculation aids in water and/or sludges and/or sediments as well as to the composite material comprising the surface-treated calcium carbonate and impurities defined herein and vice versa (as far as applicable). If, for example, it is set out that the surface-treated calcium carbonate provided in the inventive process preferably comprises ground calcium carbonate and/or precipitated calcium carbonate and/or surface-modified calcium carbonate, also the inventive uses as well as the inventive composite material preferably comprise ground calcium carbonate and/or precipitated calcium carbonate and/or surface-modified calcium carbonate.~~

According to one preferred embodiment of the inventive process, the water and/or sludge and/or sediment of step a) is selected from industrial waste water, drinking water, urban waste water, sludge such as harbour sludge, river sludge, coastal sludge or digested sludge, waste water or process water from breweries or other beverage industries, waste water or process water in the paper industry, colour-, paints-, or coatings industry, agricultural waste water, slaughterhouse waste water, leather industry waste water and leather tanning industry.

According to another preferred embodiment of the inventive process, the at least one surface-treated calcium carbonate of step b) comprises ground calcium carbonate and/or precipitated calcium carbonate ~~and/or surface-modified calcium carbonate, preferably surface-modified calcium carbonate~~.

According to yet another preferred embodiment of the inventive process, the source of ground calcium carbonate (GCC) is selected from marble, chalk, calcite, dolomite, limestone and mixtures thereof and/or the precipitated calcium carbonate (PCC) is selected from one or more of the aragonitic, vateritic and calcitic mineralogical crystal forms.

polymer being a homopolymer based on monomer units selected from the group consisting of diallyldialkyl ammonium salts; tertiary and quaternized amines; quaternized imines; ~~acrylamide; methacrylamide; N,N-dimethyl acrylamide; acrylic acid; methacrylic acid; vinylsulfonic acid; vinyl pyrrolidone; hydroxyl ethyl acrylate; styrene; methyl methacrylate and vinyl acetate,~~ preferably diallyldialkyl ammonium salts ~~and acrylic acid~~ and most preferably diallyldimethyl ammonium chloride ~~and acrylic acid~~.

According to another preferred embodiment of the inventive process, the coating of the at least one surface-treated calcium carbonate comprises at least one cationic polymer being a copolymer based on monomer units selected from diallyldialkyl ammonium salts ~~and methacrylic acid~~ and comonomer units selected from the group consisting of acrylamide; methacrylamide; N,N-dimethyl acrylamide; acrylic acid; methacrylic acid; vinylsulfonic acid; vinyl pyrrolidone; hydroxyl ethyl acrylate; styrene; methyl methacrylate; vinyl acetate and mixtures thereof~~, preferably the monomer units are selected from diallyldialkyl ammonium salts and methacrylic acid and comonomer units selected from acrylamide and acrylic acid~~.

According to yet another preferred embodiment of the inventive process, at least 10 % of the accessible surface area of the calcium carbonate is covered by a coating comprising a cationic polymer, preferably at least 20 % of the accessible surface area, more preferably at least 30 %, even more preferably at least 40 % and most preferably at least 50 % of the accessible surface area.

According to one preferred embodiment of the inventive process, the at least one surface-treated calcium carbonate is in powder form and/or in the form of granules or in the form of slurry.

According to another preferred embodiment of the inventive process, the process further comprises step d) of contacting the water and/or sludge and/or sediment to be

Step b): provision of at least one surface-treated calcium carbonate

According to step b) of the process of the present invention, at least one surface-treated calcium carbonate is provided.

In accordance with the inventive process, at least 1 % of the accessible surface area of the calcium carbonate is covered by a coating comprising at least one cationic polymer.

In one preferred embodiment, the surface-treated calcium carbonate comprises ground (or natural) calcium carbonate (GCC) or precipitated (or synthetic) calcium carbonate (PCC) ~~or surface-modified calcium carbonate (MCC)~~. In another preferred embodiment, the surface-treated calcium carbonate comprises a mixture of at least two calcium carbonates selected from GCC, PCC and MCC. ~~For example, the surface-treated calcium carbonate comprises a mixture of GCC and PCC.~~ Alternatively, the surface-treated calcium carbonate comprises a mixture of GCC and MCC. Alternatively, the surface-treated calcium carbonate comprises a mixture of PCC and MCC.

~~In one especially preferred embodiment, the surface-treated calcium carbonate comprises surface-modified calcium carbonate (MCC).~~

Ground (or natural) calcium carbonate (GCC) is understood to be a naturally occurring form of calcium carbonate, mined from sedimentary rocks such as limestone or chalk, or from metamorphic marble rocks. Calcium carbonate is known to exist as three types of crystal polymorphs: calcite, aragonite and vaterite. Calcite, the most common crystal polymorph, is considered to be the most stable crystal form of calcium carbonate. Less common is aragonite, which has a discrete or clustered needle orthorhombic crystal structure. Vaterite is the rarest calcium carbonate

polymorph and is generally unstable. Ground calcium carbonate is almost exclusively of the calcitic polymorph, which is said to be trigonal-rhombohedral and represents the most stable of the calcium carbonate polymorphs.

Preferably, the source of the ground calcium carbonate is selected from the group comprising marble, chalk, calcite, dolomite, limestone and mixtures thereof. In a preferred embodiment, the source of the ground calcium carbonate is calcite.

The term "source" of the calcium carbonate in the meaning of the present invention refers to the naturally occurring mineral material from which the calcium carbonate is obtained. The source of the calcium carbonate may comprise further naturally occurring components such as magnesium carbonate, alumino silicate etc.

Additionally ~~or alternatively~~, the surface-treated calcium carbonate comprises a precipitated calcium carbonate (PCC). Calcium carbonate polymorphs of the PCC type often include, in addition to calcites, less stable polymorphs of the aragonitic-type, which has an orthorhombic, acicular crystal shape, and hexagonal vateritic-type, which has an even lower stability than aragonite. The different PCC forms may be identified according to their characteristic x-ray powder diffraction (XRD) peaks. PCC synthesis most commonly occurs by a synthetic precipitation reaction that includes a step of contacting carbon dioxide with a solution of calcium hydroxide, the latter being most often provided on forming an aqueous suspension of calcium oxide, also known as burnt lime, and the suspension of which is commonly known as milk of lime. Depending on the reaction conditions, this PCC can appear in various forms, including both stable and unstable polymorphs. Indeed, PCC often represents a thermodynamically unstable calcium carbonate material. When referred to in the context of the present invention, PCC shall be understood to mean synthetic calcium carbonate products obtained notably by carbonation of a slurry of calcium hydroxide, commonly referred to in the art as a slurry of lime or milk of lime when derived from finely divided calcium oxide particles in water.

