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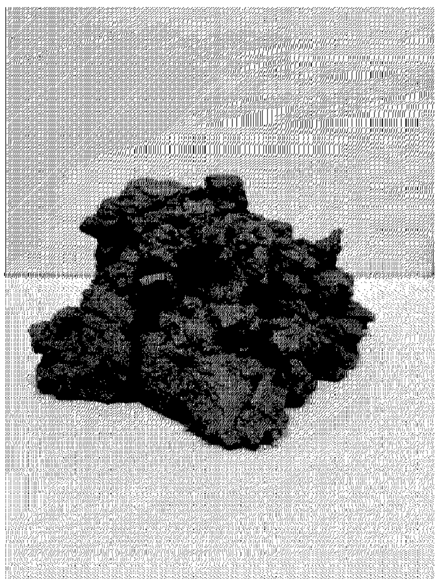
(54) Titre : LIANT ET METHODE DE FORMATION DE LIANT POUR LA GRANULATION, L'AGREGATION ET LA STRUCTURATION DE SOLIDES MINERAUX
(54) Title: BINDER AND METHOD OF FORMING THE BINDER FOR GRANULATION, AGGREGATION AND STRUCTURING OF MINERAL SOLIDS



(57) Abrégé/Abstract:
There is provided a method for treating fine tailings of a slurry comprising water, solid mineral component(s), and/or organic components derived from oil sands extractions to form a granulated aggregated material and an aqueous component. The method comprising subjecting tailings of a slurry comprising water, solid mineral component(s), and/or organic components to a sufficient dosage of an anionic polymer flocculant and to a sufficient dosage of a cationic polymer coagulant so as to convert the fine tailings into a granulated aggregated material and an aqueous component. There is also provided a granulating binder for immobilizing mineral solids within a waste stream of mineral solids-containing water slurry obtained from a mining process.

ABSTRACT

There is provided a method for treating fine tailings of a slurry comprising water, solid mineral component(s), and/or organic components derived from oil sands extractions to form a granulated aggregated material and an aqueous component. The method comprising subjecting tailings of a slurry comprising water, solid mineral component(s), and/or organic components to a sufficient dosage of an anionic polymer flocculant and to a sufficient dosage of a cationic polymer coagulant so as to convert the fine tailings into a granulated aggregated material and an aqueous component. There is also provided a granulating binder for immobilizing mineral solids within a waste stream of mineral solids-containing water slurry obtained from a mining process.

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Binder and method of forming the binder for granulation, aggregation and structuring of mineral solids

TECHNICAL FIELD

[0001] The present invention relates to composition and method for granulation, aggregation and structuring of mineral solids.

BACKGROUND

[0002] Mining processes world-wide produce waste streams of solids-containing water slurries. Generally these water slurries are sent to ponds where, within months to a few years, the solids settle to a reclaimable condition and the supernatant water is returned to process.

[0003] The mining and processing of oil sands is a major industry in the province of Alberta, Canada. As in virtually all mining processes, mine waste disposal is a major cost and a major environmental concern.

[0004] From the inception of Alberta oil sands processing by hot water extraction, a fine particle slurry containing predominantly clays has been produced. Unfortunately the usual tailings pond gravity separation process has not been effective in settling the fine clays from the water. Instead, the fine clay solids have concentrated and remained in stable suspensions of up to 40% clay solids, and these suspensions are projected to be stable for hundreds of years. It is a government requirement that these clay solids be separated and recovered to be used in restoration of the mine site. Clay slurries that have not been sent to tailings ponds are referred to as fresh fine tailings (FFT). Ponded clay slurries are referred to as mature fine tailings (MFT).

[0005] Industry efforts over the last decades have focused on essentially two routes to fine tailings reclamation. The first route involves

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blending the clay tailings slurry, usually MFT, with sand separated from oil sands ore during bitumen extraction. Weight ratios in these sand-to-clay blends are described as Sand:Fines ratios (SFR's). One particular process, referred to as Combined Tailings (CT), could have SFR's of from 4:1 to 6:1, which results in immense quantities of sand compared to the fines being sequestered. In order to assist dewatering of these sand-to-fines blends gypsum or alum are often added. Unfortunately, these inorganic salts add undesirable dissolved-solids loading to the process water and these sulfur-containing salts may eventually produce dangerous gases on the mine site.

[0006] The obvious drawback of the CT process is that huge quantities of sand are required to sequester disproportionately small amounts of clay. Handling and controlled-metering of these volumes of clay and sand is both a difficult and expensive in process. Large volumes of sand are required for mine-site construction including building dykes to contain ever increasing volumes of MFT. Because of these uses, sand has become a scarce commodity.

[0007] A second route to dewatering MFT has been to treat the MFT with flocculants and other chemical additives to accelerate the solids settling process, using reduced amounts of sand. This treated MFT is pumped to what are essentially small tailings ponds called Dedicated Deposition Areas (DDAs).

[0008] A desired result is that the clay solids in the DDA will, within an acceptable time-frame, settle and consolidate to facilitate incorporation of the settled fines in mine-site reclamation. However, regardless of any significant reduction of settling times in the DDA, the fines will still be fines. Any mine site reclamation process seeks to prevent re-release of unconsolidated fines back to process water or the environment.

[0009] Additionally, the water slurries of fine clays may also contain residual bitumen from the hot water bitumen extraction process. Residual

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bitumen, as well as other chemicals added in or following the extraction process inhibit the effective separation and disposal of clay from the water slurry. It is highly desirable that residual bitumen be trapped in the solids.

[0010] The present disclosure relates to the treatment and disposal of oil sands fine clay tailings from (e.g. Alberta) oil sands bitumen production as part of mine-site reclamation.

[0011] To address the deficiencies in current practices in oil sands operations, there is a need to provide a binder composition, use of the binder composition, and to provide a granulation process for fine clay particles that does not require the incorporation of sand and/or is broadly applicable and therefore not limited to the different types of water swelling clays.

SUMMARY OF THE INVENTION:

[0012] It is an embodiment of the present invention to provide a method to produce a binder that granulates, aggregates and structures fine clay particles. According to an embodiment, granulation is produced in a fine clay tailings slurry by the sequential addition of two water soluble organic polymers that react to form in situ a granulated binder. In one aspect, the disclosed binder granulates the fine tailings particles and the granulated tailings particles aggregate to form a structure that can be stacked, centrifuged, or sub-aqueously deposited without re-release of fines to process or to the environment.

[0013] According to an embodiment, there is provided a method of producing *in-situ* (i.e. on-site and in the presence of fines) a granulating binder in an aqueous dispersed mineral slurry, the process comprising:

[0014] (a) providing an aqueous slurry comprising slurrying water and solid mineral component(s), and

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[0015] (b) adding to the dispersed slurry of (a) sufficient quantities of an anionic flocculant, and

[0016] (c) adding to the dispersed slurry of (b) sufficient quantities of a cationic coagulant, to

[0017] (d) cause the two components in (b) and (c) to react to form a granulating binder that granulates and aggregates the mineral components of the aqueous slurry.

