



(51) International Patent Classification:

E21B 33/13 (2006.01) *E21B 49/00* (2006.01)
C09K 8/42 (2006.01)

(21) International Application Number:

PCT/US2017/018930

(22) International Filing Date:

22 February 2017 (22.02.2017)

(25) Filing Language:

English

(26) Publication Language:

English

(71) Applicant: **HALLIBURTON ENERGY SERVICES, INC.** [US/US]; 3000 N. Sam Houston Parkway E., Houston, Texas 77032-3219 (US).

(72) Inventors: **MORGAN, Ronnie Glen**; 14069 North 2770 Road, Waurika, Oklahoma 73573 (US). **PISKLAK, Thomas Jason**; 14122 Cellini Drive, Cypress, Texas 77429 (US). **RIGGIO, Sean William**; 3433 West Dallas St., Houston, Texas 77056 (US). **LEWIS, Samuel J.**; 3 Dahlia Trail Pl, Spring, Texas 77382 (US).

(74) Agent: **TUMEY, Corey, S.**; Tumey L.L.P., P.O. Box 22188, Houston, Texas 77227-2188 (US).

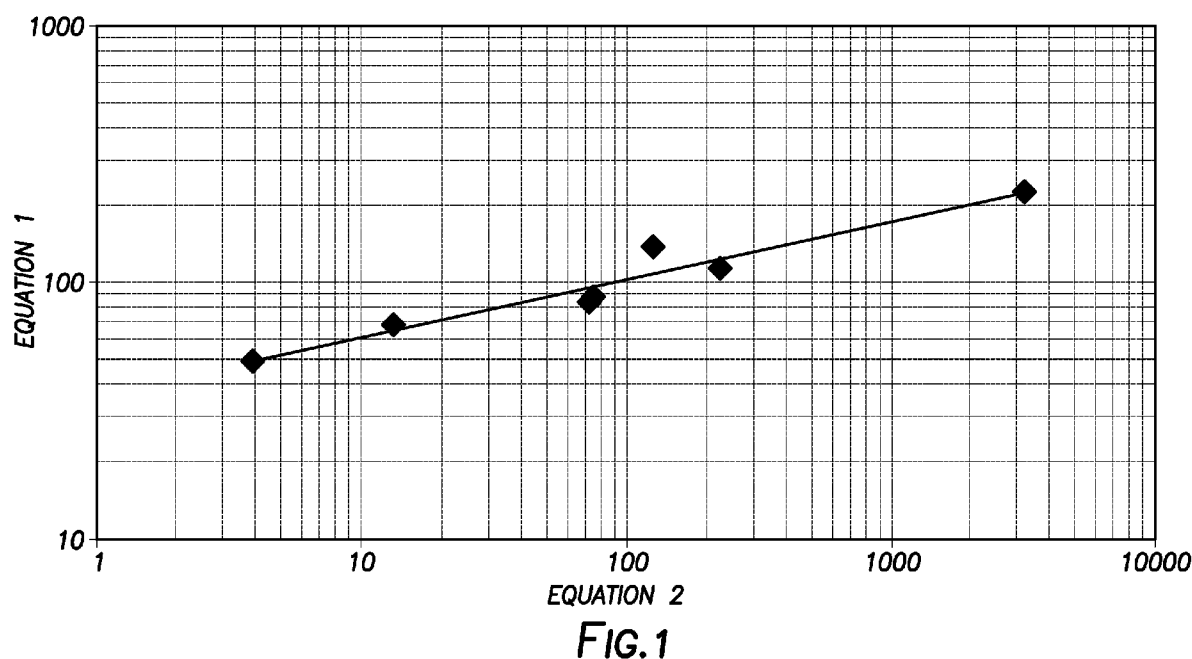
(81) Designated States (*unless otherwise indicated, for every kind of national protection available*): AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DJ, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IR, IS, JP, KE, KG, KH, KN, KP, KR, KW, KZ, LA, LC, LK, LR, LS, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) Designated States (*unless otherwise indicated, for every kind of regional protection available*): ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, ST, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, KM, ML, MR, NE, SN, TD, TG).

Declarations under Rule 4.17:

— *of inventorship (Rule 4.17(iv))*

(54) Title: APPLICATION OF WATER REQUIREMENT MEASUREMENTS TO APPROXIMATE SPECIFIC SURFACE AREA



(57) Abstract: Methods of wellbore cementing are provided. A method of analyzing a solid particulate including: measuring a water requirement of the solid particulate; and determining an approximation of specific surface area of the solid particulate from the water requirement.

Published:

— *with international search report (Art. 21(3))*

APPLICATION OF WATER REQUIREMENT MEASUREMENTS TO APPROXIMATE SPECIFIC SURFACE AREA

BACKGROUND

[0001] In well cementing, such as well construction and remedial cementing, cement compositions are commonly utilized. Cement compositions may be used in a variety of subterranean applications. For example, in subterranean well construction, a pipe string (*e.g.*, casing, liners, expandable tubulars, etc.) may be run into a well bore and cemented in place. The process of cementing the pipe string in place is commonly referred to as “primary cementing.” In a typical primary cementing method, a cement composition may be pumped into an annulus between the walls of the well bore and the exterior surface of the pipe string disposed therein. The cement composition may set in the annular space, thereby forming an annular sheath of hardened, substantially impermeable cement (*i.e.*, a cement sheath) that may support and position the pipe string in the well bore and may bond the exterior surface of the pipe string to the subterranean formation. Among other things, the cement sheath surrounding the pipe string functions to prevent the migration of fluids in the annulus, as well as protecting the pipe string from corrosion. Cement compositions also may be used in remedial cementing methods, for example, to seal cracks or holes in pipe strings or cement sheaths, to seal highly permeable formation zones or fractures, to place a cement plug, and the like.

[0002] A particular challenge in well cementing is the development of satisfactory mechanical properties in a cement composition within a reasonable time period after placement in the subterranean formation. Oftentimes several cement compositions with varying additives are tested to see if they meet the material engineering requirements for a particular well. The process of selecting the components of the cement composition are usually done by a best guess approach by utilizing previous slurries and modifying them until a satisfactory solution is reached. The process may be time consuming and the resulting slurry may be expensive. Furthermore, the cement components available in any one particular region may vary in composition from those of another region thereby further complicating the process of selecting a correct slurry.

BRIEF DESCRIPTION OF THE DRAWINGS

[0003] These drawings illustrate certain aspects of some of the embodiments of the present invention, and should not be used to limit or define the invention.

[0004] FIG. 1 is a chart showing simulated results for compressive strength index calculations.

[0005] FIG. 2 is a chart showing simulated results for compressive strength index calculations.

[0006] FIG. 3 is a schematic illustration of an example system for analyzing cement components.

[0007] FIG. 4 is a schematic illustration of an example system for generating cement compositions.

[0008] FIG. 5 is a schematic illustration of showing introduction of a cement composition into a wellbore.

DETAILED DESCRIPTION

[0009] The present disclosure may generally relate to cementing methods and systems. Provided herein are methods of identifying and categorizing silica sources, cements, and other materials based on physiochemical properties. In some examples, water requirement measurements may be correlated to specific surface area so that specific surface area of the cement component may be approximated. The physiochemical properties of each cement component of a cement composition may affect the final set mechanical properties of the slurry as well as the dynamic or time based properties such as mixability, rheology, viscosity, and others. Every cement component may affect one or more of the properties mentioned. For example, a locally sourced fly ash may be added to a cement composition. The added fly ash may increase the compressive strength of the cement composition and may have no effect on for example, the thickening time of the cement composition. In another region, a locally sourced fly ash may also increase the compressive strength of the cement composition but may also increase the thickening time. The unpredictable behavior of a cement composition may not be realized until multiple lab tests have been performed. As specific surface area measurements may require specialized equipment that may not always be available, water requirement measurement may be used to approximate the specific surface area. Once the specific surface area is available, the reactivity of the cement component may be determined and used in designing a cement composition.

[0010] The cement compositions generally may comprise water and a cement additive. The cement additive may comprise two or more cement components, which may be dry blended to form the cement additive prior to combination with the water. Alternatively, the cement components may not be combined until mixture with the water. The cement components may generally be described as alkali soluble. While a number of different embodiments are contemplated, a cement composition may comprise water and a cement additive, wherein the cement additive comprises hydraulic cement and two or more silica sources, such as cement kiln dust and a natural pozzolan. As described in more detail herein, the cement compositions may be foamed and/or extended as desired by those of ordinary skill in the art.

[0011] The cement compositions may have a density suitable for a particular application. The cement compositions may have a density in the range of about 8 pounds per gallon (“ppg”) to about 16 ppg. In the foamed examples, the foamed cement compositions of the present invention may have a density in the range of about 8 ppg to about 13 ppg (or even lower).

[0012] The water used in the cement compositions may include, for example, freshwater, saltwater (e.g., water containing one or more salts dissolved therein), brine (e.g., saturated saltwater produced from subterranean formations), seawater, or combinations thereof. Generally, the water may be from any source, provided that it does not contain an excess of compounds that may undesirably affect other components in the cement composition. The water may be included in an amount sufficient to form a pumpable slurry. The water may be included in the cement compositions in the range of about 40% to about 200% by weight of the cement additive (“bwoc”). In some examples, the water may be included in an amount in the range of about 40% to about 150% bwoc.

[0013] The cement additive may comprise two or more cement components. A variety of hydraulic cements may be utilized in accordance with the present disclosure, including, but not limited to, those comprising calcium, aluminum, silicon, oxygen, iron, and/or sulfur, which set and harden by reaction with water. Suitable hydraulic cements may include Portland cements, gypsum, and high alumina content cements, among others. Portland cements that are suited for use in the present disclosure may be classified as Classes A, C, G, and H cements according to American Petroleum Institute, API Specification for Materials and Testing for Well Cements, API Specification 10, Fifth Ed., Jul. 1, 1990. In addition, in some examples, cements suitable for use in the present invention may be

classified as ASTM Type I, II, III, or V. Cement compositions that may be considered “low Portland” may be designed by use of the techniques disclosed herein.

[0014] Where present, the hydraulic cement generally may be included in the cement compositions in an amount sufficient to provide the desired compressive strength, density, and/or cost. The hydraulic cement may be present in the cement compositions in any suitable concentration, including in an amount in the range of about 0% to about 99% bwoc. The hydraulic cement may be present in an amount ranging between any of and/or including any of about 1%, about 5%, about 10%, about 20%, about 40%, about 60%, about 80%, or about 90% bwoc. The cement component may be considered “low Portland” in that the Portland cement (where used) may be present in the cement composition in an amount of about 40% or less bwoc and, alternatively, about 10% or less. Cement compositions may also be designed that are free (or essentially free) of Portland cement. Those of ordinary skill in the art, with the benefit of this disclosure, should be able to select an appropriate amount of hydraulic cement for a particular application.