Preferred precipitated calcium carbonate is selected from aragonitic, vateritic or calcitic mineralogical crystal forms or mixtures thereof.

~~Additionally or alternatively, said GCC or PCC may be surface-reacted to form a surface~~ modified calcium carbonate~~, which~~ is a material comprising GCC and/or PCC and an insoluble, at least partially crystalline, non-carbonate calcium salt extending from the surface of at least part of the calcium carbonate. Such surface-modified products may, for example, be prepared according to WO 00/39222, WO 2004/083316, WO 2005/121257, WO 2009/074492, EP 2 264 108 A1, EP 2 264 109 A1.

~~For example, the~~ surface-modified calcium carbonate is obtained by reacting a natural calcium carbonate and/or precipitated calcium carbonate with an acid and with carbon dioxide prior to the preparation of the surface-treated calcium carbonate, wherein the carbon dioxide is formed in situ by the acid treatment and/or is supplied from an external source. The acid treatment can be carried out with an acid having a pK_a at 25 °C of 6 or less. If the pK_a at 25 °C is 0 or less, the acid is preferably selected from sulphuric acid, hydrochloric acid, or mixtures thereof. If the pK_a at 25 °C is from 0 to 2.5, the acid is preferably selected from H_2SO_3, $M^+HSO_4^-$ (M^+ is an alkali metal ion selected from the group comprising sodium and potassium), H_3PO_4, oxalic acid or mixtures thereof. If the pK_a at 25 °C is from 2.5 to 6, the acid is preferably selected from acetic acid, formic acid, propanoic acid and mixtures thereof. ~~Furthermore, the subject-matters of EP 2 264 108 A1 and EP2 264 109 A1 relating to the acid treatment and the acid used for the acid treatment are hereby incorporated by reference in its entirety.~~

In an especially preferred embodiment, the calcium carbonate particles of the present surface-treated calcium carbonate have a weight median particle diameter d_{50} value of from 0.01 μm to 250 μm before surface treatment, preferably from 0.06 μm to

In the process of the present invention, the surface-treated calcium carbonate is covered by a coating comprising a homopolymer and/or a copolymer of the at least one cationic polymer.

In one preferred embodiment, the coating of the at least one surface-treated calcium carbonate comprises a homopolymer of the at least one cationic polymer. That is to say, the cationic polymer consists substantially, i.e. of equal or below than 99.5 wt.-%, of the respective monomer units.

In one preferred embodiment, only monomer units selected from the group consisting of diallyldialkyl ammonium salts, tertiary amines, quaternized amines, quaternized imines~~, acrylamide, methacrylamide, N,N-dimethyl acrylamide, acrylic acid, methacrylic acid, vinylsulfonic acid, vinyl pyrrolidone, hydroxyl ethyl acrylate, styrene, methyl methacrylate and vinyl acetate~~ are detectable in the homopolymer.

In one preferred embodiment of the present invention, the coating of the at least one surface-treated calcium carbonate comprises a homopolymer based on diallyldialkyl ammonium salt monomers. In one preferred embodiment, the diallyldialkyl ammonium salt monomers are diallyldimethyl ammonium chloride.

~~In another preferred embodiment of the present invention, the coating of the at least one surface-treated calcium carbonate comprises a homopolymer based on acrylic acid monomers.~~

In case the cationic polymer is a copolymer, it is appreciated that the copolymer comprises monomers copolymerizable with suitable comonomers. Preferably, the cationic polymer being a copolymer according to this invention comprises, preferably consists of, monomer units selected from diallyldialkyl ammonium salts ~~and methacrylic acid~~ and comonomer units selected from the group consisting of acrylamide, methacrylamide, N,N-dimethyl acrylamide, acrylic acid, methacrylic

acid, vinylsulfonic acid, vinyl pyrrolidone, hydroxyl ethyl acrylate, styrene, methyl methacrylate, vinyl acetate and mixtures thereof.

For example, the coating of the surface-treated calcium carbonate may comprise a cationic polymer as described as comb polymer in US 2009/0270543 A1. ~~The subject matter of US 2009/0270543 A1 relating to the polymer is hereby incorporated by reference in its entirety.~~

~~In one preferred embodiment, the cationic polymer is a copolymer prepared from 92 wt.-% methoxy polyethylene glycol methacrylate of molecular weight 2,000 g/mole and 8 wt.-% acrylic acid and at least partially neutralised by soda. In a further preferred embodiment, the cationic polymer is a copolymer prepared from 92 wt.-% methoxy polyethylene glycol methacrylate of molecular weight 2,000 g/mole and 8 wt.-% acrylic acid and totally neutralised by soda.~~

If the monomer and/or comonomer units of the homopolymer or copolymer are diallyldialkyl ammonium salts, they are preferably selected from the group consisting of diallyldimethyl ammonium bromide, diallyldimethyl ammonium chloride, diallyldimethyl ammonium phosphate, diallyldiethyl ammonium sulfate, diallyldiethyl ammonium bromide, diallyldiethyl ammonium chloride, diallyldiethyl ammonium phosphate, diallyldiethyl ammonium sulphate, diallyldipropyl ammonium bromide, diallyldipropyl ammonium chloride, diallyldipropyl ammonium phosphate and diallyldipropyl ammonium sulphate. In one preferred embodiment, the diallyldialkyl ammonium salt monomers are diallyldimethyl ammonium chloride monomers.

In an especially preferred embodiment, the cationic polymer is a homopolymer based on diallyldimethyl ammonium chloride (PolyDADMAC).

If the monomer and/or comonomer units of the homopolymer or copolymer are quaternized amines, they are preferably epichlorhydrin reaction products such as polyamine epichlorhydrin.

If the monomer and/or comonomer units of the homopolymer or copolymer are quaternized imines, they are preferably polyethyleneimine.

In one preferred embodiment, the cationic polymer of this invention being a copolymer comprising monomer units selected from diallyldialkyl ammonium salts and methacrylic acid, and acrylamide or acrylic acid as comonomer units.