[0018] According to an embodiment, there is provided a method for treating tailings derived from oil sands extractions to form a granulated aggregated material and an aqueous component.

[0019] According to an embodiment, there is provided use of a composition for treating fine tailings derived from oil sands extractions comprising a slurry comprising water, solid mineral component(s), and/or organic components to form aggregated material and an aqueous component, the composition comprising: an anionic polymer flocculant and a cationic polymer coagulant, wherein when the composition is reacted *in situ* with tailings, will convert the tailings into a granulated aggregated material and an aqueous component.

[0020] According to an embodiment, there is provided a method for treating fine tailings of a slurry comprising water, solid mineral component(s), and/or organic components derived from oil sands extractions to form a granulated aggregated material and an aqueous component, the method comprising:

subjecting tailings to a sufficient dosage of an anionic polymer flocculant and to a sufficient dosage of a cationic polymer coagulant so as to convert the tailings into a granulated aggregated material and an aqueous component.

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[0021] In one aspect, the subjecting the tailings comprises subjecting the tailings to the sufficient dosage of the anionic polymer flocculant to form a paste material; and then subjecting the paste material to the sufficient dosage of the cationic polymer coagulant, wherein the reaction of the anionic polymer flocculant with the cationic polymer coagulant forms a granulating binder that converts the paste material into the granulated aggregated material and the aqueous component.

[0022] The method further comprising one or more of mixing the paste material before the subjecting the paste material to the cationic polymer coagulant and mixing after the subjecting the paste material to the cationic polymer coagulant.

[0023] In one aspect, the sufficient dosage of the anionic polymer flocculant is greater than about 250 g/ton of tailing solids; is greater than about 450 g/ton of tailing solids; is greater than about 1000 g/ton of tailing solids; or is about 1,115 g/ton of tailing solids.

[0024] In one aspect, the sufficient dosage of the cationic polymer coagulant (active) is greater than about 25 g/ton of tailing solids; is greater than about 100 g/ton of tailing solids; or is about 995 g/ton of tailing solids.

[0025] In one aspect, the sufficient dosage of the anionic polymer flocculant is at least about 1.5 to about 2 times the dosage of conventional flocculation and the sufficient dosage of the cationic coagulant at least about 18 to about 40 times the active dosage of conventional coagulation.

[0026] In one aspect, the anionic polymer is a copolymer or terpolymer anionic flocculant, or is a high-molecular-weight copolymer or terpolymer anionic flocculant.

[0027] In one aspect, the anionic polymer flocculant is a sodium acrylate/acrylamide copolymer, a potassium acrylate/acrylamide copolymer,

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ammonium acrylate/acrylamide copolymer, or a calcium diacrylate/acrylamide copolymer.

[0028] In one aspect, the sodium acrylate/acrylamide copolymer is a 35 wt.% or a 46 wt.% sodium acrylate/acrylamide copolymer.

[0029] In one aspect, the sodium acrylate/acrylamide copolymer is a high molecular weight copolymer.

[0030] In one aspect, the calcium diacrylate/acrylamide copolymer is a 40 wt.% calcium diacrylate/acrylamide copolymer.

[0031] In one aspect, the calcium diacrylate/acrylamide copolymer is a medium or a high molecular weight copolymer.

[0032] In one aspect, the cationic polymer coagulant is a high molecular weight diallyl dimethyl ammonium chloride polymer (DADMAC) or a high molecular weight dimethylamine/epichlorohydrin copolymer (DMA/EPI).

[0033] In one aspect, the method further comprising admixing a dry cationic flocculant with the liquid cationic polymer coagulant before the step of subjecting the tailings to the sufficient dosage of the cationic polymer coagulant. In one aspect, the admixing produces a blend of cationic polymer flocculant and high molecular weight dimethylamine/epichlorohydrin copolymer (DMA/EPI).

[0034] In one aspect, the blend comprises up to 20 wt.% cationic polymer flocculant; comprises less than or about 10 wt.% cationic polymer flocculant; or is 5 wt.% cationic polymer flocculant and 95 wt.% DMA/EPI (actives) blend.

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[0035] In one aspect, the method further comprising the step of diluting the cationic polymer coagulant with water before the step of admixing of the cationic polymer flocculant.

[0036] In one aspect, the cationic polymer flocculant is a quaternary/acrylamide cationic dry flocculant.

[0037] In one aspect, the further comprising diluting the anionic polymer flocculant solution with water before the step of subjecting the tailings to the sufficient dosage of the anionic polymer flocculant.

[0038] In one aspect, the method further comprising separating the granulated aggregated material from the aqueous component.

[0039] In one aspect, the aqueous component comprises water.

[0040] In one aspect, the tailings are FFT or MFT.

[0041] In one aspect, the tailings are extraction tailings which are tailings which are obtained after a first extraction process.

[0042] In one aspect, the granulated aggregated material comprises sequestered contaminants. In one aspect, the sequestered contaminants are one or more of metalloids, polyatomic non-metals, and surfactants. In one aspect, the sequestered contaminants comprise arsenic, selenium, and naphthenate.

[0043] In one aspect, the tailings are particulates that are less than or equal to 44 microns.

[0044] According to an embodiment, there is provided a granulating binder for immobilizing mineral solids within a waste stream of mineral solids-containing water slurry obtained from a mining process, the

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granulating binder comprises a sufficient dosage of an anionic flocculant with a sufficient dosage of a cationic coagulant, wherein the reaction of the anionic flocculant with the cationic coagulant in the presence of mineral solids within a waste stream of mineral solids-containing water slurry forms the granulated binder that will immobilize the mineral solids into a granulated aggregated material.

[0045] In one aspect, the sufficient dosage of the anionic polymer flocculant is mixed with the mineral solids to form a paste material; and the sufficient dosage of the cationic polymer coagulant is mixed with the paste material to convert the paste material into the granulated aggregated material.

BRIEF DESCRIPTION OF THE DRAWINGS

[0046] Figure 1 is a photo showing the formation of the white haze after initial admixing anionic polymer flocculant and a cationic polymer coagulant, using a method in accordance with an embodiment of the invention;

[0047] Figure 2 is a photo showing the formation of a coalesced form of an insoluble white cocoon (binder) upon continued stirring of the white haze of figure 1;

[0048] Figure 3 is a photo showing the wet aggregated structure obtained by using a method in accordance with an embodiment of the invention;

[0049] Figure 4 is a photo of a deposit from Figure 3 obtained by using a method in accordance with an embodiment of the invention after drying and re-submerged in water;

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[0050] Figure 5 is a photo of a larger volume of the stackable aggregate obtained by using a method in accordance with an embodiment of the invention dropped from one-half meter height onto a 10 mesh screen and allowed to dry;

[0051] Figure 6 is a photo showing the dried stackable solid in isolation from the screen obtained by using a method in accordance with an embodiment of the invention;

[0052] Figure 7 is a photo showing the granulated aggregate in being dropped into water;

[0053] Figure 8 is a photo showing the aggregate of figure 7 settling in water; and

[0054] Figure 9 is a photo showing a dried aggregated structure that had been submerged in water for 10 days and capable of supporting a brick thereon.