[0015] In addition to Portland cement, additional cement components may be used that can be considered alkali soluble. A cement component is considered alkali soluble where it is at least partially soluble in an aqueous solution of pH 7.0 or greater. Certain of the alkali soluble cement components may comprise a geopolymer cement, which may comprise an aluminosilicate source, a metal silicate source, and an activator. The geopolymer cement may react to form a geopolymer. A geopolymer is an inorganic polymer that forms long-range, covalently bonded, non-crystalline networks. Geopolymers may be formed by chemical dissolution and subsequent re-condensation of various aluminosilicates and silicates to form a 3D-network or three-dimensional mineral polymer. The activator may include, but is not limited to, metal hydroxides chloride salts such as KCl, CaCl₂, NaCl, carbonates such as Na₂CO₃, silicates such as sodium silicate, aluminates such as sodium aluminate, and ammonium hydroxide. The aluminosilicate source may comprise any suitable aluminosilicate. Aluminosilicate is a mineral comprising aluminum, silicon, and oxygen, plus counter-cations. There are potentially hundreds of suitable minerals that may be an aluminosilicate source in that they may comprise aluminosilicate minerals. Each aluminosilicate source may potentially be used in a particular case if the specific properties, such as composition, may be known. Some minerals such as andalusite, kyanite, and sillimanite are naturally occurring aluminosilicate sources that have the same composition, Al₂SiO₅, but differ in crystal structure. Each mineral andalusite, kyanite, or sillimanite may

react more or less quickly and to different extents at the same temperature and pressure due to the differing crystal structures. Other suitable aluminosilicate sources may include, but are not limited to, calcined clays, partially calcined clays, kaolinite clays, lateritic clays, illite clays, volcanic rocks, mine tailings, blast furnace slag, and coal fly ash. The metal silicate source may comprise any suitable metal silicate. A silicate is a compound containing an anionic silicon compound. Some examples of a silicate include the orthosilicate anion also known as silicon tetroxide anion, SiO_4^{4-} as well as hexafluorosilicate $[\text{SiF}_6]^{2-}$. Other common silicates include cyclic and single chain silicates which may have the general formula $[\text{SiO}_{2+n}]^{2n-}$ and sheet-forming silicates $([\text{SiO}_{2.5}]^-)_n$. Each silicate example may have one or more metal cations associated with each silicate molecule. Some suitable metal silicate sources and may include, without limitation, sodium silicate, magnesium silicate, and potassium silicate.

[0016] Where present, the geopolymer cement generally may be included in the cement compositions in an amount sufficient to provide the desired compressive strength, density, and/or cost. The geopolymer cement may be present in the cement compositions in any suitable concentration, including an amount in the range of about 0% to about 99% bwoc. The geopolymer cement may be present in an amount ranging between any of and/or including any of about 1%, about 5%, about 10%, about 20%, about 40%, about 60%, about 80%, or about 90% bwoc. Those of ordinary skill in the art, with the benefit of this disclosure, should be able to select an appropriate amount of geopolymer cement for a particular application.

[0017] Additional cement components that are alkali soluble may include a silica source. The silica source may be any suitable material that provides silica to the cement composition. By inclusion of the silica source, a different path may be used to arrive at a similar product as from Portland cement. A pozzolanic reaction may be induced wherein silicic acid (H_4SiO_4) and portlandite ($\text{Ca}(\text{OH})_2$) react to form a cement product (calcium silicate hydrate). If other compounds, such as, aluminate, are present in the silica source, additional reactions may occur to form additional cement products, such as calcium aluminate hydrates. Calcium hydroxide necessary for the reaction may be provide from other cement components, such as Portland cement, or may be separately added to the cement composition. Examples of suitable silica sources may include fly ash, slag, silica fume, crystalline silica, silica flour, cement kiln dust ("CKD"), volcanic rock, perlite, metakaolin, diatomaceous earth, zeolite, shale, and agricultural waste ash (e.g., rice husk ash, sugar cane ash, and bagasse ash), among other. Some specific examples of the silica source will be

discussed in more detail below. Where present, the silica source generally may be included in the cement compositions in an amount sufficient to provide the desired compressive strength, density, and/or cost. The silica source may be present in the cement compositions in any suitable concentration, including in an amount in the range of about 0% to about 99% bwoc. The silica source may be present in an amount ranging between any of and/or including any of about 1%, about 5%, about 10%, about 20%, about 40%, about 60%, about 80%, or about 90% bwoc. Those of ordinary skill in the art, with the benefit of this disclosure, should be able to select an appropriate amount of silica source for a particular application.

[0018] An example of a suitable silica source may comprise fly ash. A variety of fly ash may be suitable, including fly ash classified as Class C and Class F fly ash according to American Petroleum Institute, API Specification for Materials and Testing for Well Cements, API Specification 10, Fifth Ed., July 1, 1990. Class C fly ash comprises both silica and lime, so it may set to form a hardened mass upon mixing with water. Class F fly ash generally does not contain a sufficient amount of lime to induce a cementitious reaction, therefore, an additional source of calcium ions is necessary for a set-delayed cement composition comprising Class F fly ash. Where used, lime may be mixed with Class F fly ash in any suitable amount, including in an amount in the range of about 0.1% to about 100% by weight of the fly ash. In some instances, the lime may be hydrated lime. Suitable examples of fly ash include, but are not limited to, POZMIX[®] A cement additive, commercially available from Halliburton Energy Services, Inc., Houston, Texas.

[0019] Another example of a suitable silica source may comprise slag. Slag is generally a by-product in the production of various metals from their corresponding ores. By way of example, the production of cast iron can produce slag as a granulated, blast furnace by-product with the slag generally comprising the oxidized impurities found in iron ore. Slag generally does not contain sufficient basic material, so slag cement may be used that further may comprise a base to produce a settable composition that may react with water to set to form a hardened mass. Examples of suitable sources of bases include, but are not limited to, sodium hydroxide, sodium bicarbonate, sodium carbonate, lime, and combinations thereof.

[0020] Another example of a suitable silica source may comprise CKD. Cement kiln dust or "CKD", as that term is used herein, refers to a partially calcined kiln feed which is removed from the gas stream and collected, for example, in a dust collector during the manufacture of cement. Usually, large quantities of CKD are collected in the production of cement that are commonly disposed of as waste. Disposal of the CKD as waste can add undesirable costs to the manufacture of the cement, as well as the environmental concerns

associated with its disposal. CKD is another component that may be included in examples of the cement compositions.

[0021] Another example of a suitable silica source may comprise volcanic rock. Certain volcanic rocks can exhibit cementitious properties, in that they may set and harden in the presence of hydrated lime and water. The volcanic rock may also be ground, for example. Generally, the volcanic rock may have any particle size distribution as desired for a particular application. In certain embodiments, the volcanic rock may have a mean particle size in a range of from about 1 micron to about 200 microns. The mean particle size corresponds to d50 values as measured by particle size analyzers such as those manufactured by Malvern Instruments, Worcestershire, United Kingdom. One of ordinary skill in the art, with the benefit of this disclosure, should be able to select a particle size for the volcanic rock suitable for use for a chosen application.

[0022] Another example of a suitable silica source may comprise metakaolin. Generally, metakaolin is a white pozzolan that may be prepared by heating kaolin clay, for example, to temperatures in the range of about 600° to about 800°C.

[0023] Another example of a suitable silica source may comprise shale. Among other things, shale included in the cement compositions may react with excess lime to form a suitable cementing material, for example, calcium silicate hydrate. A variety of shales are suitable, including those comprising silicon, aluminum, calcium, and/or magnesium. An example of a suitable shale comprises vitrified shale. Generally, the shale may have any particle size distribution as desired for a particular application. In certain embodiments, the shale may have a particle size distribution in the range of about 37 micrometers to about 4,750 micrometers.

[0024] Another example of a suitable silica source may comprise zeolite. Zeolites generally are porous aluminosilicate minerals that may be either a natural or synthetic material. Synthetic zeolites are based on the same type of structural cell as natural zeolites, and may comprise aluminosilicate hydrates. As used herein, the term “zeolite” refers to all natural and synthetic forms of zeolite. Examples of zeolites may include, without limitation, mordenite, zsm-5, zeolite x, zeolite y, zeolite a, etc. Furthermore, examples comprising zeolite may comprise zeolite in combination with a cation such as Na⁺, K⁺, Ca²⁺, Mg²⁺, etc. Zeolites comprising cations such as sodium may also provide additional cation sources to the cement composition as the zeolites dissolve.

[0025] The cement compositions may further comprise hydrated lime. As used herein, the term “hydrated lime” will be understood to mean calcium hydroxide. In some examples, the hydrated lime may be provided as quicklime (calcium oxide) which hydrates when mixed with water to form the hydrated lime. The hydrated lime may be included in examples of the cement compositions, for example, to form a hydraulic composition with the silica source. The hydrated lime may be included in any suitable concentration, including, but not limited to, in a silica source-to-hydrated-lime weight ratio of about 10:1 to about 1:1 or a ratio of about 3:1 to about 5:1. Where present, the hydrated lime may be included in the cement compositions in an amount in the range of from about 10% to about 100% by weight of the silica source, for example. The hydrated lime may be present in an amount ranging between any of and/or including any of about 10%, about 20%, about 40%, about 60%, about 80%, or about 100% by weight of the silica source. One of ordinary skill in the art, with the benefit of this disclosure, should recognize the appropriate amount of hydrated lime to include for a chosen application.

[0026] The cement compositions may also comprise a calcium source other than hydrated lime, which may be used in addition, or in place of the hydrated lime. In general, calcium and a high pH, for example a pH of 7.0 or greater, may be needed for certain cementitious reactions to occur. A potential advantage of hydrated lime may be that calcium ions and hydroxide ions are supplied in the same molecule. In another example, the calcium source may be $\text{Ca}(\text{NO}_3)_2$ or CaCl_2 with the hydroxide being supplied from NaOH or KOH, for example. One of ordinary skill would understand the alternate calcium source and hydroxide source may be included in a cement composition in the same way as hydrated lime. For example, the calcium source and hydroxide source may be included in any suitable amount, including, but not limited to, a silica source-to-hydrated-lime weight ratio of about 10:1 to about 1:1 or a ratio of about 3:1 to about 5:1. Where present, the alternate calcium source and hydroxide source may be included in the cement compositions in an amount in the range of from about 10% to about 100% by weight of the silica source, for example. The alternate calcium source and hydroxide source may be present in an amount ranging between any of and/or including any of about 10%, about 20%, about 40%, about 60%, about 80%, or about 100% by weight of the silica source. One of ordinary skill in the art, with the benefit of this disclosure, should recognize the appropriate amount of alternate calcium source and hydroxide source to include for a chosen application.

[0027] A target silica lime ratio may be defined and a cement additive comprising two or more cement components may be identified that meets the silica lime ratio. In some examples, the target silica lime ratio may range from about 80/20 silica to free lime by weight to about 60/40 silica to free lime by weight, for example, be about 80/20 silica to free lime by weight, about 70/30 silica to free lime by weight, or about 60/40 silica to free lime by weight. The silica lime ratio may be determined by measuring the available silica and lime for a given cement component.

[0028] Other additives suitable for use in cementing operations also may be included in the cement compositions as needed for a particular application. Examples of such additives include, but are not limited to: weighting agents, activators, lightweight additives, gas-generating additives, mechanical-property-enhancing additives, lost-circulation materials, filtration-control additives, fluid-loss-control additives, defoaming agents, foaming agents, dispersants, thixotropic additives, and combinations thereof. One of ordinary skill in the art, with the benefit of this disclosure, should be able to select an appropriate additive for a particular application.

[0029] As mentioned previously, in order to determine if two or more of the aforementioned cement components are compatible, several lab tests may be run. Additionally, any potential synergistic effects of the cement component may not be known unless several laboratory tests are performed. Typically, a known cement composition may be first formulated and tested for properties such as, for example, the 24 hour compressive strength, fluid loss, and thickening time. Then, varying amounts of additives may be added to a fresh batch of cement compositions and the tests are re-run. The results are gathered from each test and compared. A new set of tests may then run with new concentrations of additives, for example, to adjust properties of the cement composition. The process of testing various additives in varying concentrations may go on for several trials until an acceptable cement composition or compositions is formulated. An acceptable cement composition may be one that meets certain design requirements, such as compressive strength, fluid loss, and thickening time. The cement composition design process may be done in a heuristic manner leading to a cement composition that may have the required engineering properties but may not be optimized for cost. Additionally, silica sources such as, for example, CKD, have been previously used as either pure fillers or in some examples, reactive components, in Portland based cement compositions. CKD will contribute a portion of silica which requires a portion

of lime to react. In methods of cement composition formulation described above, the heuristic process does not take into account the silica to lime ratio of a composition.