For example, the coating of the at least one surface-treated calcium carbonate comprises a copolymer of the at least one cationic polymer, wherein the monomer and comonomer units are derivable from diallyldialkyl ammonium salts and acrylamide only. In one preferred embodiment, the cationic polymer being a copolymer of this invention comprises monomer and comonomer units derivable from diallyldimethyl ammonium chloride and acrylamide only. ~~Alternatively, the coating of the at least one surface-treated calcium carbonate comprises a copolymer of the at least one cationic polymer, wherein the monomer and comonomer units are derivable from methacrylic acid and acrylic acid only.~~

~~Additionally or alternatively, the coating of the at least one surface-treated calcium carbonate comprises a copolymer of the at least one cationic polymer, wherein the monomer and comonomer units are derivable from acrylic acid and acrylamide only.~~

Additionally, it is appreciated that the copolymer has preferably a comonomer content of more than 2.0 wt.-%, more preferably more than 5 wt.-%, yet more preferably more than 7.5 wt.-%. For example, the copolymer has preferably a comonomer content in the range between 2 wt.-% and 80 wt.-%, more preferably in the range between 5 wt.-% and 60 wt.-% and most preferably in the range between

7.5 wt.-% and 40 wt.-%. The weight percentage is based on the total weight of the copolymer.

In one preferred embodiment, the coating of the at least one surface-treated calcium carbonate comprises a copolymer, wherein the molar ratio of monomer units and comonomer units is from 5:1 to 1:5, more preferably from 4:1 to 1:4, even more preferably from 3:1 to 1:3 and most preferably from 3:1 to 1:1.

In one preferred embodiment, the cationic polymer comprises a mixture of at least two cationic polymers. Preferably, if the cationic polymer comprises a mixture of at least two cationic polymers, one cationic polymer is a homopolymer based on diallyldimethyl ammonium chloride. ~~Alternatively, if the cationic polymer comprises a mixture of at least two cationic polymers, one cationic polymer is a homopolymer based on acrylic acid.~~

~~In a further preferred embodiment, the cationic polymer comprises a mixture of two cationic polymers, wherein one cationic polymer is a homopolymer based on diallyldimethyl ammonium chloride and the other one is selected from the group consisting of a homopolymer based on acrylic acid, a copolymer based on diallyldimethyl ammonium chloride and acrylamide and a copolymer based on methacrylic acid and acrylic acid. Alternatively, if the cationic polymer comprises a mixture of two cationic polymers, wherein one cationic polymer is a homopolymer based on acrylic acid, the other one is selected from the group consisting of a homopolymer based on diallyldimethyl ammonium chloride, a copolymer based on diallyldimethyl ammonium chloride and acrylamide and a copolymer based on methacrylic acid and acrylic acid.~~

If the cationic polymer comprises a mixture of two cationic polymers, the molar ratio of the homopolymer based on diallyldimethyl ammonium chloride and the second cationic polymer is from 99:1 to 1:99, more preferably from 50:1 to 1:50, even more

preferably from 25:1 to 1:25 and most preferably from 10:1 to 1:10. In one especially preferred embodiment of the present invention, the molar ratio of the homopolymer based on diallyldimethyl ammonium chloride and the second cationic polymer is from 90:1 to 1:1, more preferably from 90:1 to 10:1 and most preferably from 90:1 to 50:1.

~~In another preferred embodiment, the molar ratio of the homopolymer based on acrylic acid and the second cationic polymer is from 99:1 to 1:99, more preferably from 50:1 to 1:50, even more preferably from 25:1 to 1:25 and most preferably from 10:1 to 1:10. In one especially preferred embodiment of the present invention, the mole ratio of the homopolymer based on acrylic acid and the second cationic polymer is from 90:1 to 1:1, more preferably from 90:1 to 10:1 and most preferably from 90:1 to 50:1.~~

The at least one cationic polymer is preferably present in the coating covering the calcium carbonate in a quantity such that the total weight of said at least one cationic polymer on the surface of the surface-treated calcium carbonate product is between 0.01% w/w and 80 % w/w of the calcium carbonate.

In one preferred embodiment, the at least one cationic polymer is present in the coating covering the calcium carbonate in a quantity such that the total weight of said at least one cationic polymer on the surface of the surface-treated calcium carbonate product is less than 80 % w/w, more preferably less than 60 % w/w and most preferably less than 50 % w/w of the calcium carbonate.

In another preferred embodiment, the at least one cationic polymer is present in the coating covering at least 1 % of the accessible surface area of the calcium carbonate in an amount of about 0.1 wt.-% to 30 wt.-%, more preferably of about 0.1 wt.-% to 20 wt.-%, even more preferably of about 0.2 wt.-% to 15 wt.-% and most preferably of about 0.2 wt.-% to 10 wt.-%, based on the dry weight of the calcium carbonate.

Alternatively, at least 10 % of the accessible surface area of the calcium carbonate particles is covered by a coating comprising the at least one cationic polymer. In a preferred embodiment, at least 20 % of the accessible surface area of the calcium carbonate particles is covered by a coating comprising the at least one cationic polymer, preferably at least 30 % of the accessible surface area, more preferably at least 40 % of the accessible surface area and most preferably at least 50 % of the accessible surface area. In another preferred embodiment, at least 75 % of the accessible surface area of the calcium carbonate particles is covered by a coating comprising the at least one cationic polymer. For example, at least 90 % of the accessible surface area of the calcium carbonate particles is covered by a coating comprising the at least one cationic polymer.

In one preferred embodiment, at least 75 % of the aliphatic carboxylic acid accessible surface area of the calcium carbonate particles is covered by a coating comprising a homopolymer based on diallyldimethyl ammonium chloride. ~~In another preferred embodiment, at least 75 % of the aliphatic carboxylic acid accessible surface area of the calcium carbonate particles is covered by a coating comprising a homopolymer based on acrylic acid.~~

In one preferred embodiment, the at least one cationic polymer has a solubility in water of above 50 g/100 ml of water, preferably of above 75 g/100 ml of water, even more preferably of above 100 g/100 ml of water and most preferably of above 150 g/100 ml of water. In one especially preferred embodiment, the at least one cationic polymer is readily soluble in water.

Preferably, the surface-treated calcium carbonate used in the present process is prepared by mixing the ground calcium carbonate and/or precipitated calcium carbonate and/or surface-modified calcium carbonate, preferably in form of slurry,

An anionic polyacrylamide, i.e. a polyacrylamide having a negative overall charge, can be obtained by introducing appropriate comonomer units, e.g. derived from (meth)acrylic acid.

A cationic polyacrylamide, i.e. a polyacrylamide having a positive overall charge, can be obtained by introducing appropriate comonomer units, e.g. derived from aminoalkyl(meth)acrylates such as dimethylaminomethyl(meth)acrylate, dimethylaminoethyl(meth)acrylate, dimethylaminopro-pyl(meth)acrylate, diethylaminomethyl(meth)acrylate, diethylaminoethyl(meth)acrylate or diethylaminopropyl(meth)acrylate which can be quaternized by alkyl halides.