DETAILED DESCRIPTION

[0055] Reference will be made below in detail to exemplary embodiments of the invention, examples of which are illustrated in the accompanying drawings. Wherever possible, the same reference numerals used throughout the drawings refer to the same or like parts.

[0056] Examples

[0057] Example 1 - Binder formation

[0058] To examine the formation of binders, various combinations of anionic and cationic components were tested. Anionic components were

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selected from commercial anionic flocculants and the cationic components were cationic coagulants with or without a cationic flocculant.

[0059] As the anionic component, four commercial anionic polymer flocculants were evaluated:

(a) a 35wt.% and a 46 wt.% sodium acrylate/acrylamide high molecular weight copolymer.

(b) two, 40wt. % calcium diacrylate/acrylamide copolymers, medium and high molecular weights.

[0060] As the cationic component, four commercial polymer coagulants and one cationic flocculant were evaluated;

(a) a low and high molecular weight diallyl/dimethyl/ammonium chloride (DADMAC) copolymer, both 20% actives.

(b) a low and high molecular weight dimethylamine/epichlorohydrin copolymer (DMA/EPI) both 49% actives. (a) and (b) are considered to be coagulants in water treatment.

(c) a 10wt.% quaternary/acrylamide cationic dry flocculant.

[0061] To demonstrate the formation of the binder alone, 39 ml of water was placed in a clear container and 5.8 ml of a 0.4% solution of the high molecular weight, 46wt.% anionic copolymer flocculant was added with mixing. Then, 3 ml of a 0.69% (active) high molecular DMA/EPI solution was added with mixing.

[0062] As shown in figures 1 and 2, a white haze formed immediately (see figure 1) upon initial mixing of the anionic copolymer flocculant and high molecular weight DMA/EPI solution and with continued stirring the haze coalesced to form an insoluble white cocoon (see figure 2).

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[0063] The above example demonstrates that the formation of the binder alone can be generated by placing in an amount of water that is contained in the sample of tailings being aggregated (sample weight less weight of solids), adding to the water a volume of anionic polymer solution (with mixing). Then adding to the container, with rapid mixing, a volume of high-molecular-weight cationic coagulant solution. With rapid mixing a white haze will quickly develop. As mixing continues the haze coalesces into a white, insoluble cocoon-like deposit in clear water.

[0064] When the ratio of anionic to cationic disclosed herein is used, the haze will quickly disappear and the cocoon forms. This test or similar tests can be used to determine a ratio and quantity of the reactants to produce the binder.

[0065] <u>Example 2 – Treatment of Tailings</u>

[0066] Figures 3 to 9 show the treatment of the 34.8 % fine tailing solids to produce granules and aggregate structure. Other MFT samples have 25% and 33.8% solids. . The two FFT samples were 11% and 12.4% solids. All of the additional four fine tailings produced granulated and aggregated tailings at the disclosed dosages.

[0067] A 50 ml sample of the undiluted 34.8% solids MFT (a specific gravity of 1.2) was placed in a clear container. 5.8 ml of a 0.4% solution of the high molecular weight, 46 wt..% anionic copolymer flocculant was added with vigorous hand stirring, until the sample began to express coloured water. The sample at this point was paste-like. The dosage of anionic copolymer flocculant was 1,115 g/ton (i.e. 1,115 ppm) of MFT solids.

[0068] Next, 3 ml of a 0.69% (active) sample of the high molecular weight DMA/EPI coagulant, again with vigorous hand stirring. Shortly after mixing began, the consistency of the sample began to visually change, developing a gritty sand-like character. The formation of granules could be

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clearly seen. As mixing continued, the mix began to sound like stirring sand. Mixing was continued until no more change in consistency was noted. Colourless (i.e. no residual oil), clear water began to drain from the sample. Some granules were observed leaving the aggregated mass with the draining water but these granules immediately settled and were easily captured and reincorporated into the aggregated mass. The dosage of the DMA/EPI polymer actives was 995g/ton of MFT solids.

[0069] At this point the sample was a free-standing mass. Figure 3 shows the wet aggregated structure pushed by a spatula up the wall of the container, with the container angled to drain more clear water. This clear water (which is the water not bound within the swollen clay particles) is vicinal water that was released from the aggregated structure and as can be seen, within the vicinal water there is a small amount of intact granules which importantly do not disperse in the vicinal water and are heavy.

[0070] These solids are stackable as the solids, and when left to dry, become a basalt-like 'rock'. If immersed in water the 'rock' does not disintegrate. Figure 4 shows a deposit produced according to one embodiment of the method of the invention which was dried and then re-submerged in water.

[0071] <u>Example 3 – Treatment of Tailings</u>

[0072] The conditions of Example 2 were repeated, but in this instance the 5.8 ml of anionic flocculant was diluted with 12 ml of water (e.g. reclaim) before adding the flocculant to the MFT sample. This created 25% MFT and reduced the mixing energy required to thoroughly mix the flocculant to produce the paste material and to achieve vicinal water break-out. The 3 ml of coagulant solution was then added with mixing and the granulated aggregated structure was again produced, draining clear water. This structure centrifuged easily to a solid that does not disintegrate in water.

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[0073] Example 4 – Treatment of Tailings

[0074] The conditions of Example 1 were repeated, but with 900g of 34.8% MFT in the smaller bowl of a MixMaster using its double cage-blades for intensive mixing. After the aggregate was produced, it was dropped from 1.2 meter height onto a 10 mesh screen, drainage collected, and the aggregated structure sitting on the screen left to dry, as shown in figure 5. Figure 5 demonstrates the stability of the granulated aggregated structure when wet. On the other hand a typical flocced structure would adhere to and/or fall through the screen. The granulated aggregate according to the present disclosure is supported by the screen and does not fall through the screen.

[0075] Figure 6 shows the same dried granulated aggregated structure of figure 5, but now removed from the screen. As shown, the granulated aggregated structure did not penetrate nor adhere to the screen.

[0076] Figures 7 and 8 show the granulated aggregate being dropped into and descending through the water.

[0077] Figure 9 shows a granulated aggregated structure, that had been dried and then submerged in water for 10 days and is capable of supporting a brick.

[0078] Discussion

[0079] The present disclosure describes formation of a binder that granulates, aggregates and structures the fine clay particles from tailings. Unlike current practices in oil sands operations this granulation process for fine clay particles does not require the incorporation of sand.

[0080] In one embodiment, granulation is produced in a fine clay tailings slurry by the sequential addition of two water soluble organic

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polymers that react to form in situ a granulating binder. This binder granulates the fine tailings particles. The granulated tailings particles aggregate to form a structure that can be stacked, centrifuged, or sub-aqueously deposited without re-release of fines to process or to the environment.