[0030] The method described herein may reduce or eliminate the heuristic search for by a process that identifies cement components for use in a cement composition through a process of measuring and categorizing a variety of cement components referred to as reactivity mapping. Reactivity mapping may comprise several steps. One step may comprise measuring the physical and chemical properties of different materials through standardized tests. Another step may comprise categorizing the materials through analysis of data collected and the predicted effect on cement slurry properties. Yet another step may comprise utilizing the data to estimate material reactivity, optimizing cement performance, predicting blend mechanical properties mathematically based on analytical results, and/or predict slurry density dependence of compressive strength.

[0031] Measuring physical and chemical properties of each selected cement component may comprise many laboratory techniques and procedures including, but not limited to, microscopy, spectroscopy, x-ray diffraction, x-ray fluorescence, particle size analysis, water requirement analysis, scanning electron microscopy, energy-dispersive X-ray spectroscopy, surface area, specific gravity analysis, thermogravimetric analysis, morphology analysis, infrared spectroscopy, ultraviolet-visible spectroscopy, mass spectroscopy, secondary ion mass spectrometry, electron energy mass spectrometry, dispersive x-ray spectroscopy, auger electron spectroscopy, inductively coupled plasma analysis, thermal ionization mass spectroscopy, glow discharge mass spectroscopy x-ray photoelectron spectroscopy, mechanical property testing, Young's Modulus testing, rheological properties, Poisson's Ratio. One or more of the preceding tests may be consider API tests, as set forth in the API recommended practice for testing well cements (published as ANSI/API recommended practice 10B-2). Additional API tests not specifically listed above may also be used for the measurements. The physical and chemical properties may be measured for a group of cement components. Two or more of the cement components measured may be different types of cement components (e.g., volcanic rock, CKD, fly ash, etc.). Two or more of the cement components may be the same type but from different sources (e.g., volcanic rock from source 1, volcanic rock from source 2, etc.).

[0032] X-ray powder diffraction is one analysis technique that may be used for measuring the physical and chemical properties of the cement components. X-ray powder diffraction is a technique of exposing a sample to x-rays, neutrons, or electrons and

measuring the amount of inter-atomic-diffraction. The sample acts a diffraction grating thereby producing a differing signal at different angles. The typical properties that may be measured are the phase identification for the identification and characterization of a crystalline solid. Other properties may be crystallinity, lattice parameters, expansion tensors, bulk modulus, and phase transitions.

[0033] X-ray fluorescence is another analysis technique that may be used for measuring the physical and chemical properties of the cement components. X-ray fluorescence may use short wave x-rays to ionize atoms in a sample thereby causing them to fluoresce at certain characteristic wavelengths. The characteristic radiation released by a sample may allow accurate identification of the component atoms in the sample as well as their relative amounts.

[0034] Particle size analysis is another analysis technique that may be used for measuring the physical and chemical properties of the cement components. Particle size analysis may be accomplished through analysis by various laboratory techniques including but not limited to laser diffraction, dynamic light scattering, static image analysis, and dynamic image analysis. Particle size analysis may also provide information about the morphology of a particular sample. Morphology may include parameters such as sphericity and roundness as well as the general shape of a particle such as disk, spheroid, blade, or roller. With a knowledge of the morphology and particle size, the average surface area and volume may be estimated. Surface area and volume may be important in determining the water requirement as well as reactivity. In general, a relatively smaller particle size may react more quickly than a relatively larger particle size. Also the relatively smaller particle size may have a greater water requirement to completely hydrate than a relatively larger particle size.

[0035] Energy dispersive x-ray spectroscopy is another analysis technique that may be used for measuring the physical and chemical properties of the cement components. Energy dispersive x-ray spectroscopy is an analytical technique used to analyze the elements present in a sample and determine the chemical characterization of a sample. Other techniques may include fourier transform infrared spectroscopy, ultraviolet-visible spectroscopy, mass spectroscopy, secondary ion mass spectrometry, electron energy mass spectrometry, dispersive x-ray spectroscopy, auger electron spectroscopy, and x-ray photoelectron spectroscopy.

[0036] The cement components may be analyzed to determine their water requirement. Water requirement is typically defined as the amount of mixing water that is required to be added to a powdered, solid material to form a slurry of a specified consistency. The consistency may vary for a particular application. The following example technique for determining water requirement holds the consistency and amount of water constant while varying the amount of the solid material. However, techniques may also be applied that vary the amount of the water, the consistency, and/or the amount of solid material in any combination. The following technique also estimates the specified consistency based on the size of the vortex at the surface of the mixture in the blender. Water requirement for a particular cement component may be determined by a process that includes a) preparing a blender (e.g., Waring® blender) with a specified amount of water (e.g., about 100 grams to about 500 grams), b) agitating the water at a specified blender rpm (e.g., 4,000 to 15,000 rpm), c) adding the powdered solid that is being investigated to the water until a specified consistency is obtained, and d) calculating the water requirement based on the ratio of water to solids required to obtain the desired consistency. A specific example for determining water requirement may include, but is not limited to: 1) preparing a blender (e.g., Waring® blender) with a specified amount of water (e.g., about 100 grams to about 500 grams or about 200 grams in one example); 2) agitating the water at a specified blender rpm (e.g., about 4,000 to about 15,000 rpm or about 12,000 rpm in one example); 3) adding a specified amount (e.g., about 1 gram to about 1,000 grams or about 400 grams in one example) of the cement component to the water; 4) observing mixture to determine if a specified consistency is obtained, for example, the cement component can be considered thoroughly wet and mixed if the vortex formed at the surface of the mixture in the blender is about 0 inches (0 mm) to about 2 inch (50 mm) or about 0.004 inches (0.1 mm) to about 1 inch (25 mm); 5) if the desired consistency is not obtained, add more cement component until desired consistency is obtained, for example, the vortex formed in the blender is about the size of a dime; and 6) calculate the water requirement based on the ratio of water to cement component to obtain the desired consistency. In some examples, the specific consistency may be where a vortex at the surface of the mixture in the blender is the size of a dime or about 0.7 in (17.9 mm). Other suitable techniques for determining the water requirement may also be used as will be appreciated by those of ordinary skill in the art.

[0037] The cement components may be analyzed to determine their specific surface area. Specific surface area generally refers to the total surface area and may be reported as the

total surface area per unit mass. Values obtained for specific area are dependent on the analysis technique. Any suitable analysis technique may be used, including, without limitation, adsorption based methods such as Brunauer-Emmett-Teller (BET) analysis, methylene blue staining, ethylene glycol monoethyl ether adsorption, and a protein-retention method, among other.

[0038] Thermogravimetric analysis is another analysis technique that may be used for measuring the physical and chemical properties of the cement components. Thermogravimetric analysis is a method of thermal analysis wherein changes in physical and chemical properties of a sample may be measured. In general the properties may be measured as a function of increasing temperature, such as with a constant heating rate, or as a function of time with a constant temperature or a constant mass change. Properties determined by thermogravimetric analysis may include first-order phase transitions and second-order phase transitions such as vaporization, sublimation, adsorption, desorption, absorption, chemisorption, desolvation, dehydration, decomposition, oxidation and reduction reactions, ferromagnetic transition, superconducting transition, and others.

[0039] In addition to determining physical and chemical properties of the cement components themselves, laboratory tests may also be run to determine behavior of the cement components in a cement composition. For example, the cement components may be analyzed in a cement composition to determine their compressive strength development and mechanical properties. For example, a preselected amount of the cement component may be combined with water and lime (if needed for setting). The mechanical properties of the cement composition may then be determined including, compressive strength, tensile strength, and Young's modulus. Any of a variety of different conditions may be used for the testing so long as the conditions are consistent for the different cement components.

[0040] Compressive strength is generally the capacity of a material or structure to withstand axially directed pushing forces. The compressive strength of the cement component may be measured at a specified time after the cement component has been mixed with water and the resultant cement composition is maintained under specified temperature and pressure conditions. For example, compressive strength can be measured at a time in the range of about 24 to about 48 hours (or longer) after the fluid is mixed and the fluid is maintained at a temperature of from 100 °F to about 200 °F and atmospheric pressure. Compressive strength can be measured by either a destructive method or non-destructive method. The destructive method physically tests the strength of treatment fluid samples at various points in time by

crushing the samples in a compression-testing machine. The compressive strength is calculated from the failure load divided by the cross-sectional area resisting the load and is reported in units of pound-force per square inch (psi). Non-destructive methods typically may employ an Ultrasonic Cement Analyzer (“UCA”), available from Fann[®] Instrument Company, Houston, TX. Compressive strengths may be determined in accordance with API RP 10B-2, *Recommended Practice for Testing Well Cements*, First Edition, July 2005.

[0041] Tensile strength is generally the capacity of a material to withstand loads tending to elongate, as opposed to compressive strength. The tensile strength of the cement component may be measured at a specified time after the cement component has been mixed with water and the resultant cement composition is maintained under specified temperature and pressure conditions. For example, tensile strength can be measured at a time in the range of about 24 to about 48 hours (or longer) after the fluid is mixed and the fluid is maintained at a temperature of from 100 °F to about 200 °F and atmospheric pressure. Tensile strength may be measured using any suitable method, including, without limitation, in accordance with the procedure described in ASTM C307. That is, specimens may be prepared in briquette molds having the appearance of dog biscuits with a one square inch cross-sectional area at the middle. Tension may then be applied at the enlarged ends of the specimens until the specimens break at the center area. The tension in pounds per square inch at which the specimen breaks is the tensile strength of the material tested.

[0042] Young’s modulus also referred to as the modulus of elasticity is a measure of the relationship of an applied stress to the resultant strain. In general, a highly deformable (plastic) material will exhibit a lower modulus when the confined stress is increased. Thus, the Young’s modulus is an elastic constant that demonstrates the ability of the tested material to withstand applied loads. A number of different laboratory techniques may be used to measure the Young’s modulus of a treatment fluid comprising a cementitious component after the treatment fluid has been allowed to set for a period of time at specified temperature and pressure conditions.

[0043] Although only some select laboratory techniques may have been mentioned, it should be understood that there may many analytical techniques that may be appropriate or not appropriate for a certain sample. One of ordinary skill in the art with the benefit of this disclosure should be able to select an appropriate analytical technique to determine a certain property of interest.

[0044] Once the analytical techniques have been performed on the cement components, the data may be categorized and correlated. Some categories may include, but are not limited to, specific surface area, morphology, specific gravity, water requirement, etc. In some examples, the components may be categorized by relative amounts, including amount of at least one following: silica, alumina, iron, iron, calcium, calcium, sodium, potassium, magnesium, sulfur, oxides thereof, and combinations thereof. For example, the components may be categorized based on an oxide analysis that includes without limitation, silica content, calcium oxide content, and alumina content among other oxides that may be present in the cement component.. In addition, correlations between the cement components may be generated based on the categorization of the data. For example, the various categories of properties may be plotted against one another. In some examples, water requirement versus specific surface area may be plotted. Accordingly, the water requirement of the cement component may be correlated to the specific surface area so that the specific surface area is a function of water requirement. Specific surface area may be used to predict reactivity of a cement component (or components). However, specific surface area may not always be available for each material as specific surface area analysis typically requires a specialized instrument. Accordingly, if the water requirement may be obtained for the cement component, the correlation between water requirement and specific surface area may be used to obtain an approximation for specific surface area, which may then be used to predict reactivity. The correlation between water requirement and specific surface may include, but not be limited to, a graph of water requirement versus specific surface or an equation that assigns an output of specific surface area based on an input of water requirement. In addition to correlations between specific surface area and reactivity, correlations may also be made between specific surface area and other mechanical properties such as tensile strength and Young's modulus.