In another preferred embodiment, polyacrylate is used as a preferred polymeric flocculation aid in the process of the present invention. Preferably, the polyacrylate is used as a cationic polymeric flocculation aid. More specifically, the polyacrylate used as a cationic polymeric flocculation aid is free of acrylamide.

Preferably, the polyacrylate contains at least 50 mol-%, more preferably at least 60 mol-%, even more preferably at least 75 mol-% monomer units derived from aminoalkyl(meth)acrylates such as dimethylaminomethyl(meth)acrylate, dimethylaminoethyl(meth)acrylate, dimethylaminopro-pyl(meth)acrylate, diethylaminomethyl(meth)acrylate, diethylaminoethyl(meth)acrylate or diethylaminopropyl(meth)acrylate which can be quaternized by alkyl halides.

Alternatively, the polymeric flocculation aid may be a polymer as described as comb polymer in US 2009/0270543 A1. ~~The subject-matter of US 2009/0270543 A1 relating to the polymer is hereby incorporated by reference in its entirety.~~

In one preferred embodiment, the polymeric flocculation aid is a copolymer prepared from 92 wt.-% methoxy polyethylene glycol methacrylate of molecular weight 2,000 g/mole and 8 wt.-% acrylic acid and at least partially neutralised by soda. In a further

purification of water and/or dewatering of sludges and/or sediments. According to another aspect of the present invention, the use of the surface-treated calcium carbonate for reducing the amount of polymeric flocculation aids in water and/or sludges and/or sediments is provided.

~~According to a further aspect of the present invention, a composite material comprising the surface-treated calcium carbonate and impurities is provided.~~

Preferably, the composite material further comprises a polymeric flocculation aid as defined above. When the surface-treated calcium carbonate is used in combination with a polymeric flocculation aid as defined above, it has surprisingly been found that a flocculated composite material of improved compactness is obtained while the concentration of polymeric flocculation aid in the filtrate is considerably reduced.

If the flocculated composite material is separated from the water and/or sludge and/or sediment by filtration, sedimentation and/or centrifugation, the composite material can be present in the form of a filter cake.

With regard to the definition of the surface-treated calcium carbonate and preferred embodiments thereof, reference is made to the statements provided above when discussing the technical details of the process of the present invention.

The following examples may additionally illustrate the invention, but are not meant to restrict the invention to the exemplified embodiments.

Claims

1. A process for the purification of water and/or dewatering of sludges and/or sediments, comprising the following steps of:

a) providing water to be purified and/or sludge and/or sediment to be dewatered comprising impurities;

b) providing at least one surface-treated calcium carbonate, wherein at least 1 % of the accessible surface area of the calcium carbonate is covered by a coating comprising at least one cationic polymer, and

c) contacting the water and/or sludge and/or sediment of step a) with the at least one surface-treated calcium carbonate of step b) for obtaining a composite material of surface-treated calcium carbonate and impurities.

2. The process according to claim 1, wherein the water and/or sludge and/or sediment of step a) is selected from industrial waste water, drinking water, urban waste water, sludge such as harbour sludge, river sludge, coastal sludge or digested sludge, waste water or process water from breweries or other beverage industries, waste water or process water in the paper industry, colour-, paints-, or coatings industry, agricultural waste water, slaughterhouse waste water, leather industry waste water and leather tanning industry.

3. The process according to claims 1 or 2, wherein the at least one surface-treated calcium carbonate of step b) comprises ground calcium carbonate and/or precipitated calcium carbonate and/or surface-modified calcium carbonate, preferably surface-modified calcium carbonate.

4. The process according to any one of claims 1 to 3, wherein the source of ground calcium carbonate (GCC) is selected from marble, chalk, calcite, dolomite, limestone and mixtures thereof and/or the precipitated calcium carbonate (PCC) is

selected from one or more of the aragonitic, vateritic and calcitic mineralogical crystal forms.

5. The process according to any one of claims 1 to 4, wherein the calcium carbonate particles of the at least one surface-treated calcium carbonate has a weight median particle diameter d_{50} value of between 0.01 μm and 250 μm, preferably between 0.06 μm and 225 μm, more preferably between 1 μm and 200 μm, even more preferably between 1 μm and 150 μand most preferably between 1 μm and 100 μm and/or the calcium carbonate particles of the at least one surface-treated calcium carbonate has a specific surface area of from 1 to 250 m^2/g, more preferably from 20 to 200 m^2/g, even more preferably from 30 to 150 m^2/g and most preferably from 30 to 100 m^2/g.

6. The process according to any one of claims 1 to 5, wherein the coating of the at least one surface-treated calcium carbonate comprises at least one cationic polymer having a positive charge density in the range of 1 mEq/g and 15 mEq/g, more preferably in the range of 2.5 mEq/g and 12.5 mEq/g and most preferably in the range of 5 μEq/g and 10 mEq/g and/or the coating of the at least one surface-treated calcium carbonate comprises at least one cationic polymer in which at least 60 % of the monomer units have a cationic charge, preferably at least 70 %, more preferably at least 80 %, even more preferably at least 90 % and most preferably equal to 100 %.

7. The process according to any one of claims 1 to 6, wherein the coating of the at least one surface-treated calcium carbonate comprises at least one cationic polymer having a weight average molecular weight M_w of below 1,000,000 g/mole, more preferably from 50,000 to 750,000 g/mole, even more preferably from 50,000 to 650,000 g/mole and most preferably from 100,000 to 300,000 g/mole.

8. The process according to any one of claims 1 to 7, wherein the coating of the at least one surface-treated calcium carbonate comprises at least one cationic polymer being a homopolymer based on monomer units selected from the group consisting of diallyldialkyl ammonium salts; tertiary and quaternized amines; quaternized imines; acrylamide; methacrylamide; N,N-dimethyl acrylamide; acrylic acid; methacrylic acid; vinylsulfonic acid; vinyl pyrrolidone; hydroxyl ethyl acrylate; styrene; methyl methacrylate and vinyl acetate, preferably diallyldialkyl ammonium salts and acrylic acid.