[0081] The Examples above clearly demonstrate methods to produce a granulated, draining, semi-solid from a mineral slurry. In particular, all the tested FFT and MFT responded similarly in the formation of a granular deposit. The dosage levels of binder required to produce granular aggregation were essentially the same relative to tailings solids.

[0082] The present disclosure demonstrates the binder's ability to handle different sources of fine tailings. In one embodiment, the only significant difference in granulation and structuring of all these fine tailings was the intensity of mixing required with higher slurry viscosity.

[0083] Accordingly, the present invention relates, in one embodiment, relates to a method of producing a granulated, draining, semi-solid from a mineral slurry. In one aspect, the invention relates to a method for producing a granulated aggregate from an aqueous, dispersed slurry from an oil sands operation comprising:

[0084] (a) providing an aqueous, dispersed slurry from an oil sands operation (FFT or MFT) comprising slurrying water, solid mineral components and possibly organic components such as bitumen;

[0085] (b) adding to the dispersed slurry of (a) sufficient quantities of a water solution of an anionic polymeric flocculant, such addition resulting in a paste structure that begins to release slurry water. In one aspect, high-solids tailings slurries may require intense mixing to achieve the paste structure.

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[0086] (c) adding, with mixing, to the paste structure of (b) a cationic coagulant, such addition resulting in the *in-situ* formation of a granulating binder that converts the paste structure into a gritty, stiff, draining, free-standing granulated aggregate.

[0087] The granular nature of the produced free-standing aggregate resembles that of a structure of wet, course beach sand. Any granules leaving with the clear, initially-draining water are clearly visible and fall instantly for easy recovery and re-addition to the aggregate.

[0088] At conventional dosages, the anionic flocculant will flocculate the suspended solids. The anionic flocculant dosage needed to produce flocced material is around 450 g/ton of tailing solids. At an effective dosage for producing the binder, the anionic flocculant will produce a paste-like deposit, releasing water. According to the present embodiment, when an excess amount of anionic flocculant is selected (i.e. greater than about 250 g/ton of tailing solids), only then does the material become a desired paste-like deposit. Therefore, the paste-like material is a dispersed material and is obtained when the amount of the anionic flocculant that is used is in excess of the amounts typically used to flocculate mineral solids.

[0089] In one embodiment, the desired amount of anionic flocculant is greater than about 450 g/ton of tailing solids. In another embodiment, the desired amount of anionic flocculant is greater than about 1000 g/ton of tailing solids.

[0090] In one embodiment, the anionic flocculant is a high-molecular-weight anionic flocculant. In one embodiment, the anionic flocculant is an anionic polymeric flocculant. In one embodiment, the anionic flocculant is a copolymer or terpolymer anionic flocculant or is a high-molecular-weight copolymer or terpolymer anionic flocculant.

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[0091] As would be understood, the term anionic polymer can mean a homopolymer of an anionic monomer or a copolymer of an anionic monomer and a nonionic monomer. The term anionic terpolymer could be understood to mean a polymer of two anionic monomers (e.g. sodium acrylate and calcium diacrylate) and a nonionic monomer (e.g. acrylamide).

[0092] In one aspect, the anionic flocculant can be a water-soluble, high-molecular-weight acrylate/acrylamide-type copolymer or terpolymer. In one aspect, the anionic flocculant is a commercial dry anionic flocculant, Zetag 4145 by Solenis LLC of Wilmington DE USA. Zetag 4145 is a 46 wt.% sodium acrylate/acrylamide copolymer in dry form. In one embodiment, the dosage of Zetag 4145 used in the Examples was 1,115 g/per ton of MFT solids.

[0093] In one embodiment, the cationic coagulant is a cationic polymeric coagulant. While not wishing to be bound by any particular theory, Applicant believes that, if used in the desired amounts, the cationic coagulant is able to convert the anionic flocculant-treated and paste-like material to granules. Thus, in certain embodiments the use of the desired amounts of the cationic coagulant means a dosage in excess of what is known in the water treatment industry for usual coagulation (which is about 25 ppm). In one aspect, the commercial liquid cationic coagulant in these tests was Floquat FL 3249 by SNF Inc. of Riceboro, GA USA. Floquat FL 3249 is a 49% actives dimethylamine/epichlorohydrin viscous liquid copolymer. The dosage of DMA/EPI actives was 995g (active)/ton of MFT solids.

[0094] In one aspect, the commercial dry cationic copolymer flocculant in these tests was Zetag 7563 supplied by Solenis LLC. It is a supplement to the DMA/EPI, as described.

[0095] Using the components as disclosed in the Examples, an effective granulation, aggregation and structuring was developed when the

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anionic copolymer was added to the tailings first. In one aspect, the addition sequence of the anionic constituent first, cationic constituent second, is one preferred addition sequence according to an embodiment of the invention. However, in another aspect, the addition sequence could be the cationic constituent first and the anionic constituent second.

[0096] In one aspect, the sufficient dosage (in g/ton tailing solids) of high-molecular-weight anionic flocculant to produce the binder for aggregate formation (and to begin water release) has been found to be in the range of about 1.5 to 2 times that of anionic flocculant required in conventional tailings flocculation which is about 250-500 g/ton of tailing solids. In some aspects, the required dosage (g/ton tailing solids) of high-molecular-weight organic cationic coagulant (active) is in the same g/ton range as that of the anionic flocculant.

[0097] From the Examples, the performance of the anionic component copolymers as binder reactants, one preferred embodiment was the 46 wt.% sodium acrylate/acrylamide copolymer, followed closely in order by the 35wt.% sodium acrylate/acrylamide copolymer, then the high molecular weight 40 wt.% calcium diacrylate/acrylamide copolymer, then the medium molecular weight 40 wt.% calcium diacrylate/acrylamide copolymer.

[0098] Using the components as disclosed in the Examples, the high molecular weight DMA/EPI coagulant was the most effective in granulation, aggregation and structuring the MFT, regardless of which one of the anionic copolymers was used.

[0099] The 10 wt.% cationic flocculant was not effective in replacing the DMA/EPI in the initial formation of the granular structure (results not shown). However, if 2.5 wt.% of the cationic flocculant was blended with the 97.5 wt.% DMA/EPI product (effectively creating a 5 wt.% flocculant/95wt.% DMA/EPI actives blend), granulation was maintained. In one embodiment, this blend reduced the amount of granules that left the

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deposit with the initial drainage water and appeared to strengthened the structure of the deposit.

[00100] Materials handling in oil sands processes, particularly of dry flocculants, is often a problem. In some embodiments, handling problems with the addition of another flocculant to this process can be avoided if the dry cationic flocculant product is blended with the DMA/EPI product, adding water to the blend to produce a 40wt.% actives product. Without being limited to any particular theory it is believed that the dry flocculant will essentially dissolve in the diluted DMA/EPI and therefore simplifying the process of applying the cationic component as used in the Examples.