[0045] Some cement components that are alkali soluble may comprise reclaimed or natural materials. Specifically silica containing cement components may comprise materials such as mined materials, for example volcanic rock, perlite, waste materials, such as fly ash and CKD, and agricultural ashes as previously described. In some examples the cement component that is alkali soluble may have synergistic effects with a Portland cement while others may be incompatible. In some examples a cement component that is alkali soluble may cause gelation, high heat generation, water retention, among other effects. These and other effects may be realized during laboratory testing of the cement component in a cement

composition comprising Portland cement. Laboratory equipment may be configured to detect the effects of the cement component on the composition. In some examples, equipment such as a calorimeter may measure and quantify the amount of heat generation per unit mass of the cement component. Viscometers may measure the increase in gelation caused by the cement component. Each of the physical effects caused by the addition of the cement component may be measured at several concentrations and then categorized, e.g., plotted or mapped. Once a component is mapped, the effect of adding the component to a cement composition may be predicted by referencing the categorization.

[0046] As mentioned previously, some cement components that are alkali soluble may induce gelling when included in a cement composition. Although a higher gelling rate may be undesirable in some examples, in other examples, a higher gelling rate may be advantageous or necessary to meet the engineering design criteria. Usually one of ordinary skill in the art would select a suitable gelling agent or viscosifier for use in the cement composition. With the benefit of mapping, one of ordinary skill should be able to select a cement component that is alkali soluble that may serve a dual purpose. For example, a cement component may increase the compressive strength of a cement composition but also increase the gelling during mixing. If the engineering design criteria require a higher gelling during mixing, it may be advantageous to include the cement component that increases the compressive strength while also increasing gelling. The inclusion of a cement component that exhibits multiple effects may reduce the amount of additional additives, such as gelling agents or viscosifiers, needed, which may be high cost. Since the component's gelling effect may have been documented in a map, the amount of component to include in a cement composition may be readily determined.

[0047] Another potentially advantageous physical effect that may be mapped is dispersing ability. Some cement components may comprise relatively spherical particles. The relatively spherical particles may exert a "roller bearing" effect in a cement composition with water. The effect may cause the other components in the cement composition to become more mobile thereby dispersing the components in the cement composition. Another potentially advantageous physical property that may be mapped is surface area. Surface area may relate to density wherein a relatively higher surface area particle may lower the density of a cement composition. Particles which lower the density may be used as a low density additive. Another potentially advantageous effect that may be mapped is particle size. Components with relatively smaller particle sizes may have the ability to form a filter cake

against a formation thereby blocking cement from escaping into a formation. Cement components with a small particle size may be used as a fluid loss control agent. With the benefit of the present disclosure, one of ordinary skill should be able to select a cement component and map its properties. One of ordinary skill should also be able to select a secondary property of interest of the cement component and with the benefit of the map, create a slurry with the desired properties.

[0048] Another potential benefit of replacing traditional cement additives with silica based cement components is a reduction in cost. A silica based cement component may partially or fully replace a relatively more expensive cement additive as discussed above. The cost of the cement composition may be optimized by balancing the required engineering parameters such as compressive strength, mix ability, free water content, and others in order to maximize the amount of relatively lower cost silica based cement components. Any remaining deviation from the engineering requirement may be “made up” with the relatively more expensive cement additive. In this way, the cement composition may be reduced to a minimum cost per pound since the engineering requirements are met with a blend of primarily lower cost components.

[0049] Once the data is collected by the chosen laboratory techniques, categorized, and mapped, several operations may be performed on the data in order to yield predictions about a cement composition that comprises mapped cement components. Set properties, for example, may be estimated. A method of estimating the material reactivity based on the reactive index will be described below. Material reactivity may be based on many parameters such as specific surface area and specific gravity, among others. Another use for the mapped data may be to optimize cement slurry performance based on parameters such as particle shape, particle size, and particle reactivity. The data may also be used to predict and capture slurry density dependence of compressive strength and use the insight gathered to design optimized cement formulations. The data may also be used to predict a slurry composition to achieve an optimal cement formulation. The criteria for just right may be compressive strength, cost, rheology, mechanical properties, fluid loss control properties, thickening times, and others.

[0050] Reactivity mapping may be used to estimate various mechanical properties of a cement component, including compressive strength, tensile strength, and Young’s modulus. As previously described, correlations may be made between specific surface area and certain mechanical properties, such as reactivity, tensile strength, and Young’s modulus. Using these

correlations the mechanical properties for a cement component or combination of cement components may be predicted.

[0051] One technique that may be used to correlate reactivity and specific surface area is the reactive index. Without being limited by theory, the reactive index of a cement component may be referred to as a measure of the cement component's reactivity as adjusted for differences in surface area. It is important to note that the term "cement component" refers to any material that is cementitious when mixed with water and/or lime and a suspending agent, when necessary, such that the slurry is stable. A "cementitious reactive index" CRI_i can be defined as, but not limited to, Equation [1] as follows:

$$CRI_i = f_{CRI}(CS_i, \rho_i, SSA_{PSDi}) \quad [1]$$

Where:

CS_i = Unconfined UCS (ultimate compressive strength) obtained from samples cured at specific reference temperature, pressure and age.

ρ_i = Density of slurry that was prepared and cured for measuring UCS

SSA_{PSDi} = Specific surface area obtained by typical particle size analysis methods.

A "physicochemical index" (PCI) of the cementitious component may be defined as, but not limited to Equation [2]:

$$PCI_i = f_{PCI}(BETSA_i, SG_i, D_{50}, C_{Si}, C_{Ca}, C_{Al}, C_{Na}, C_{Fe}, C_{other\ species}) \quad [2]$$

Where:

$BETSA_i$ = Surface area obtained by a nitrogen adsorption method of cementitious component i,

SG_i = specific gravity of the cementitious component i,

D_{50} = mass average or volume average diameter of the particle size distribution of cementitious component i,

C_{Si} = Mass concentration of silica oxide of component i,

C_{Ca} = Mass concentration of calcium oxide of component i,

C_{Al} = Mass concentration of Aluminum oxide of component i,

C_{Na} = Mass concentration of sodium oxide of component i,

C_{Fe} = Mass concentration of iron oxide of component i,

[0052] It should be noted that the mass concentrations referenced above and here to for, may be measured, but is not limited to X-ray fluorescence spectroscopy measuring technique and a reference to “component i” is equivalent to “cementitious component i”. The functions in Equations [1] and [2] that define CRI_i and PCI_i , when properly defined, the following universal relationship may hold for a wide range of cementitious materials such as, but not limited to, Portland cements; fly ash; other pozzolanic materials; other ashes; etc.

$$CRI_i = f_{CRI-PCI}(PCI_i) \quad [3]$$

FIG. 1 is a graph of Equation [1] versus Equation [2], , illustrating the accuracy of Equations [1], [2] and [3] when applied to five different types of cementitious material sources and three samples of similar materials but from different sources. The simulated data was found to have a relationship of $y=36.252x^{0.2256}$, wherein $R^2=0.9406$.

[0053] In some examples, the form of Equation [3] may be a power law, such as in Equation 4.

$$CRI_i = A\{PCI_i\}^B \quad [4]$$

A and B are coefficients that may be unique the various species and sources of cementitious materials selected. Once the generalized function defined in Equation [4] is defined for a given population or group of cementitious components, a linear or nonlinear summation relationship further defined below, may be used in conjunction with Equation [5] to predict the UCS of various combinations of cementitious materials for specified slurry densities, temperatures, pressures and curing age.

$$CRI_c = A\{PCI_c\}^B \quad [5]$$

Where,

CRI_c is defined as the CRI for the unique combination of n cementitious components as the composite, and similarly

PCI_c is defined as the Physicochemical Index for the composite.

A given composite with mass of m_c is defined as:

$$m_c = f_i + f_{i+1} + f_{i+2} + f_n \quad [6]$$

Where: f_i is defined as the mass fraction of the cementitious component i , and n is the total number of independent cementitious components. Once the function is defined in Equation [5], then the composite value of the physicochemical reactive index may be computed using Equation [7] as follows:

$$PCI_c = f_1 PCI_1 + f_2 PCI_2 + f_3 PCI_3 + \dots + f_n PCI_n \quad [7]$$

[0054] Where: PCI_c is defined as the overall reactive index for a blend of n number of uniquely independent cementitious components, f_i is defined as the mass fraction of the cementitious component i , and n is the total number of independent cementitious components. Once PCI_c has been determined for specific assumed blend of selected cementitious components, then the linear or non-linear summations (Equations [8] and [9]) are determined for the following terms:

$$\rho_c = f_1 \rho_1 + f_2 \rho_2 + f_3 \rho_3 + \dots + f_n \rho_n \quad [8]$$

and,

$$SSA_{PSDC} = f_1 SSA_{PSD1} + f_2 SSA_{PSD2} + f_3 SSA_{PSD3} + \dots + f_n SSA_{PSDn} \quad [9]$$

PCI_c is used to compute the value of CRI_c using either Equation [5] or the more generalized form of Equation [3] for the composite terms. Once CRI_c is determined for the given composite blend, then the composite values of ρ_c and SSA_{PSDC} may be used along with Equation [10] to predict the actual compressive strength of the composite blend, CS_c .

$$CRI_c = f_{CRI}(CS_c, \rho_c, SSA_{PSDC},) \quad [10]$$

Experimental data was collected for specific composite blends and is summarized in the table below:

Table 1

Mass Fractions of Cementitious Components			
Cementitious Component	Composite Blend 1	Composite Blend 2	Composite Blend 3
A	0.36		0.53
B		0.32	
C	0.32		0.31
D		0.33	
E	0.32		
F		0.35	
G			0.16
Totals	1.00	1.00	1.00

It is important to note that each of the cementitious components above were either distinctly different species (type) of cementitious composition and/or from a different source.

[0055] FIG. 2 is another plot of Equation [1] versus Equation [2], showing the accuracy of Equations [1], [2], and [3]. Equations [1] through [10] may also be used for predicting other mechanical properties, including but not limited to, Young's Modulus of Elasticity and Tensile Strength. Additionally, it should be noted that even though a "linear summation" technique is presented in the previous development, that this invention also includes other methods such as the non-linear summation method presented in Equation [11].

$$PCI_c = (1 + f_1)^{a_1} PCI_1 + (1 + f_2)^{a_2} PCI_2 + (1 + f_3)^{a_3} PCI_3 + \dots + (1 + f_n)^{a_n} PCI_n \quad [11]$$

Where: a_i are exponents that are determined for a unique set of cementitious components.

[0056] Further examples using the reactive index, water requirement and other analytical parameters will now be discussed. A statistical table may be generated that plots reactive index against water requirement. An example is shown in Table 2.

Table 2 – Reactive Index Vs. Water Requirement

Water Requirement	High	X1	X4, X5	X8
	Medium	X2	X6	X9,X10
	Low	X3	X7	X11...Xn
		Low	Medium	High

Reactive Index

Other analytical parameters such as particle size versus reactive index, heat generation versus reactive index, and others may also be used. By ranking the reactive index against an analytical parameter, a blend of components may be selected that has a minimized cost and an optimized reactive index while still having a mixable composition. In some examples, a selected cement composition may have too much free water to set properly. In such examples, a component having a high water requirement may be selected to replace a component in the cement composition or supplement the cement composition. The selected component having the high water requirement may be selected based on the reactive index to ensure that the overall blend has sufficient reactivity. A cement composition comprising the selected cement component may exhibit less free water due to the high water requirement of the component and may also exhibit the same reactivity from selecting the appropriate reactive index. The reactivity of a cement composition may be tuned based on the selection of cement component having the desired reactivity. A component having a high reactivity may exhibit a faster set time than one with a low reactivity.

[0057] As will be appreciated by those of ordinary skill in the art, the cement compositions disclosed herein may be used in a variety of subterranean applications, including primary and remedial cementing. The cement compositions may be introduced into a subterranean formation and allowed to set. As used herein, introducing the cement composition into a subterranean formation includes introduction into any portion of the subterranean formation, into near wellbore region surrounding the wellbore, or into both. In primary cementing applications, for example, the cement compositions may be introduced into the annular space between a conduit located in a wellbore and the walls of the wellbore (and/or a larger conduit in the wellbore), wherein the wellbore penetrates the subterranean formation. The cement composition may be allowed to set in the annular space to form an annular sheath of hardened cement. The cement composition may form a barrier that prevents the migration of fluids in the wellbore. The cement composition may also, for example, support the conduit in the wellbore. In remedial cementing applications, the cement compositions may be used, for example, in squeeze cementing operations or in the placement of cement plugs. By way of example, the cement compositions may be placed in a wellbore to plug an opening (e.g., a void or crack) in the formation, in a gravel pack, in the conduit, in the cement sheath, and/or between the cement sheath and the conduit (e.g., a microannulus).