9. The process according to any one of claims 1 to 7, wherein the coating of the at least one surface-treated calcium carbonate comprises at least one cationic polymer being a copolymer based on monomer units selected from diallyldialkyl ammonium salts and methacrylic acid and comonomer units selected from the group consisting of acrylamide; methacrylamide; N,N-dimethyl acrylamide; acrylic acid; methacrylic acid; vinylsulfonic acid; vinyl pyrrolidone; hydroxyl ethyl acrylate; styrene; methyl methacrylate; vinyl acetate and mixtures thereof, preferably the monomer units are selected from diallyldialkyl ammonium salts and methacrylic acid and comonomer units selected from acrylamide and acrylic acid.

10. The process according to any one of claims 1 to 9, wherein at least 10 % of the accessible surface area of the calcium carbonate is covered by a coating comprising a cationic polymer, preferably at least 20 % of the accessible surface area, more preferably at least 30 %, even more preferably at least 40 % and most preferably at least 50 % of the accessible surface area.

11. The process according to any one of claims 1 to 10, wherein the at least one surface-treated calcium carbonate is in powder form and/or in the form of granules or in the form of a slurry.

12. The process according to any one of claims 1 to 11, wherein the process further comprises step d) of contacting the water to be purified and/or sludge and/or sediment to be dewatered of step a) with at least one polymeric flocculation aid.

13. The process according to claim 12, wherein the polymeric flocculation aid has a weight average molecular weight M_w in the range from 100,000 to 10,000,00 g/mole, preferably in the range from 300,000 to 5,000,000 g/mole, more preferably in the range from 300,000 to 1,000,000 g/mole and most preferably in the range from 300,000 to 800,000 g/mole and/or the polymeric flocculation aid is non-ionic or ionic, preferbly a cationic or anionic polymer selected from polyacrylamides, polyacrylates, poly(diallyldimethylammonium chloride), polyethyleneimines, polyamines, starches and mixtures thereof.

14. The process according to any one of claims 12 or 13, wherein step c) and step d) are carried out simultaneously or separately, preferably simultaneously.

15. The process according to any one of claims 1 to 14, wherein step c) and/or step d) are carried out by at least partially covering the surface of the water and/or sludge and/or sediment to be treated of step a) with the at least one surface-treated calcium carbonate of step b) and/or mixing the water and/or sludge and/or sediment to be treated of step a) with the at least one surface-treated calcium carbonate of step b).

16. The process according to any one of claims 1 to 15, wherein step c) and/or step d) are repeated one or more times.

17. The process according to any one of claims 1 to 16, wherein the composite material of the at least one surface-treated calcium carbonate and impurities is removed from the water and/or sludge and/or sediment phase by filtration, sedimentation and/or centrifugation.

18. The process according to any one of claims 1 to 17, wherein the water and/or sludge and/or sediment obtained by the process contains an amount of flocculation aid of at least 10 wt.-%, preferably at least 20 wt.-%, more preferably at least 30 wt.-%, even more preferably at least 40 wt.-%, still more preferably at least 50 wt.-% and most preferably at least 60 wt.-% below the amount of flocculation aid contained in a corresponding water and/or sludge and/or sediment being treated the same way but in the absence of the at least one surface-treated calcium carbonate.

19. Use of a surface-treated calcium carbonate for water purification and/or dewatering of sludges and/or sediments, wherein at least 1 % of the accessible surface area of the calcium carbonate is covered by a coating comprising at least one cationic polymer.

20. Use of a surface-treated calcium carbonate for reducing the amount of polymeric flocculation aids in water and/or sludges and/or sediments, wherein at least 1 % of the accessible surface area of the calcium carbonate is covered by a coating comprising at least one cationic polymer.

21. The use according to any one of claims 19 or 20, wherein the surface-treated calcium carbonate comprises ground calcium carbonate and/or precipitated calcium carbonate and/or surface-modified calcium carbonate, preferably surface-modified calcium carbonate.

22. The use according to any one of claims 19 to 21, wherein the source of ground calcium carbonate (GCC) is selected from marble, chalk, calcite, dolomite, limestone and mixtures thereof and/or the precipitated calcium carbonate (PCC) is selected from one or more of the aragonitic, vateritic and calcitic mineralogical crystal forms.

23. The use according to any one of claims 19 to 22, wherein the calcium carbonate particles of the at least one surface-treated calcium carbonate has a weight median particle diameter d_{50} value of between 0.01 μm and 250 μm, preferably between 0.06 μm and 225 μm, more preferably between 1 μm and 200 μm, even more preferably between 1 μm and 150 μm and most preferably between 1 μm and 100 μm and/or the calcium carbonate particles of the surface-treated calcium carbonate has a specific surface area of from 1 to 250 m^2/g, more preferably from 2 to 200 m^2/g, even more preferably from 30 to 150 m^2/g and most preferably from 30 to 100 m^2/g.

24. The use according to any one of claims 19 to 23, wherein the coating of the surface-treated calcium carbonate comprises at least one cationic polymer having a positive charge density in the range of 1 mEq/g and 15 mEq/g, more preferably in the range of 2.5 mEq/g and 12.5 mEq/g and most preferably in the range of 5 mEq/g and 10 mEq/g and/or the coating of the surface-treated calcium carbonate comprises at least one cationic polymer in which at least 60 % of the monomer units have a cationic charge, preferably at least 70 %, more preferably at least 80 %, even more preferably at least 90 % and most preferably equal to 100 %.

25. The use according to any one of claims 19 to 24, wherein the coating of the surface-treated calcium carbonate comprises at least one cationic polymer having a weight average molecular weight M_w of below 1,000,000 g/mole, more preferably from 50,000 to 750,000 g/mole, even more preferably from 50,000 to 650,000 g/mole and most preferably from 100,000 to 300,000 g/mole.

26. The use according to any one of claims 19 to 25, wherein the coating of the surface-treated calcium carbonate comprises at least one cationic polymer being a homopolymer based on monomer units selected from the group consisting of diallyldialkyl ammonium salts; tertiary and quaternized amines; quaternized imines; acrylamide; methacrylamide; N,N-dimethyl acrylamide; acrylic acid; methacrylic acid; vinylsulfonic acid; vinyl pyrrolidone; hydroxyl ethyl acrylate; styrene; methyl methacrylate and vinyl acetate, preferably diallyldialkyl ammonium salts and acrylic acid.

27. The use according to any one of claims 19 to 25, wherein the coating of the surface-treated calcium carbonate comprises at least one cationic polymer being a copolymer based on monomer units selected from diallyldialkyl ammonium salts and methacrylic acid and comonomer units selected from the group consisting of acrylamide; methacrylamide; N,N-dimethyl acrylamide; acrylic acid; methacrylic acid; vinylsulfonic acid; vinyl pyrrolidone; hydroxyl ethyl acrylate; styrene; methyl methacrylate; vinyl acetate and mixtures thereof, preferably the monomer units are selected from diallyldialkyl ammonium salts and methacrylic acid and comonomer units selected from acrylamide and acrylic acid.