[00101] The present inventor has surprisingly discovered that water-soluble organic polymers can be added sequentially to FFT or MFT, forming a water-insoluble or granulating binder that produces granules *in-situ* from clay tailings. In preferred embodiments, the organic polymers are commercial water treatment organic polymers. The formed granules are easily visible and aggregate to form a draining semi-solid structure that can be wet-stacked.

[00102] The semi-solid wet structure can be formed directly from high-solids tailings without dilution, or from dilute tailings with initial increased water release. The structure of this deposit releases clear water initially and continues to release oil-free, clear, solids-free water under (simulated) stacked-compression.

[00103] Any granulated tailings released during initial dewatering of the aggregated structure settle instantly from the water and are easily recovered. Residual bitumen is bound in the granules and aggregate. If taken to dryness, the structure resembles basalt and will not collapse in water. The semi-solid wet-stacked structure is not disrupted by freeze-thawing, as the granules and structure remain intact.

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[00104] Importantly, the wet granulated structure can also be centrifuged for additional water release. Importantly, the granulated structure can be sub-aqueously deposited without release of fines while being deposited, or over time.

[00105] In some embodiments, the granulated structure could be subjected to compression and drying sufficient to produce the basalt-like structure of desired stack thicknesses.

[00106] Beneficially, sand-free fluid tailings of any solids content could be pumped to a mined-out area of the mine pit and there treated continuously, producing wet, free-draining solids and clear water. The solids could be conveyor-drained and stacked with conventional mining equipment for mine site reclamation, never to be handled again, which is in contrast to current industry practice. Existing centrifuge applications would be enhanced. In some embodiments, sub-aqueous deposition may well be the economic choice.

[00107] In some embodiments, this sub-aqueous deposition could be done with continuous processing of MFT and deposition in an oil sands mined-out pit for permanent sequestering of oil sands fines. Importantly, no further handling would ever be required.

[00108] According to an embodiment, the granulation process of the present disclosure may sequester process water contaminants such as arsenic (metalloids), selenium (polyatomic non-metals), and/or naphthenates (surfactants) within the granulated and aggregated tailings structure. These substances can be considered contaminants and therefore, undesirable for various reasons (e.g. environmental impact). Without being limited to any particular theory, the high charge cationic coagulant component (e.g. the second step in the formation of the binder) will insolublize and sequester arsenic, selenium, and naphthenates, in the formed granulated solids.

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[00109] The embodiments of the present application described above are intended to be examples only. Those of skill in the art may effect alterations, modifications and variations to the particular embodiments without departing from the intended scope of the present application. In particular, features from one or more of the above-described embodiments may be selected to create alternate embodiments comprised of a subcombination of features which may not be explicitly described above. In addition, features from one or more of the above-described embodiments may be selected and combined to create alternate embodiments comprised of a combination of features which may not be explicitly described above. Features suitable for such combinations and subcombinations would be readily apparent to persons skilled in the art upon review of the present application as a whole. Any dimensions provided in the drawings are provided for illustrative purposes only and are not intended to be limiting on the scope of the invention. The subject matter described herein and in the recited claims intends to cover and embrace all suitable changes in technology.

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CLAIMS

1. A method for treating fine tailings of a slurry comprising water, solid mineral component(s), and/or organic components derived from oil sands extractions to form a granulated aggregated material and an aqueous component, the method comprising:

   subjecting tailings to a sufficient dosage of an anionic polymer flocculant and to a sufficient dosage of a cationic polymer coagulant so as to convert the tailings into a granulated aggregated material and an aqueous component,

   wherein the cationic polymer coagulant is a high molecular weight diallyl dimethyl ammonium chloride polymer (DADMAC) or a high molecular weight dimethylamine/epichlorohydrin copolymer (DMA/EPI),

   wherein the sufficient dosage of the anionic polymer flocculant is greater than about 250 g/ton tailing solids, and wherein the sufficient dosage of the cationic polymer coagulant is greater than about 25 g/ton of tailing solids.

2. The method of claim 1 wherein the subjecting the tailings comprises subjecting the tailings to the sufficient dosage of the anionic polymer flocculant to form a paste material; and then subjecting the paste material to the sufficient dosage of the cationic polymer coagulant, wherein the reaction of the anionic polymer flocculant with the cationic polymer coagulant forms a granulating binder that converts the paste material into the granulated aggregated material and the aqueous component.

3. The method of claim 1 or 2 further comprising one or more of mixing the paste material before the subjecting the paste material to the cationic

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polymer coagulant and mixing after the subjecting the paste material to the cationic polymer coagulant.

4. The method of claim 1 wherein the sufficient dosage of the anionic polymer flocculant is greater than about 1000 g/ton of tailing solids.

5. The method of any one of claims 1 to 4 wherein the sufficient dosage of the anionic polymer flocculant is about 1,115 g/ton of tailing solids.

6. The method of any one of claims 1 to 5 wherein the sufficient dosage of the cationic polymer coagulant is about 995 g/ton of tailing solids.

7. The method of any one of claims 1 to 3 wherein the sufficient dosage of the anionic polymer flocculant is at least about 1.5 to about 2 times the dosage of conventional flocculation which is about 250 to 500 ppm and the sufficient dosage of the cationic coagulant is at least about 18 to about 40 times the dosage of conventional coagulation which is about 25 ppm.

8. The method of any one of claims 1 to 7 wherein the anionic polymer is a copolymer or terpolymer anionic flocculant, or is a high-molecular-weight copolymer or terpolymer anionic flocculant.

9. The method of any one of claims 1 to 8 wherein the anionic polymer flocculant is a sodium acrylate/acrylamide copolymer, a potassium acrylate/acrylamide copolymer, ammonium acrylate/acrylamide copolymer, or a calcium diacrylate/acrylamide copolymer.

10. The method of claim 9 wherein the sodium acrylate/acrylamide copolymer is a 35wt.% or a 46 wt.% sodium acrylate/acrylamide copolymer.

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11. The method of claim 9 wherein the sodium acrylate/acrylamide copolymer is a high molecular weight copolymer.

12. The method of claim 9 wherein the calcium diacrylate/acrylamide copolymer is a 40 wt.% calcium diacrylate/acrylamide copolymer.

13. The method of claim 9 wherein the calcium diacrylate/acrylamide copolymer is a medium or a high molecular weight copolymer.

14. The method of any one of claims 1 to 13 further comprising admixing a cationic polymer flocculant with the cationic polymer coagulant before the step of subjecting the tailings to the sufficient dosage of the cationic polymer coagulant.

15. The method of claim 14 wherein the admixing produces a blend of cationic polymer flocculant and high molecular weight dimethylamine/epichlorohydrin copolymer (DMA/EPI).

16. The method of claim 15 wherein the blend comprises up to a 20 wt.% cationic polymer flocculant.

17. The method of claim 15 wherein the blend comprises less than or about a 10 wt.% cationic polymer flocculant.

18. The method of claim 15 wherein the blend is a 5 wt.% cationic polymer flocculant and 95wt.% DMA/EPI (actives) blend.

19. The method of any one of claims 14 to 18 further comprising the step of diluting the cationic polymer coagulant with water before the step of admixing of the cationic polymer flocculant.