[0058] While the present description refers to cement compositions and cement components, it should be understood that the techniques disclosed herein may be used with any suitable wellbore treatment composition and corresponding solid particulates of which cement compositions and cement components are one example. Additional examples of slurry compositions may include spacer fluids, drilling fluids, cleanup pills, lost circulation pills, and fracturing fluids, among others. Suitable solid particulates may include any of a variety of inorganic particles commonly used in well treatments.

[0059] Accordingly, this disclosure describes systems, compositions, and methods relating to slurry design process. Without limitation, the systems, compositions and methods may further be characterized by one or more of the following statements:

[0060] Statement 1: A method of analyzing a solid particulate comprising: measuring a water requirement of the solid particulate; and determining an approximation of specific surface area of the solid particulate from the water requirement.

[0061] Statement 2: The method of statement 1 wherein the water requirement is a weight ratio of water to the solid particulate required to obtain a predetermined consistency.

[0062] Statement 3: The method of statement 1 or statement 2 wherein the measuring the water requirement comprises preparing a blender with a specified amount of water, agitating the blender at a specified blender speed, adding the solid particulate to the water until a predetermined consistency is obtained, and calculating the water requirement based on a weight ratio of the water to the solid particulate to obtain the predetermined consistency.

[0063] Statement 4: The method of statement 3 wherein the specified consistency is obtained when a vortex formed at a surface in the blender is about 0 mm to about 50 mm in diameter while mixing the solid particulate and the water.

[0064] Statement 5: The method of any preceding statement wherein the determining an approximation of the specific surface area comprises inputting the water requirement into an equation to obtain an output of the approximation of the specific surface area.

[0065] Statement 6: The method of any preceding statement wherein the solid particulate comprises a silica source that is alkali soluble.

[0066] Statement 7: The method of any preceding statement wherein the solid particulate comprises at least one silica source selected from the group consisting of fly ash, slag, silica fume, crystalline silica, silica flour, cement kiln dust, volcanic rock, perlite,

metakaolin, diatomaceous earth, zeolite, shale, agricultural waste ash, rice husk ash, sugar cane ash, Portland cement, bagasse ash, and combinations thereof.

[0067] Statement 8: The method of any preceding statement further comprising measuring at least one additional property for the solid particulate selected from the group consisting of compressive strength, Young's modulus, and tensile strength.

[0068] Statement 9: The method of any preceding statement further comprising determining a reactive index for the solid particulate based on the specific surface area.

[0069] Statement 10: The method of any preceding statement further comprising estimating a compressive strength of a cement composition comprising the solid particulate and one or more additional solid particulates, wherein the estimating uses the approximation of the specific surface for the solid particulate and specific surface areas for the one or more additional solid particulates as inputs to an equation that outputs the compressive strength, wherein the solid particulate and additional solid particulate are each cementitious.

[0070] Statement 11: The method of any preceding statement further comprising including the solid particulate in a cement composition and allowing the cement composition to set.

[0071] Statement 12. A method of cementing comprising: measuring a water requirement of a solid particulate; determining an approximation of specific surface area of the solid particulate from the water requirement; determining an approximation of compressive strength for a cement composition comprising the solid particulate; preparing the cement composition, wherein the cement composition comprises the solid particulate, one or more additional solid particulates, and water; and allowing the cement composition to set in a predetermined location.

[0072] Statement 13: The method of statement 12 further comprising introducing the cement composition into a wellbore.

[0073] Statement 14: The method of statement 13 wherein the cement composition is introduced into the wellbore using one or more pumps.

[0074] Statement 15: The method of any one of statements 12 to 14 wherein the cement composition is used in primary cementing to form a set cement sheath in a wellbore annulus

[0075] Statement 16: The method of any one of statements 12 to 15 wherein the preparing comprising mixing components of the cement composition using mixing

equipment, the components comprising the solid particulate, the one or more additional solid particulates, and the water.

[0076] Statement 17: The method of any one of statements 12 to 16 wherein the water requirement is a ratio of weight of water to weight of the solid particulate required to obtain a predetermined consistency.

[0077] Statement 18: The method of any one of statements 12 to 17 wherein the measuring the water requirement comprises preparing a blender with a specified amount of water, agitating the blender at a specified blender rpm, adding the solid particulate to the water until a specified consistency is obtained, and calculating the water requirement based on a weight ratio of the water to the solid particulate to obtain the specified consistency.

[0078] Statement 19: The method of any one of statements 12 to 18 wherein the determining an approximation of the specific surface area comprises inputting the water requirement into an equation to obtain an output of the approximation of the specific surface area.

[0079] Statement 20: The method of any one of statements 12 to 19 wherein the solid particulate comprises at least one silica source selected from the group consisting of fly ash, slag, silica fume, crystalline silica, silica flour, cement kiln dust, volcanic rock, perlite, metakaolin, diatomaceous earth, zeolite, shale, agricultural waste ash, rice husk ash, sugar cane ash, bagasse ash, and combinations thereof.

[0080] Statement 21: The method of any one of statements 12 to 20 further comprising measuring at least one additional property for the solid particulate selected from the group consisting of compressive strength, Young's modulus, and tensile strength and determining a reactive index for the solid particulate based on the approximation of specific surface area.

[0081] Statement 22: A system comprising: a solid particulate; a blender configured to mix the solid particulate with water; and a computer system configured to accept inputs of a water requirement for the solid particulate and output an approximation of specific surface area of the solid particulate.

[0082] Statement 23. The system of statement 22 wherein the computer system is configured to input the water requirement into an equation to obtain the output of the approximation of the specific surface area.

[0083] Statement 24: The system of statement 22 or statement 23 wherein the water requirement is a ratio of weight of water to weight of the solid particulate required to obtain a predetermined consistency.

[0084] Statement 25: The system of any one of statements 22 to 24 further comprising: a cement composition comprising the solid particulate, one or more additional solid particulates, and water; a pump fluidly coupled to a tubular in fluid communication with a wellbore, wherein the tubular is configured to convey the cement composition to the wellbore; and a vessel disposed upstream of the pump, wherein the cement composition is disposed in the vessel.

[0085] Examples of the methods of using the reactivity mapping technique will now be described in more detail with reference to FIG. 3. A system 300 for analyzing the cement component is illustrated. The system 300 may comprise a cement component sample 305, analytical instrument 310, and computer system 315. Cement component sample 305 may be any cement component of interest. Cement components as previously described may be generally categorized as alkali soluble. The cement component sample may be placed or fed into analytical instrument 310. In some examples, analytical instrument 310 may be configured to automatically feed cement component sample 305 into analytical instrument 310. Analytical instrument 310 may be configured to analyze the physical and chemical properties of cement component sample 305. As previously described, physical and chemical properties may comprise, without limitation, morphology, chemical composition, water requirement, and others. By way of example, the analytical instrument 310 may be used to measure the water requirement for the cement component. The data generated by analytical instrument 310 may be sent to computer system 315 for processing. Computer system 315 may comprise a processor, memory, internal storage, input and output means, network connectivity means, and/or other components common to computer systems. Computer system 315 may take the data from analytical instrument 310 as input and store it in the storage for later processing. Processing the data may comprise inputting the data into algorithms which compute a result. Processing the data may also comprise organizing the data and mapping the data as previously described. In particular, the computer system may comprise algorithms configured to process the data to generate a predictive model of the physical and chemical behavior of cement component sample 305. Predictive models may be stored in a predictive model database 320 which may be stored locally or on a network. The

predictive model database 320 may comprise all previous predictive models generated by the algorithms as well as maps of the generated data as well as the raw data.

[0086] Referring now to FIG. 4, a system 400 for generating cement compositions is illustrated. The system 400 may comprise a predictive model database 320 and computer system 410. In some examples, computer system 410 may be the same computer system 315 of FIG. 3. A user input 420 may define engineering parameters such as the required compressive strength of a cement slurry, the bottom hole static temperature of the wellbore, the required rheological properties of the slurry, the thickening time of the slurry, cement materials, cement additives, free fluid, permeability, pore pressure, frac gradient, mud weight, density, acid resistance, salt tolerance, and other parameters. Computer system 410 may be configured to input user input 420 and the predictive models, maps, and data stored in predictive model database 320 into a predictive cement algorithm. The predictive cement algorithm may generate a cement composition or compositions that meet the engineering requirements define by the user input 420. The output 430 of the predictive cement algorithm may contain the relative amounts of each cement component in the generated cement composition as well as the predicted material properties of the cement composition.

[0087] For example, if a user selects Portland cement, fly ash, and volcanic rock as the cement materials available the computer system may query predictive model database 320 for the required models, maps, and data corresponding to the cement materials. As previously described, there may be many different parameters such as particle size, regional source of the cement material, among others that may determine which set of data that is retrieved from predictive model database 320. The predictive cement algorithm may be configured to optimize the output cement slurry based on one or more parameters such as cost, compressive strength, or any other chosen parameter. In some examples, the predictive cement algorithm may determine an approximation of specific surface area from a measured water requirement. In some examples the predictive cement algorithm may optimize on two or more variable. The output of the algorithm in this example may be for example, 30% Portland by weight, 30 % volcanic rock by weight, 20% fly ash, and 20 % lime, with a 120% excess by weight of water. The generated slurry may conform within a margin of error to the engineering parameters supplied by user input 420. The generated slurry may be added to predictive model database 320 to be used in future calculations.

[0088] As previously discussed, the cement components may have secondary effects such as gelling, dispersive properties, and other secondary effects previously mentioned in

addition to the primary effect of being cementitious when included in a cement composition. The predictive cement algorithm may calculate the secondary effects of each component in the cement slurry and optimize the relative amounts of each component to ensure the target parameters are met. User input 420 may specify, for example, a relatively higher free water requirement for the cement slurry. The predictive cement algorithm may choose to include a cement component that requires less water based on the maps and data to ensure that the free water requirement specified by user input 420 is met.

[0089] Reference is now made to FIG. 5, illustrating use of a cement composition 500. Cement composition 500 may comprise any of the components described herein. Cement composition 500 may be designed, for example, using reactivity mapping as described herein. Turning now to FIG. 5, the cement composition 500 may be placed into a subterranean formation 505 in accordance with example systems, methods and cement compositions. As illustrated, a wellbore 510 may be drilled into the subterranean formation 505. While wellbore 510 is shown extending generally vertically into the subterranean formation 505, the principles described herein are also applicable to wellbores that extend at an angle through the subterranean formation 505, such as horizontal and slanted wellbores. As illustrated, the wellbore 510 comprises walls 515. In the illustration, a surface casing 520 has been inserted into the wellbore 510. The surface casing 520 may be cemented to the walls 515 of the wellbore 510 by cement sheath 525. In the illustration, one or more additional conduits (e.g., intermediate casing, production casing, liners, etc.), shown here as casing 530 may also be disposed in the wellbore 510. As illustrated, there is a wellbore annulus 535 formed between the casing 530 and the walls 515 of the wellbore 510 and/or the surface casing 520. One or more centralizers 540 may be attached to the casing 530, for example, to centralize the casing 530 in the wellbore 510 prior to and during the cementing operation.