28. The use according to any one of claims 19 to 27, wherein at least 10 % of the accessible surface area of the calcium carbonate is covered by a coating comprising a cationic polymer, preferably at least 20 % of the accessible surface area, more preferably at least 30 %, even more preferably at least 40 % and most preferably at least 50 % of the accessible surface area.

29. The use according to any one of claims 19 to 28, wherein the surface-treated calcium carbonate is in powder form and/or in the form of granules or in the form of slurry.

30. The use according to any one of claims 19 to 29, wherein the surface-treated calcium carbonate is used in combination with at least one polymeric flocculation aid.

31. The use according to claim 30, wherein the polymeric flocculation aid has a weight average molecular weight M_w in the range from 100,000 to 10,000,000 g/mole, preferably in the range from 300,000 to 5,000,000 g/mole, more preferably in the range from 300,000 to 1,000,000 g/mole and most preferably in the range from 300,000 to 800,000 g/mole and/or the polymeric flocculation aid is non-ionic or ionic, preferbly a cationic or anionic polymer selected from polyacrylamides, polyacrylates, poly(diallyldimethylammonium chloride), polyethyleneimines, polyamines, starches and mixtures thereof.

32. A composite material comprising a surface-treated calcium carbonate and impurities obtainable by the process according to any one of claims 1 to 18.

filter out. Due to the restriction to cationic polymers, the process flexibility is reduced.

A known polymeric flocculation aid is polyacrylamide. By using of specific comonomers, anionic as well as cationic, polyacrylamide can be provided. However, as already indicated above, when used in combination with inorganic flocculants such as iron(III) chloride, only cationic polyacrylamide is effective.

Furthermore, reference is made to EP 0 273 335 A2 that relates to flocculation and filtration aids. The flocculation and filtration aids are used for the separation of fine particles and particulate solids from liquid phases such that they are bound on the surface of the polycationic particles. The polycationic material preferably comprises quaternary ammonium groups.

CA 2 734 310 A1 refer to the removal of contaminants from waste streams by using polymeric additives. More precisely, tethering polymers like chitosan, poly(DADMAC), epi/DMA, SMAI and PEI are disclosed, that complex with a capture polymer.

However, one problem with this approach is that these polymeric flocculation aids are usually overdosed to a large extent in order to ensure the agglomeration of all fine solid particles in the water to be treated. Thus, after the separation of the flocculated material from the water phase, the content of polyacrylamide in the filtrate is usually increased due to the high amounts of polymeric flocculating aids used. However, as there are severe environmental concerns regarding water containing polymeric flocculation aids, and especially polyacrylamide, the filtrate cannot be readily disposed in nature and, thus, further time and cost consuming purification steps are required to remove the polymeric flocculation aid from the filtrate.

Therefore, there is a continuous need for alternative water treatment processes, which provide a better performance than existing processes and effectively decrease the concentration of impurities and especially inorganic impurities and the concentration of polymeric flocculation aids in waste water to be treated but still enables easy performance at low cost.

This and other objects are solved by the subject-matter of the present invention. According to a first aspect of the present invention, a process for the purification of water and/or dewatering of sludges and/or sediments, comprising the following steps of:

a) providing water to be purified and/or sludge and/or sediment to be dewatered comprising impurities;

b) providing at least one surface-treated calcium carbonate, wherein at least 1 % of the accessible surface area of the calcium carbonate is covered by a coating comprising at least one cationic polymer, and

c) contacting the water and/or sludge and/or sediment of step a) with the at least one surface-treated calcium carbonate of step b) for obtaining a composite material of surface-treated calcium carbonate and impurities,

wherein the surface-treated calcium carbonate comprises a surface-modified calcium carbonate that has been processed with cationic polymers through an additional treatment step,

wherein the surface-modified calcium carbonate is obtained by reacting a natural calcium carbonate and/or precipitated calcium carbonate with an acid and with carbon dioxide prior to the preparation of the surface-treated calcium carbonate,

wherein the carbon dioxide is formed in situ by the acid treatment and/or is supplied from an external source.

The inventors surprisingly found that the foregoing process according to the present invention leads to an improved quality of the obtained filter cake and purified water providing a lower amount of polymeric flocculation aids than water, sludges and/or sediments treated the same way but without contacting it with the at least one surface-treated calcium carbonate (step c)). More precisely, the inventors found that the quality of water and of a filter cake being obtained by a purification process can be improved by a defined calcium carbonate that is surface-treated with cationic polymers.

It should be understood that for the purposes of the present invention, the following terms have the following meaning:

The term "purification" in the meaning of the present invention refers to the removal of harmful compounds and/or other compounds not tolerated in the water. Furthermore, the term refers to the reduction in concentration of naturally occurring compounds in the water.

The term "dewatering" in the meaning of the present invention refers to the removal of residual liquid from sludges and/or sediments.

particles. Thus, the presence of anionic monomer units is not excluded as long as there are still sufficient cationic monomer units providing a positive overall charge. The same applies for amphotheric polymers which provide for an overall positive charge when bound to the calcium carbonate particles.

The term "accessible surface area" in the meaning of the present invention refers to the surface of the calcium carbonate particle that is accessible or exposed to the cationic polymer applied by mixing and/or coating techniques known to the skilled person and thereby forming a monolayer of cationic polymer on the surface of the calcium carbonate particle. In this regard, it should be noted that the amount of cationic polymer required for full saturation of the accessible surface area is defined as a monolayer concentration. Higher concentrations thus can be chosen thereby forming bilayered or multi-layered structures on the surface of the calcium carbonate particle. Such monolayer concentrations can be readily calculated by the skilled person, based on the publication of Papirer, Schultz and Turchi (Eur. Polym. J., Vol. 20, No. 12, pp. 1155-1158, 1984).