20. The method of any one of claims 14 to 19 wherein the cationic polymer flocculant is a quaternary/acrylamide cationic dry flocculant.

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21. The method of any one of claims 1 to 20 further comprising diluting the anionic polymer flocculant solution with water before the step of subjecting the tailings to the sufficient dosage of the anionic polymer flocculant.

22. The method of any one of claims 1 to 21 further comprising separating the granulated aggregated material from the aqueous component.

23. The method of any one of claims 1 to 22 where the aqueous component comprises water.

24. The method of any one of claims 1 to 23 wherein the tailings are fresh fine tailings (FFT) or mature fine tailings (MFT).

25. The method of any one of claims 1 to 23 wherein the tailings are extraction tailings.

26. The method of any one of claims 1 to 25 wherein the granulated aggregated material comprises sequestered contaminants.

27. The method of claim 26 wherein the sequestered contaminants are one or more of metalloids, polyatomic non-metals, and surfactants.

28. The method of claim 26 wherein the sequestered contaminants comprise arsenic, selenium, and naphthenate.

29. The method of any one of claims 1 to 28 wherein the fine tailings are particulates that are less than or equal to 44 microns.

30. A method for treating fine tailings of a slurry comprising water, solid mineral component(s), and/or organic components derived from oil sands extractions to form a granulated aggregated material and an aqueous component, the method comprising:

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subjecting tailings to a sufficient dosage of an anionic polymer flocculant and to a sufficient dosage of a cationic polymer coagulant so as to convert the tailings into a granulated aggregated material and an aqueous component,

wherein the sufficient dosage of the cationic polymer coagulant is about 995 g/ton of tailing solids.

31. The method of claim 30 wherein the subjecting the tailings comprises subjecting the tailings to the sufficient dosage of the anionic polymer flocculant to form a paste material; and then subjecting the paste material to the sufficient dosage of the cationic polymer coagulant, wherein the reaction of the anionic polymer flocculant with the cationic polymer coagulant forms a granulating binder that converts the paste material into the granulated aggregated material and the aqueous component.

32. The method of claim 30 or 31 further comprising one or more of mixing the paste material before the subjecting the paste material to the cationic polymer coagulant and mixing after the subjecting the paste material to the cationic polymer coagulant.

33. The method of any one of claims 30 to 32 wherein the sufficient dosage of the anionic polymer flocculant is greater than about 250 g/ton tailing solids.

34. The method of claim 33 wherein the sufficient dosage of the anionic polymer flocculant is greater than about 1000 g/ton of tailing solids.

35. The method of any one of claims 30 to 34 wherein the sufficient dosage of the anionic polymer flocculant is about 1,115 g/ton of tailing solids.

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36. The method of any one of claims 30 to 35 wherein the sufficient dosage of the anionic polymer flocculant is at least about 1.5 to about 2 times the dosage of about 250 to 500 ppm as in conventional flocculation.

37. The method of any one of claims 30 to 36 wherein the anionic polymer is a copolymer or terpolymer anionic flocculant, or is a high-molecular-weight copolymer or terpolymer anionic flocculant.

38. The method of any one of claims 30 to 37 wherein the anionic polymer flocculant is a sodium acrylate/acrylamide copolymer, a potassium acrylate/acrylamide copolymer, ammonium acrylate/acrylamide copolymer, or a calcium diacrylate/acrylamide copolymer.

39. The method of claim 38 wherein the sodium acrylate/acrylamide copolymer is a 35wt.% or a 46 wt.% sodium acrylate/acrylamide copolymer.

40. The method of claim 38 wherein the sodium acrylate/acrylamide copolymer is a high molecular weight copolymer.

41. The method of claim 38 wherein the calcium diacrylate/acrylamide copolymer is a 40 wt.% calcium diacrylate/acrylamide copolymer.

42. The method of claim 38 wherein the calcium diacrylate/acrylamide copolymer is a medium or a high molecular weight copolymer.

43. The method of any one of claims 30 to 42 further comprising admixing a cationic polymer flocculant with the cationic polymer coagulant before the step of subjecting the tailings to the sufficient dosage of the cationic polymer coagulant.

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44. The method of claim 43 wherein the admixing produces a blend of cationic polymer flocculant and high molecular weight dimethylamine/epichlorohydrin copolymer (DMA/EPI).

45. The method of claim 44 wherein the blend comprises up to a 20 wt.% cationic polymer flocculant.

46. The method of claim 44 wherein the blend comprises less than or about a 10 wt.% cationic polymer flocculant.

47. The method of claim 44 wherein the blend is a 5 wt.% cationic polymer flocculant and 95wt.% DMA/EPI (actives) blend.

48. The method of any one of claims 43 to 47 further comprising the step of diluting the cationic polymer coagulant with water before the step of admixing of the cationic polymer flocculant.

49. The method of any one of claims 43 to 48 wherein the cationic polymer flocculant is a quaternary/acrylamide cationic dry flocculant.

50. The method of any one of claims 30 to 49 further comprising diluting the anionic polymer flocculant solution with water before the step of subjecting the tailings to the sufficient dosage of the anionic polymer flocculant.

51. The method of any one of claims 30 to 50 further comprising separating the granulated aggregated material from the aqueous component.

52. The method of any one of claims 30 to 51 where the aqueous component comprises water.

53. The method of any one of claims 30 to 52 wherein the tailings are FFT or MFT.

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54. The method of any one of claims 30 to 53 wherein the tailings are extraction tailings.

55. The method of any one of claims 30 to 54 wherein the granulated aggregated material comprises sequestered contaminants.

56. The method of claim 55 wherein the sequestered contaminants are one or more of metalloids, polyatomic non-metals, and surfactants.

57. The method of claim 55 wherein the sequestered contaminants comprise arsenic, selenium, and naphthenate.

58. The method of any one of claims 30 to 57 wherein the fine tailings are particulates that are less than or equal to 44 microns.

59. A method for treating fine tailings of a slurry comprising water, solid mineral component(s), and/or organic components derived from oil sands extractions to form a granulated aggregated material and an aqueous component, the method comprising:

admixing a cationic polymer flocculant with a cationic polymer coagulant, wherein the cationic polymer coagulant is a high molecular weight dimethylamine/epichlorohydrin copolymer (DMA/EPI) to produce a blend, wherein the blend comprises up to a 20 wt.% cationic polymer flocculant,

subjecting tailings to a sufficient dosage of an anionic polymer flocculant to form a paste material, wherein the sufficient dosage of the anionic polymer flocculant is greater than about 250 g/ton tailing solids and then subjecting the paste material to a sufficient dosage of the blend having a dosage of the cationic polymer coagulant of greater than about 25 g/ton tailing solids, wherein the reaction of the anionic polymer flocculant with

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the blend forms a granulating binder that converts the paste material into a granulated aggregated material and an aqueous component.