[0090] With continued reference to FIG. 5, the cement composition 500 may be pumped down the interior of the casing 530. The cement composition 500 may be allowed to flow down the interior of the casing 530 through the casing shoe 545 at the bottom of the casing 530 and up around the casing 530 into the wellbore annulus 535. The cement composition 500 may be allowed to set in the wellbore annulus 535, for example, to form a cement sheath that supports and positions the casing 530 in the wellbore 510. While not illustrated, other techniques may also be utilized for introduction of the cement composition 500. By way of example, reverse circulation techniques may be used that include introducing the cement composition 500 into the subterranean formation 505 by way of the wellbore

annulus 535 instead of through the casing 530. As it is introduced, the cement composition 500 may displace other fluids 550, such as drilling fluids and/or spacer fluids that may be present in the interior of the casing 530 and/or the wellbore annulus 535. While not illustrated, at least a portion of the displaced fluids 550 may exit the wellbore annulus 535 via a flow line and be deposited, for example, in one or more retention pits. A bottom plug 355 may be introduced into the wellbore 510 ahead of the cement composition 500, for example, to separate the cement composition 500 from the fluids 550 that may be inside the casing 530 prior to cementing. After the bottom plug 555 reaches the landing collar 580, a diaphragm or other suitable device should rupture to allow the cement composition 500 through the bottom plug 555. The bottom plug 555 is shown on the landing collar 580. In the illustration, a top plug 560 may be introduced into the wellbore 510 behind the cement composition 500. The top plug 360 may separate the cement composition 500 from a displacement fluid 565 and also push the cement composition 500 through the bottom plug 555.

[0091] The disclosed cement compositions and associated methods may directly or indirectly affect any pumping systems, which representatively includes any conduits, pipelines, trucks, tubulars, and/or pipes which may be coupled to the pump and/or any pumping systems and may be used to fluidically convey the cement compositions downhole, any pumps, compressors, or motors (e.g., topside or downhole) used to drive the cement compositions into motion, any valves or related joints used to regulate the pressure or flow rate of the cement compositions, and any sensors (i.e., pressure, temperature, flow rate, etc.), gauges, and/or combinations thereof, and the like. The cement compositions may also directly or indirectly affect any mixing hoppers and retention pits and their assorted variations.

[0092] It should be understood that the compositions and methods are described in terms of “comprising,” “containing,” or “including” various components or steps, the compositions and methods can also “consist essentially of” or “consist of” the various components and steps. Moreover, the indefinite articles “a” or “an,” as used in the claims, are defined herein to mean one or more than one of the element that it introduces.

[0093] For the sake of brevity, only certain ranges are explicitly disclosed herein. However, ranges from any lower limit may be combined with any upper limit to recite a range not explicitly recited, as well as, ranges from any lower limit may be combined with any other lower limit to recite a range not explicitly recited, in the same way, ranges from any upper limit may be combined with any other upper limit to recite a range not explicitly

recited. Additionally, whenever a numerical range with a lower limit and an upper limit is disclosed, any number and any included range falling within the range are specifically disclosed. In particular, every range of values (of the form, “from about a to about b,” or, equivalently, “from approximately a to b,” or, equivalently, “from approximately a-b”) disclosed herein is to be understood to set forth every number and range encompassed within the broader range of values even if not explicitly recited. Thus, every point or individual value may serve as its own lower or upper limit combined with any other point or individual value or any other lower or upper limit, to recite a range not explicitly recited.

[0094] Therefore, the present disclosure is well adapted to attain the ends and advantages mentioned as well as those that are inherent therein. The particular examples disclosed above are illustrative only, as the present invention may be modified and practiced in different but equivalent manners apparent to those skilled in the art having the benefit of the teachings herein. Although individual examples are discussed, the invention covers all combinations of all those examples. Furthermore, no limitations are intended to the details of construction or design herein shown, other than as described in the claims below. Also, the terms in the claims have their plain, ordinary meaning unless otherwise explicitly and clearly defined by the patentee. It is therefore evident that the particular illustrative examples disclosed above may be altered or modified and all such variations are considered within the scope and spirit of the present invention. If there is any conflict in the usages of a word or term in this specification and one or more patent(s) or other documents that may be incorporated herein by reference, the definitions that are consistent with this specification should be adopted.

CLAIMS

What is claimed is:

1. A method of analyzing a solid particulate comprising:
measuring a water requirement of the solid particulate; and
determining an approximation of specific surface area of the solid particulate from the water requirement.
2. The method of claim 1 wherein the water requirement is a weight ratio of water to the solid particulate required to obtain a predetermined consistency.
3. The method of claim 1 wherein the measuring the water requirement comprises preparing a blender with a specified amount of water, agitating the blender at a specified blender speed, adding the solid particulate to the water until a predetermined consistency is obtained, and calculating the water requirement based on a weight ratio of the water to the solid particulate to obtain the predetermined consistency.
4. The method of claim 3 wherein the specified consistency is obtained when a vortex formed at a surface in the blender is about 0 mm to about 50 mm in diameter while mixing the solid particulate and the water.
5. The method of claim 1 wherein the determining an approximation of specific surface area comprises inputting the water requirement into an equation to obtain an output of the approximation of the specific surface area.
6. The method of claim 1 wherein the solid particulate comprises a silica source that is alkali soluble.
7. The method of claim 1 wherein the solid particulate comprises at least one silica source selected from the group consisting of fly ash, slag, silica fume, crystalline silica, silica flour, cement kiln dust, volcanic rock, perlite, metakaolin, diatomaceous earth, zeolite, shale, agricultural waste ash, rice husk ash, sugar cane ash, Portland cement, bagasse ash, and combinations thereof.
8. The method of claim 1 further comprising measuring at least one additional property for the solid particulate selected from the group consisting of compressive strength, Young's modulus, and tensile strength.
9. The method of claim 1 further comprising including the solid particulate in a cement composition and allowing the cement composition to set.

10. A method of cementing comprising:
 - measuring a water requirement of a solid particulate;
 - determining an approximation of specific surface area of the solid particulate from the water requirement;
 - determining an approximation of compressive strength for a cement composition comprising the solid particulate;
 - preparing the cement composition, wherein the cement composition comprises the solid particulate, one or more additional solid particulates, and water; and
 - allowing the cement composition to set in a predetermined location.
11. The method of claim 10 further comprising introducing the cement composition into a wellbore.
12. The method of claim 11 wherein the cement composition is introduced into the wellbore using one or more pumps.
13. The method of claim 10 wherein the cement composition is used in primary cementing to form a set cement sheath in a wellbore annulus
14. The method of claim 10 wherein the preparing comprising mixing components of the cement composition using mixing equipment, the components comprising the solid particulate, the one or more additional solid particulates, and the water.
15. The method of claim 10 wherein the water requirement is a ratio of weight of water to weight of the solid particulate required to obtain a predetermined consistency.
16. The method of claim 10 wherein the measuring the water requirement comprises preparing a blender with a specified amount of water, agitating the blender at a specified blender rpm, adding the solid particulate to the water until a specified consistency is obtained, and calculating the water requirement based on a weight ratio of the water to the solid particulate to obtain the specified consistency.
17. The method of claim 10 wherein the determining an approximation of specific surface area comprises inputting the water requirement into an equation to obtain an output of the approximation of the specific surface area.
18. The method of claim 10 wherein the solid particulate comprises at least one silica source selected from the group consisting of fly ash, slag, silica fume, crystalline silica, silica flour, cement kiln dust, volcanic rock, perlite, metakaolin, diatomaceous earth, zeolite, shale, agricultural waste ash, rice husk ash, sugar cane ash, bagasse ash, and combinations thereof.

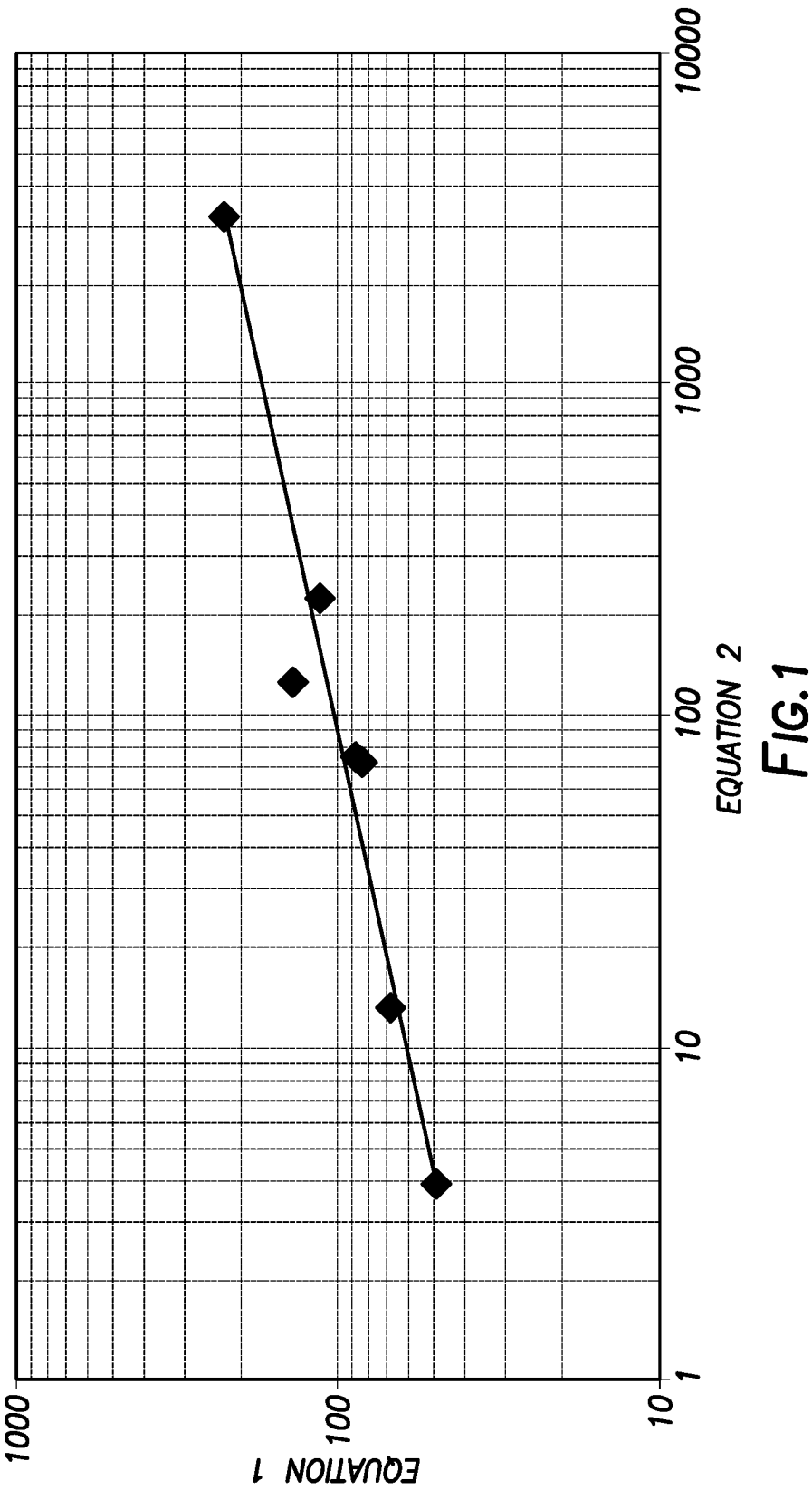
19. The method of claim 10 further comprising measuring at least one additional property for the solid particulate selected from the group consisting of compressive strength, Young's modulus, and tensile strength and determining a reactive index for the solid particulate based on the approximation of specific surface area.