It is preferred that the surface-treated calcium carbonate further comprises ground calcium carbonate and/or precipitated calcium carbonate. It is also preferred that the source of ground calcium carbonate (GCC) is selected from marble, chalk, calcite, dolomite, limestone and mixtures thereof and/or the precipitated calcium carbonate (PCC) is selected from one or more of the aragonitic, vateritic and calcitic mineralogical crystal forms. It is further preferred that the calcium carbonate particles of the surface-treated calcium carbonate have a weight median particle diameter d_{50} value of between 0.04 μm and 250 μm, preferably between 0.06 μm and 225 μm, more preferably between 1 μm and 200 μm, even more preferably between 1 μm and 150 μm, and most preferably between 1 μm and 100 μm and/or the calcium carbonate particles of the surface-treated calcium carbonate have a specific surface area of from 1 to 250 m^2/g, more preferably from 20 to 200 m^2/g, even more preferably from 30 to 150 m^2/g and most preferably from 30 to 100 m^2/g. It is still

weight average molecular weight M_w in the range from 100,000 to 10,000,000 g/mole, preferably in the range from 300,000 to 5,000,000 g/mole, more preferably in the range from 300,000 to 1,000,000 g/mole and most preferably in the range from 300,000 to 800,000 g/mole and/or the polymeric flocculation aid is non-ionic or ionic, preferbly a cationic or anionic polymer selected from polyacrylamides, polyacrylates, poly(diallyldimethylammonium chloride), polyethyleneimines, polyamines, starches and mixtures thereof.

According to one preferred embodiment of the inventive process, the water and/or sludge and/or sediment of step a) is selected from industrial waste water, drinking water, urban waste water, sludge such as harbour sludge, river sludge, coastal sludge or digested sludge, waste water or process water from breweries or other beverage industries, waste water or process water in the paper industry, colour-, paints-, or coatings industry, agricultural waste water, slaughterhouse waste water, leather industry waste water and leather tanning industry.

According to another preferred embodiment of the inventive process, the at least one surface-treated calcium carbonate of step b) further comprises ground calcium carbonate and/or precipitated calcium carbonate.

According to yet another preferred embodiment of the inventive process, the source of ground calcium carbonate (GCC) is selected from marble, chalk, calcite, dolomite, limestone and mixtures thereof and/or the precipitated calcium carbonate (PCC) is selected from one or more of the aragonitic, vateritic and calcitic mineralogical crystal forms.

Step b): provision of at least one surface-treated calcium carbonate

According to step b) of the process of the present invention, at least one surface-treated calcium carbonate comprising surface-modified calcium carbonate (MCC) is provided.

In accordance with the inventive process, at least 1 % of the accessible surface area of the calcium carbonate is covered by a coating comprising at least one cationic polymer.

In one preferred embodiment, the surface-treated calcium carbonate further comprises ground (or natural) calcium carbonate (GCC) or precipitated (or synthetic) calcium carbonate (PCC). In another preferred embodiment, the surface-treated calcium carbonate comprises a mixture of at least two calcium carbonates selected from GCC, PCC and MCC. Alternatively, the surface-treated calcium carbonate comprises a mixture of GCC and MCC. Alternatively, the surface-treated calcium carbonate comprises a mixture of PCC and MCC.

Ground (or natural) calcium carbonate (GCC) is understood to be a naturally occurring form of calcium carbonate, mined from sedimentary rocks such as limestone or chalk, or from metamorphic marble rocks. Calcium carbonate is known to exist as three types of crystal polymorphs: calcite, aragonite and vaterite. Calcite, the most common crystal polymorph, is considered to be the most stable crystal form of calcium carbonate. Less common is aragonite, which has a discrete or clustered needle orthorhombic crystal structure. Vaterite is the rarest calcium carbonate

polymorph and is generally unstable. Ground calcium carbonate is almost exclusively of the calcitic polymorph, which is said to be trigonal-rhombohedral and represents the most stable of the calcium carbonate polymorphs.

Preferably, the source of the ground calcium carbonate is selected from the group comprising marble, chalk, calcite, dolomite, limestone and mixtures thereof. In a preferred embodiment, the source of the ground calcium carbonate is calcite.

The term "source" of the calcium carbonate in the meaning of the present invention refers to the naturally occurring mineral material from which the calcium carbonate is obtained. The source of the calcium carbonate may comprise further naturally occurring components such as magnesium carbonate, alumino silicate etc.

Additionally, the surface-treated calcium carbonate may comprises a precipitated calcium carbonate (PCC). Calcium carbonate polymorphs of the PCC type often include, in addition to calcites, less stable polymorphs of the aragonitic-type, which has an orthorhombic, acicular crystal shape, and hexagonal vateritic-type, which has an even lower stability than aragonite. The different PCC forms may be identified according to their characteristic x-ray powder diffraction (XRD) peaks. PCC synthesis most commonly occurs by a synthetic precipitation reaction that includes a step of contacting carbon dioxide with a solution of calcium hydroxide, the latter being most often provided on forming an aqueous suspension of calcium oxide, also known as burnt lime, and the suspension of which is commonly known as milk of lime. Depending on the reaction conditions, this PCC can appear in various forms, including both stable and unstable polymorphs. Indeed, PCC often represents a thermodynamically unstable calcium carbonate material. When referred to in the context of the present invention, PCC shall be understood to mean synthetic calcium carbonate products obtained notably by carbonation of a slurry of calcium hydroxide, commonly referred to in the art as a slurry of lime or milk of lime when derived from finely divided calcium oxide particles in water.

Preferred precipitated calcium carbonate is selected from aragonitic, vateritic or calcitic mineralogical crystal forms or mixtures thereof.

Surface-modified calcium carbonate is a material comprising GCC and/or PCC and an insoluble, at least partially crystalline, non-carbonate calcium salt extending from the surface of at least part of the calcium carbonate. Such surface-modified products may, for example, be prepared according to WO 00/39222, WO 2004/083316, WO 2005/121257, WO 2009/074492, EP 2 264 108 A1, EP 2 264 109 A1.

The surface-modified calcium carbonate is obtained by reacting a natural calcium carbonate and/or precipitated calcium carbonate with an acid and with carbon dioxide prior to the preparation of the surface-treated calcium carbonate, wherein the carbon dioxide is formed in situ by the acid treatment and/or is supplied from an external source. The acid treatment can be carried out with an acid having a pK_a at 25 °C of 6 or less. If the pK_a at 25 °C is 0 or less, the acid is preferably selected from sulphuric acid, hydrochloric acid, or mixtures thereof. If the pK_a at 25 °C is from 0 to 2.5, the acid is preferably selected from H_2SO_3, $M^+HSO_4^-$ (M^+ is an alkali metal ion selected from the group comprising sodium and potassium), H_3PO_4, oxalic acid or mixtures thereof. If the pK_a at 25 °C is from 2.5 to 6, the acid is preferably selected from acetic acid, formic acid, propanoic acid and mixtures thereof.