60.The method of claim 59 further comprising one or more of mixing the paste material before the subjecting the paste material to the blend and mixing after the subjecting the paste material to the blend.

61.The method of claim 59 or 60 wherein the sufficient dosage of the anionic polymer flocculant is greater than about 1000 g/ton of tailing solids.

62.The method of any one of claims 59 to 61 wherein the sufficient dosage of the anionic polymer flocculant is about 1,115 g/ton of tailing solids.

63.The method of any one of claims 59 to 62 wherein the sufficient dosage of the anionic polymer flocculant is at least about 1.5 to about 2 times the dosage of about 250 to 500 ppm as in conventional flocculation.

64.The method of any one of claims 59 to 63 wherein the anionic polymer is a copolymer or terpolymer anionic flocculant, or is a high-molecular-weight copolymer or terpolymer anionic flocculant.

65.The method of any one of claims 59 to 64 wherein the anionic polymer flocculant is a sodium acrylate/acrylamide copolymer, a potassium acrylate/acrylamide copolymer, ammonium acrylate/acrylamide copolymer, or a calcium diacrylate/acrylamide copolymer.

66.The method of claim 65 wherein the sodium acrylate/acrylamide copolymer is a 35wt.% or a 46 wt.% sodium acrylate/acrylamide copolymer.

67.The method of claim 65 wherein the sodium acrylate/acrylamide copolymer is a high molecular weight copolymer.

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68.The method of claim 65 wherein the calcium diacrylate/acrylamide copolymer is a 40 wt.% calcium diacrylate/acrylamide copolymer.

69.The method of claim 65 wherein the calcium diacrylate/acrylamide copolymer is a medium or a high molecular weight copolymer.

70.The method of any one of claims 59 to 69 wherein the blend comprises less than or about a 10 wt.% cationic polymer flocculant.

71.The method of any one of claims 59 to 69 wherein the blend is a 5 wt.% cationic polymer flocculant and 95wt.% DMA/EPI (actives) blend.

72.The method of any one of claims 59 to 71 further comprising the step of diluting the cationic polymer coagulant with water before the step of admixing of the cationic polymer flocculant.

73.The method of any one of claims 59 to 72 wherein the cationic polymer flocculant is a quaternary/acrylamide cationic dry flocculant.

74.The method of any one of claims 59 to 73 further comprising diluting the anionic polymer flocculant solution with water before the step of subjecting the tailings to the sufficient dosage of the anionic polymer flocculant.

75.The method of any one of claims 59 to 74 further comprising separating the granulated aggregated material from the aqueous component.

76.The method of any one of claims 59 to 75 where the aqueous component comprises water.

77.The method of any one of claims 59 to 76 wherein the tailings are FFT or MFT.

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78. The method of any one of claims 59 to 77 wherein the tailings are extraction tailings.

79. The method of any one of claims 59 to 77 wherein the granulated aggregated material comprises sequestered contaminants.

80. The method of claim 79 wherein the sequestered contaminants are one or more of metalloids, polyatomic non-metals, and surfactants.

81. The method of claim 79 wherein the sequestered contaminants comprise arsenic, selenium, and naphthenate.

82. The method of any one of claims 59 to 81 wherein the fine tailings are particulates that are less than or equal to 44 microns.

83. A granulating binder for immobilizing mineral solids within a waste stream of mineral solids-containing water slurry obtained from a mining process, the granulating binder comprises a sufficient dosage of an anionic polymer flocculant with a sufficient dosage of a cationic polymer coagulant, wherein the reaction of the anionic polymer flocculant with the cationic polymer coagulant in the presence of mineral solids within a waste stream of mineral solids-containing water slurry forms the granulated binder that will immobilize the mineral solids into a granulated aggregated material, wherein the cationic polymer coagulant is a high molecular weight diallyl dimethyl ammonium chloride polymer (DADMAC) or a high molecular weight dimethylamine/epichlorohydrin copolymer (DMA/EPI), wherein the sufficient dosage of the anionic polymer flocculant is in an excess of the dosage of conventional flocculation which is about 250 to 500 ppm and the sufficient dosage of the cationic polymer coagulant in an excess of the dosage of conventional coagulation which is about 25 ppm.

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84. The binder of claim 83 wherein the sufficient dosage of the anionic polymer flocculant is mixed with the mineral solids to form a paste material; and the sufficient dosage of the cationic polymer coagulant is mixed with the paste material to convert the paste material into the granulated aggregated material.

85. The binder of claim 83 or 84 wherein the sufficient dosage of the anionic polymer flocculant is at least about 1.5 to about 2 times the dosage of conventional flocculation which is about 250 to 500 ppm and the sufficient dosage of the cationic coagulant at least about 18 to about 40 times the dosage of conventional coagulation which is about 25 ppm.

86. The binder of any one of claims 83 to 85 wherein the anionic polymer is a copolymer or terpolymer anionic flocculant, or is a high-molecular-weight copolymer or terpolymer anionic flocculant.

87. The binder of any one of claims 83 to 86 wherein the anionic polymer flocculant is a sodium acrylate/acrylamide copolymer, a potassium acrylate/acrylamide copolymer, ammonium acrylate/acrylamide copolymer, or a calcium diacrylate/acrylamide copolymer.

88. The binder of claim 87 wherein the sodium acrylate/acrylamide copolymer is a 35 wt.% or a 46 wt.% sodium acrylate/acrylamide copolymer.

89. The binder of claim 87 wherein the sodium acrylate/acrylamide copolymer is a high molecular weight copolymer.

90. The binder of claim 87 wherein the calcium diacrylate/acrylamide copolymer is a 40 wt.% calcium diacrylate/acrylamide copolymer.

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91. The binder of claim 87 wherein the calcium diacrylate/acrylamide copolymer is a medium or a high molecular weight copolymer.

92. The binder of any one of claims 83 to 91 further comprising a cationic polymer flocculant to form a blend of the cationic polymer flocculant and the cationic polymer coagulant.

93. The binder of claim 92 wherein the blend comprises up to a 20 wt.% cationic polymer flocculant.

94. The binder of claim 92 wherein the blend comprises less than or about a 10 wt.% cationic polymer flocculant.

95. The binder of claim 92 wherein the blend is a 5 wt.% cationic polymer flocculant and 95 wt.% DMA/EPI (actives) blend.

96. The binder of any one of claims 92 to 95 wherein the cationic polymer flocculant is a quaternary/acrylamide cationic dry flocculant.