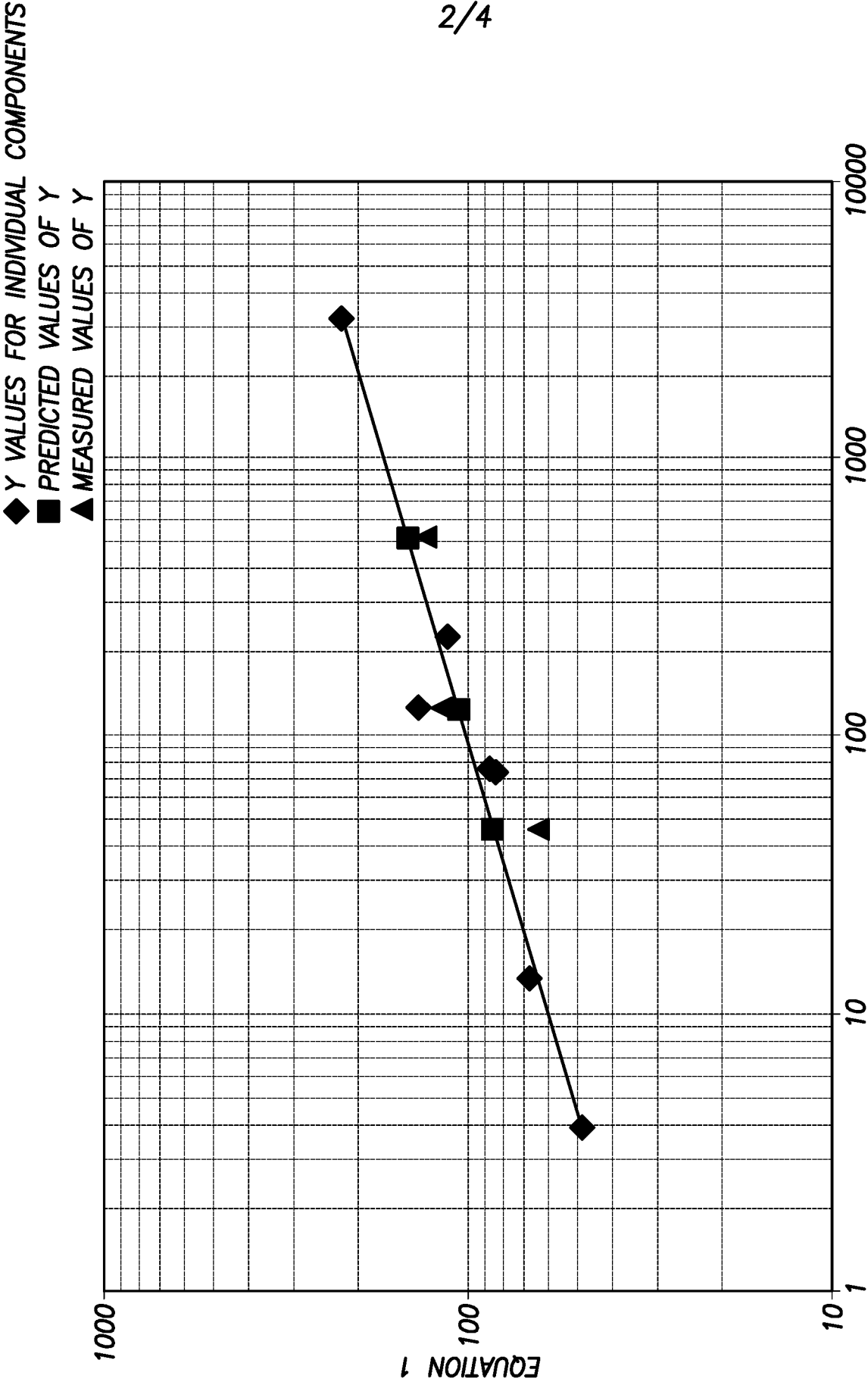
20. A system comprising:
a solid particulate;
a blender configured to mix the solid particulate with water; and
a computer system configured to accept inputs of a water requirement for the solid particulate and output an approximation of specific surface area of the solid particulate.

21. The system of claim 20 wherein the computer system is configured to input the water requirement into an equation to obtain the output of the approximation of specific surface area.

22. The system of claim 20 wherein the water requirement is a ratio of weight of water to weight of the solid particulate required to obtain a predetermined consistency.

1/4





EQUATION 2
FIG.2

3/4

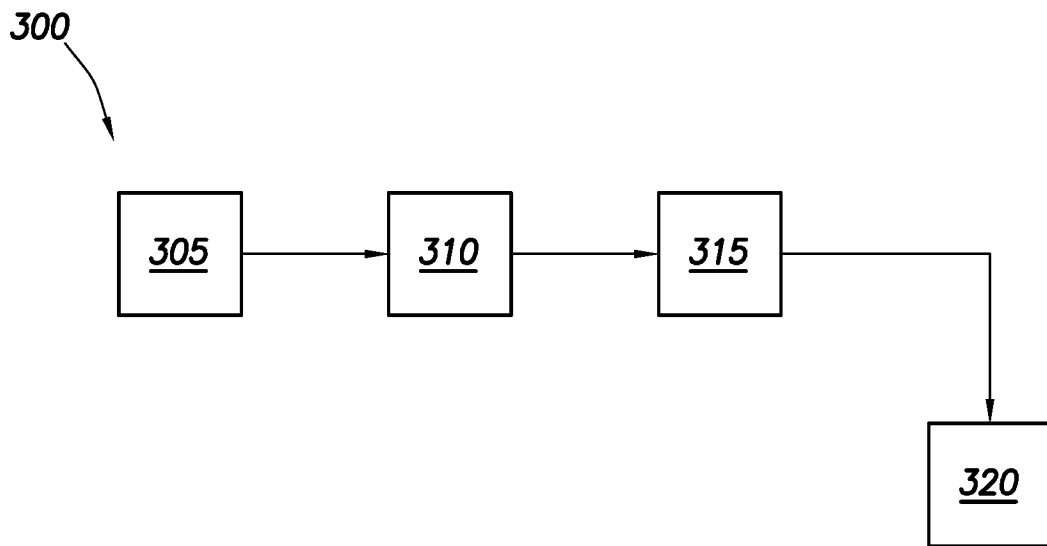


FIG.3

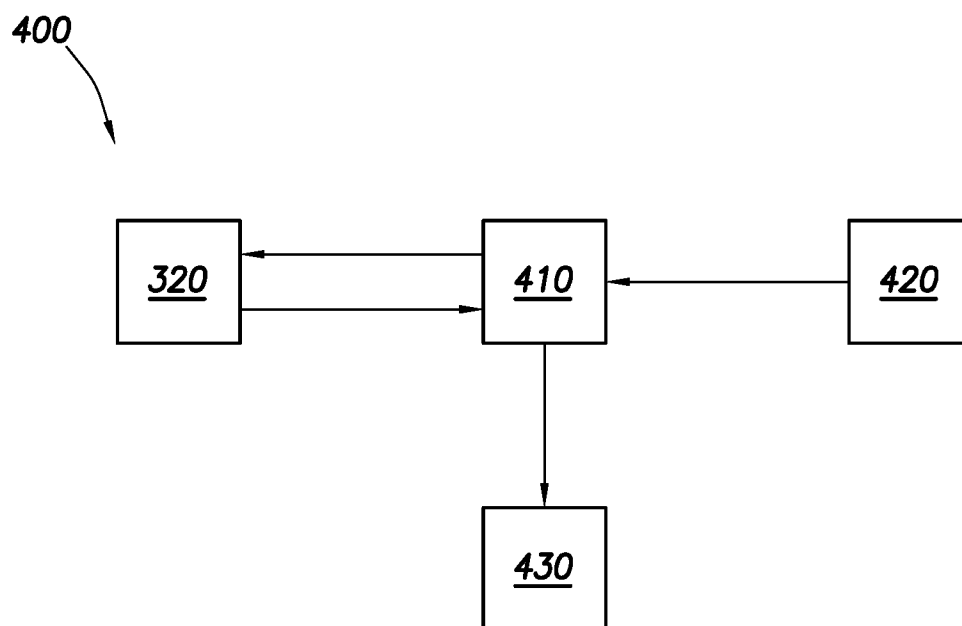


FIG.4

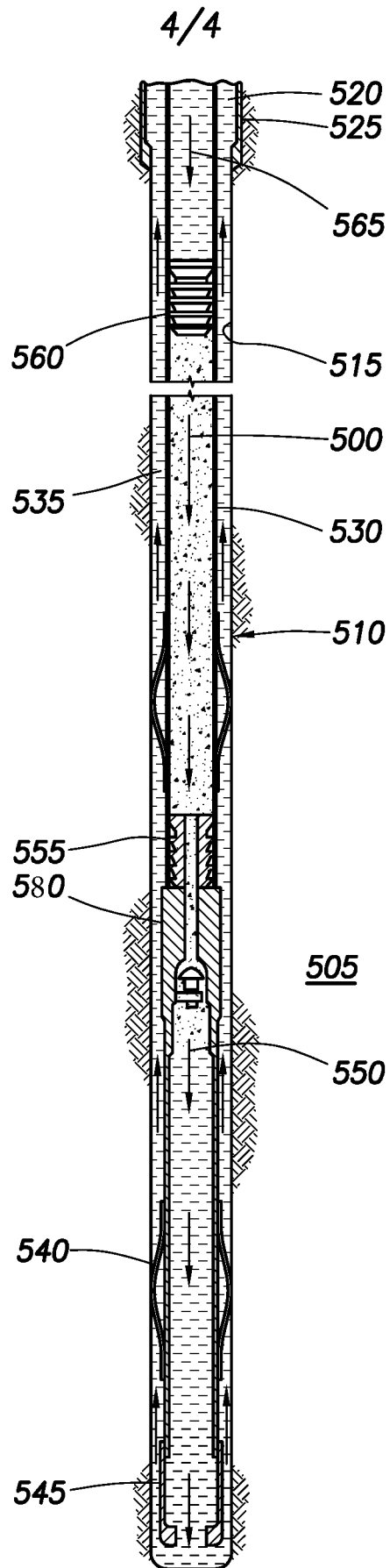


FIG. 5

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US2017/018930**A. CLASSIFICATION OF SUBJECT MATTER****E21B 33/13(2006.01)i, C09K 8/42(2006.01)i, E21B 49/00(2006.01)i**

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

E21B 33/13; C04B 16/08; C04B 14/04; C09K 8/46; C09K 8/42; C04B 28/00; E21B 33/14; C04B 28/04; E21B 49/00

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Korean utility models and applications for utility models

Japanese utility models and applications for utility models

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

eKOMPASS(KIPO internal) & Keywords: analyze, solid particle, water requirement, surface area, cement

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 2015-0260009 A1 (KING FAHD UNIVERSITY OF PETROLEUM AND MINERALS et al.) 17 September 2015 See paragraphs [0006]–[0028], [0050]–[0088]; and figures 1–16.	1–22
Y	US 2015-0184060 A1 (HALLIBURTON ENERGY SERVICES, INC.) 02 July 2015 See paragraphs [0027], [0058]; and figure 1.	1–22
A	US 2016-0264462 A1 (RESEARCH INSTITUTE OF PETROLEUM INDUSTRY) 15 September 2016 See paragraphs [0029]–[0068]; and tables 1–14.	1–22
A	EP 1900703 A1 (BJ SERVICES COMPANY) 19 March 2008 See paragraphs [0011]–[0036].	1–22
A	US 2004-0112255 A1 (BRUNO et al.) 17 June 2004 See paragraphs [0011]–[0045].	1–22



Further documents are listed in the continuation of Box C.



See patent family annex.

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search

09 November 2017 (09.11.2017)

Date of mailing of the international search report

09 November 2017 (09.11.2017)

Name and mailing address of the ISA/KR

International Application Division

Korean Intellectual Property Office

189 Cheongsa-ro, Seo-gu, Daejeon, 35208, Republic of Korea



Facsimile No. +82-42-481-8578

Authorized officer

PARK, Tae Wook

Telephone No. +82-42-481-3405



INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.