In an especially preferred embodiment, the calcium carbonate particles of the present surface-treated calcium carbonate have a weight median particle diameter d_{50} value of from 0.01 μm to 250 μm before surface treatment, preferably from 0.06 μm to

Claims

1. A process for the purification of water and/or dewatering of sludges and/or sediments, comprising the following steps of:

a) providing water to be purified and/or sludge and/or sediment to be dewatered comprising impurities;

b) providing at least one surface-treated calcium carbonate, wherein at least 1 % of the accessible surface area of the calcium carbonate is covered by a coating comprising at least one cationic polymer, and

c) contacting the water and/or sludge and/or sediment of step a) with the at least one surface-treated calcium carbonate of step b) for obtaining a composite material of surface-treated calcium carbonate and impurities,

wherein the surface-treated calcium carbonate comprises a surface-modified calcium carbonate that has been processed with cationic polymers through an additional treatment step,

wherein the surface-modified calcium carbonate is obtained by reacting a natural calcium carbonate and/or precipitated calcium carbonate with an acid and with carbon dioxide prior to the preparation of the surface-treated calcium carbonate, wherein the carbon dioxide is formed in situ by the acid treatment and/or is supplied from an external source.

2. The process according to claim 1, wherein the water and/or sludge and/or sediment of step a) is selected from industrial waste water, drinking water, urban waste water, sludge such as harbour sludge, river sludge, coastal sludge or digested sludge, waste water or process water from breweries or other beverage industries, waste water or process water in the paper industry, colour-, paints-, or coatings industry, agricultural waste water, slaughterhouse waste water, leather industry waste water and leather tanning industry.

3. The process according to claims 1 or 2, wherein the at least one surface-treated calcium carbonate of step b) further comprises ground calcium carbonate and/or precipitated calcium carbonate.

4. The process according to claim 3, wherein the source of ground calcium carbonate (GCC) is selected from marble, chalk, calcite, dolomite, limestone and mixtures thereof and/or the precipitated calcium carbonate (PCC) is selected from one or more of the aragonitic, vateritic and calcitic mineralogical crystal forms.

5. The process according to any one of claims 1 to 4, wherein the calcium carbonate particles of the at least one surface-treated calcium carbonate has a weight median particle diameter d_{50} value of between 0.01 μm and 250 μm, preferably between 0.06 μm and 225 μm, more preferably between 1 μm and 200 μm, even more preferably between 1 μm and 150 μm and most preferably between 1 μm and 100 μm and/or the calcium carbonate particles of the at least one surface-treated calcium carbonate has a specific surface area of from 1 to 250 m^2/g, more preferably from 20 to 200 m^2/g, even more preferably from 30 to 150 m^2/g and most preferably from 30 to 100 m^2/g.

6. The process according to any one of claims 1 to 5, wherein the coating of the at least one surface-treated calcium carbonate comprises at least one cationic polymer having a positive charge density in the range of 1 mEq/g and 15 mEq/g, more preferably in the range of 2.5 mEq/g and 12.5 mEq/g and most preferably in the range of 5 mEq/g and 10 mEq/g and/or the coating of the at least one surface-treated calcium carbonate comprises at least one cationic polymer in which at least 60 % of the monomer units have a cationic charge, preferably at least 70 %, more preferably at least 80 %, even more preferably at least 90 % and most preferably equal to 100 %.

7. The process according to any one of claims 1 to 6, wherein the coating of the at least one surface-treated calcium carbonate comprises at least one cationic polymer having a weight average molecular weight M_w of below 1,000,000 g/mole, more preferably from 50,000 to 750,000 g/mole, even more preferably from 50,000 to 650,000 g/mole and most preferably from 100,000 to 300,000 g/mole.

8. The process according to any one of claims 1 to 7, wherein the coating of the at least one surface-treated calcium carbonate comprises at least one cationic polymer being a homopolymer based on monomer units selected from the group consisting of diallyldialkyl ammonium salts; tertiary and quaternized amines; quaternized imines, preferably diallyldialkyl ammonium salts.

9. The process according to any one of claims 1 to 7, wherein the coating of the at least one surface-treated calcium carbonate comprises at least one cationic polymer being a copolymer based on monomer units selected from diallyldialkyl ammonium salts and comonomer units selected from the group consisting of acrylamide; methacrylamide; N,N-dimethyl acrylamide; acrylic acid; methacrylic acid; vinylsulfonic acid; vinyl pyrrolidone; hydroxyl ethyl acrylate; styrene; methyl methacrylate; vinyl acetate and mixtures thereof.

10. The process according to any one of claims 1 to 9, wherein at least 10 % of the accessible surface area of the calcium carbonate is covered by a coating comprising a cationic polymer, preferably at least 20 % of the accessible surface area, more preferably at least 30 %, even more preferably at least 40 % and most preferably at least 50 % of the accessible surface area.

11. The process according to any one of claims 1 to 10, wherein the at least one surface-treated calcium carbonate is in powder form and/or in the form of granules or in the form of a slurry.

12. The process according to any one of claims 1 to 11, wherein the process further comprises step d) of contacting the water to be purified and/or sludge and/or sediment to be dewatered of step a) with at least one polymeric flocculation aid.

13. The process according to claim 12, wherein the polymeric flocculation aid has a weight average molecular weight M_w in the range from 100,000 to 10,000,00 g/mole, preferably in the range from 300,000 to 5,000,000 g/mole, more preferably in the range from 300,000 to 1,000,000 g/mole and most preferably in the range from 300,000 to 800,000 g/mole and/or the polymeric flocculation aid is non-ionic or ionic, preferbly a cationic or anionic polymer selected from polyacrylamides, polyacrylates, poly(diallyldimethylammonium chloride), polyethyleneimines, polyamines, starches and mixtures thereof.

14. The process according to any one of claims 12 or 13, wherein step c) and step d) are carried out simultaneously or separately, preferably simultaneously.

15. The process according to any one of claims 1 to 14, wherein step c) and/or step d) are carried out by at least partially covering the surface of the water and/or sludge and/or sediment to be treated of step a) with the at least one surface-treated calcium carbonate of step b) and/or mixing the water and/or sludge and/or sediment to be treated of step a) with the at least one surface-treated calcium carbonate of step b).

16. The process according to any one of claims 1 to 15, wherein step c) and/or step d) are repeated one or more times.

17. The process according to any one of claims 1 to 16, wherein the composite material of the at least one surface-treated calcium carbonate and impurities is removed from the water and/or sludge and/or sediment phase by filtration, sedimentation and/or centrifugation.