97. The binder of any one of claims 92 to 95 wherein the cationic polymer flocculant is Zetag 7563.

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Figure 1

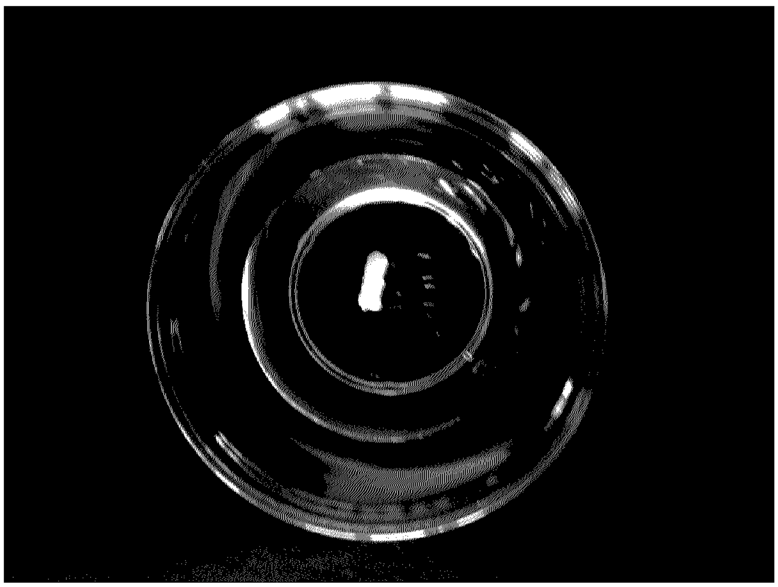

Figure 2

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Figure 3

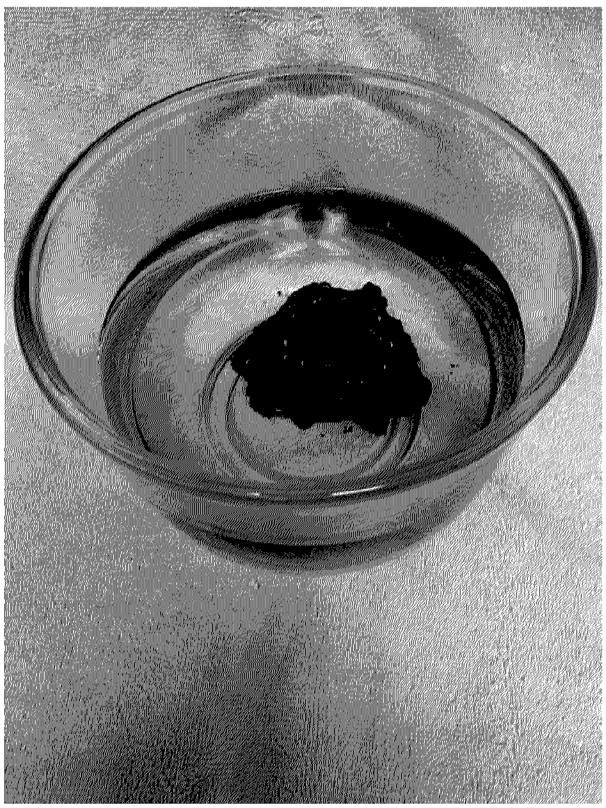

Figure 4

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Figure 5

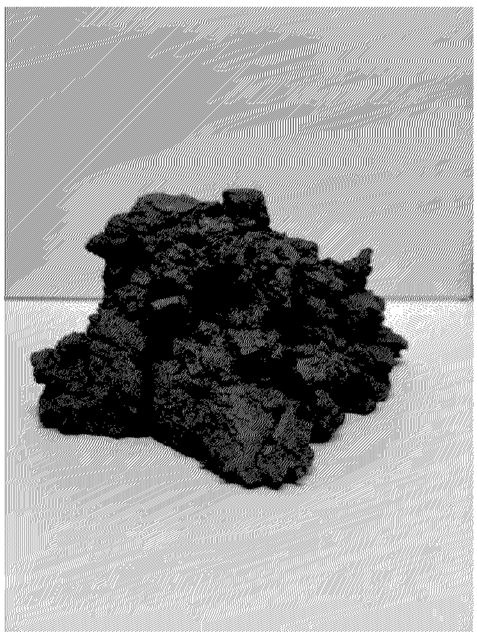

Figure 6

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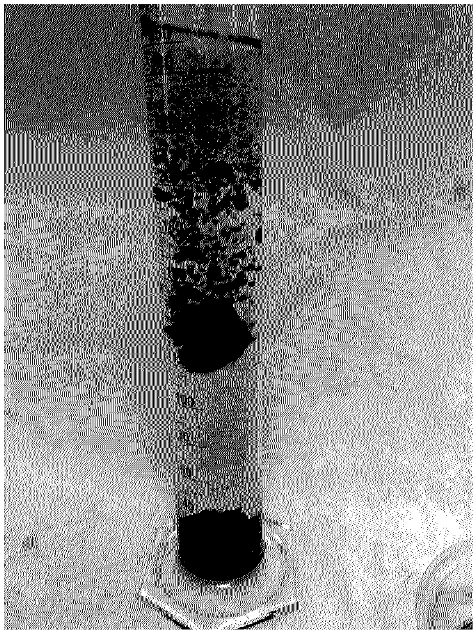

Figure 7

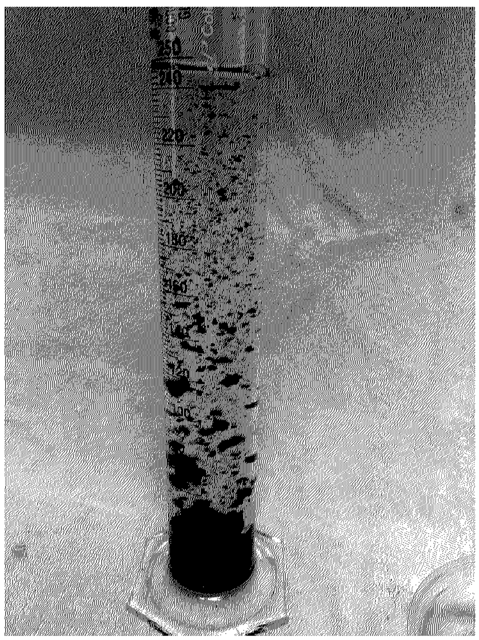

Figure 8

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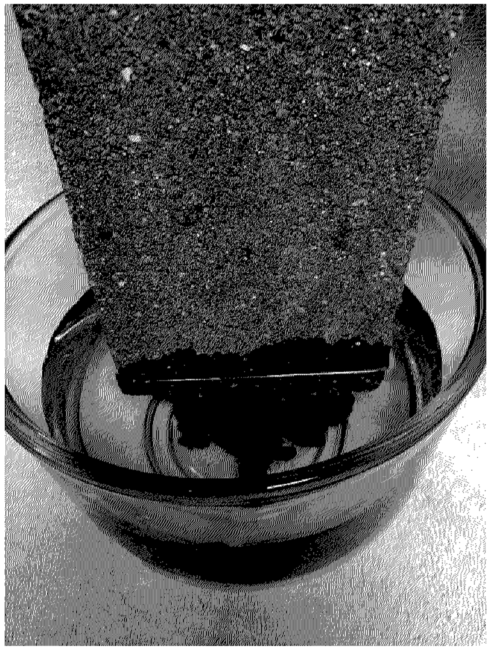

Figure 9

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