PCT/US2017/018930

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 2015-0260009 A1	17/09/2015	US 2014-0332217 A1	13/11/2014
US 2015-0184060 A1	02/07/2015	AU 2007-231193 A1	04/10/2007
		AU 2009-216602 A1	27/08/2009
		AU 2009-216602 B2	05/09/2013
		AU 2009-290758 A1	18/03/2010
		AU 2009-290758 B2	24/07/2014
		AU 2009-321421 A1	03/06/2010
		AU 2009-321421 B2	11/07/2013
		AU 2009-321422 A1	03/06/2010
		AU 2009-321422 B2	30/01/2014
		AU 2009-321423 A1	03/06/2010
		AU 2009-321423 B2	06/03/2014
		AU 2010-233555 A1	14/10/2010
		AU 2010-233555 B2	18/07/2013
		AU 2010-240744 A1	28/10/2010
		AU 2010-252793 A1	02/12/2010
		AU 2010-252793 B2	25/07/2013
		AU 2010-299648 A1	31/03/2011
		AU 2010-299648 B2	19/09/2013
		AU 2010-299649 A1	31/03/2011
		AU 2010-299649 B2	20/03/2014
		AU 2010-311158 A1	05/05/2011
		AU 2010-311158 B2	12/09/2013
		AU 2010-311178 A1	05/05/2011
		AU 2010-311178 B2	14/11/2013
		AU 2011-203389 A1	07/07/2011
		AU 2011-203389 B2	02/10/2014
		AU 2011-268758 A1	29/12/2011
		AU 2011-268758 B2	27/03/2014
		AU 2011-273259 A1	05/01/2012
		AU 2011-273259 B2	19/12/2013
		AU 2011-309957 A1	05/04/2012
		AU 2011-309957 B2	17/07/2014
		AU 2011-346883 A1	28/06/2012
		AU 2011-346883 B2	11/09/2014
		AU 2012-282775 A1	17/01/2013
		AU 2012-282775 B2	09/10/2014
		AU 2013-221468 A1	22/08/2013
		AU 2013-221468 B2	13/08/2015
		AU 2013-251467 A1	31/10/2013
		AU 2013-266319 A1	28/11/2013
		AU 2013-266319 B2	23/07/2015
		AU 2013-280260 A1	03/01/2014
		AU 2013-280260 B2	27/08/2015
		AU 2013-308769 A1	06/03/2014
		AU 2013-308769 B2	07/07/2016
		AU 2013-309038 A1	06/03/2014
		AU 2013-309038 B2	31/03/2016

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.

PCT/US2017/018930

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
		AU 2013-334222 A1	01/05/2014
		AU 2013-334222 B2	21/07/2016
		AU 2013-361111 A1	26/06/2014
		AU 2013-361111 B2	08/10/2015
		AU 2014-224072 A1	26/03/2015
		AU 2014-256987 A1	30/10/2014
		AU 2014-256987 B2	24/11/2016
		AU 2014-296231 A1	05/02/2015
		AU 2014-354985 A1	04/06/2015
		AU 2014-354985 B2	16/02/2017
		CA 2621835 A1	15/03/2007
		CA 2621835 C	28/06/2011
		CA 2642930 A1	04/10/2007
		CA 2681606 A1	20/11/2008
		CA 2681606 C	06/11/2012
		CA 2714452 A1	27/08/2009
		CA 2714452 C	31/07/2012
		CA 2736148 A1	18/03/2010
		CA 2736148 C	01/04/2014
		CA 2741491 A1	03/06/2010
		CA 2741491 C	29/12/2015
		CA 2741824 A1	03/06/2010
		CA 2741824 C	29/04/2014
		CA 2755433 A1	03/06/2010
		CA 2757109 A1	14/10/2010
		CA 2757109 C	16/02/2016
		CA 2758311 A1	28/10/2010
		CA 2758311 C	24/12/2013
		CA 2762605 A1	02/12/2010
		CA 2774302 A1	31/03/2011
		CA 2774302 C	05/05/2015
		CA 2774306 A1	31/03/2011
		CA 2774306 C	15/07/2014
		CA 2778241 A1	05/05/2011
		CA 2778241 C	14/07/2015
		CA 2778242 A1	05/05/2011
		CA 2778242 C	23/09/2014
		CA 2802959 A1	29/12/2011
		CA 2802959 C	07/04/2015
		CA 2803223 A1	05/01/2012
		CA 2803223 C	28/07/2015
		CA 2808133 A1	05/04/2012
		CA 2808133 C	03/11/2015
		CA 2821573 A1	28/06/2012
		CA 2821931 A1	17/01/2013
		CA 2821931 C	16/02/2016
		CA 2847401 A1	31/03/2011
		CA 2847401 C	16/09/2014
		CA 2847489 A1	31/03/2011
		CA 2847489 C	30/09/2014

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.

PCT/US2017/018930

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
		CA 2847647 A1	31/03/2011
		CA 2861662 A1	28/11/2013
		CA 2863283 A1	12/03/2015
		CA 2863987 A1	22/08/2013
		CA 2870367 A1	31/10/2013
		CA 2873279 A1	31/03/2011
		CA 2873279 C	21/03/2017
		CA 2873296 A1	31/03/2011
		CA 2873296 C	16/05/2017
		CA 2875660 A1	03/01/2014
		CA 2875660 C	27/06/2017
		CA 2881910 A1	06/03/2014
		CA 2882817 A1	06/03/2014
		CA 2888162 A1	01/05/2014
		CA 2891718 A1	26/06/2014
		CA 2914252 A1	05/02/2015
		CA 2940821 A1	28/06/2012
		CN 101305070 A	12/11/2008
		CN 101305070 C	12/11/2008
		CN 103140562 A	05/06/2013
		CN 103370393 A	23/10/2013
		CN 103370393 B	23/11/2016
		CN 103459348 A	18/12/2013
		CN 104114513 A	22/10/2014
		CN 104812868 A	29/07/2015
		CN 104995279 A	21/10/2015
		EP 1928975 A1	11/06/2008
		EP 1928975 B1	04/11/2015
		EP 2158288 A1	03/03/2010
		EP 2245106 A1	03/11/2010
		EP 2245106 B1	06/05/2015
		EP 2350226 A1	03/08/2011
		EP 2362887 A2	07/09/2011
		EP 2362888 A1	07/09/2011
		EP 2387603 A1	23/11/2011
		EP 2417079 A1	15/02/2012
		EP 2421929 A1	29/02/2012
		EP 2435528 A1	04/04/2012
		EP 2465910 A1	20/06/2012
		EP 2480620 A1	01/08/2012
		EP 2480621 A1	01/08/2012
		EP 2493830 A1	05/09/2012
		EP 2493999 A1	05/09/2012
		EP 2521700 A1	14/11/2012
		EP 2521700 B1	16/04/2014
		EP 2585551 A1	01/05/2013
		EP 2585552 A1	01/05/2013
		EP 2622040 A1	07/08/2013
		EP 2651849 A1	23/10/2013
		EP 2655542 A1	30/10/2013

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.

PCT/US2017/018930

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
		EP 2743242 A2	18/06/2014
		EP 2814787 A2	24/12/2014
		EP 2841523 A1	04/03/2015
		EP 2848666 A1	18/03/2015
		EP 2855393 A1	08/04/2015
		EP 2867326 A1	06/05/2015
		EP 2867326 B1	02/11/2016
		EP 2888335 A1	01/07/2015
		EP 2890756 A1	08/07/2015
		EP 2907862 A1	19/08/2015
		EP 2912137 A1	02/09/2015
		EP 2935506 A1	28/10/2015
		EP 2989290 A1	02/03/2016
		EP 3002323 A1	06/04/2016
		EP 3118278 A1	18/01/2017
		EP 3121245 A1	25/01/2017
		GB 2451007 A	14/01/2009
		GB 2529960 A	09/03/2016
		GB 2537236 A	12/10/2016
		US 2005-0173117 A1	11/08/2005
		US 2006-0162926 A1	27/07/2006
		US 2006-0166834 A1	27/07/2006
		US 2007-0056475 A1	15/03/2007
		US 2007-0056734 A1	15/03/2007
		US 2008-0110619 A1	15/05/2008
		US 2008-0156491 A1	03/07/2008
		US 2008-0277116 A1	13/11/2008
		US 2009-0071650 A1	19/03/2009
		US 2009-0088348 A1	02/04/2009
		US 2009-0114126 A1	07/05/2009
		US 2009-0120644 A1	14/05/2009
		US 2009-0124522 A1	14/05/2009
		US 2009-0139719 A1	04/06/2009
		US 2009-0200029 A1	13/08/2009
		US 2009-0236097 A1	24/09/2009
		US 2009-0260544 A1	22/10/2009
		US 2009-0283269 A1	19/11/2009
		US 2009-0312445 A1	17/12/2009
		US 2009-0320720 A1	31/12/2009
		US 2010-0016183 A1	21/01/2010
		US 2010-0025039 A1	04/02/2010
		US 2010-0041792 A1	18/02/2010
		US 2010-0044043 A1	25/02/2010
		US 2010-0095871 A1	22/04/2010
		US 2010-0096135 A1	22/04/2010
		US 2010-0258312 A1	14/10/2010
		US 2010-0273912 A1	28/10/2010
		US 2010-0282466 A1	11/11/2010
		US 2010-0292365 A1	18/11/2010
		US 2011-0000400 A1	06/01/2011

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.

PCT/US2017/018930

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
		US 2011-0017452 A1	27/01/2011
		US 2011-0100626 A1	05/05/2011
		US 2011-0162845 A1	07/07/2011
		US 2012-0145393 A1	14/06/2012
		US 2012-0152539 A1	21/06/2012
		US 2012-0160131 A1	28/06/2012
		US 2012-0167803 A1	05/07/2012
		US 2012-0186494 A1	26/07/2012
		US 2012-0190769 A1	26/07/2012
		US 2012-0192768 A1	02/08/2012
		US 2012-0193097 A1	02/08/2012
		US 2012-0211227 A1	23/08/2012
		US 2012-0227631 A1	13/09/2012
		US 2012-0234541 A1	20/09/2012
		US 2012-0260828 A1	18/10/2012
		US 2012-0267107 A1	25/10/2012
		US 2012-0291674 A1	22/11/2012
		US 2012-0318506 A1	20/12/2012
		US 2012-0325119 A1	27/12/2012
		US 2012-0325476 A1	27/12/2012
		US 2012-0325477 A1	27/12/2012
		US 2012-0328377 A1	27/12/2012
		US 2013-0008351 A1	10/01/2013
		US 2013-0008352 A1	10/01/2013
		US 2013-0048286 A1	28/02/2013
		US 2013-0061779 A1	14/03/2013
		US 2013-0112405 A1	09/05/2013
		US 2013-0153214 A1	20/06/2013
		US 2013-0157903 A1	20/06/2013
		US 2013-0210685 A1	15/08/2013
		US 2013-0213642 A1	22/08/2013
		US 2013-0213643 A1	22/08/2013
		US 2013-0233538 A1	12/09/2013
		US 2013-0244911 A1	19/09/2013
		US 2013-0312641 A1	28/11/2013
		US 2014-0008067 A1	09/01/2014
		US 2014-0048266 A1	20/02/2014
		US 2014-0060389 A1	06/03/2014
		US 2014-0083699 A1	27/03/2014
		US 2014-0123879 A1	08/05/2014
		US 2014-0221257 A1	07/08/2014
		US 2014-0326446 A1	06/11/2014
		US 2015-0107838 A1	23/04/2015
		US 2015-0247383 A1	03/09/2015
		US 2016-0053158 A1	25/02/2016
		US 7086466 B2	08/08/2006
		US 7341104 B2	11/03/2008
		US 7353870 B2	08/04/2008
		US 7424913 B2	16/09/2008
		US 7445669 B2	04/11/2008

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.

PCT/US2017/018930

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
		US 7478675 B2	20/01/2009
		US 7559369 B2	14/07/2009
		US 7607482 B2	27/10/2009
		US 7607484 B2	27/10/2009
		US 7617870 B1	17/11/2009
		US 7631692 B2	15/12/2009
		US 7674332 B2	09/03/2010
		US 7743828 B2	29/06/2010
		US 7784542 B2	31/08/2010
		US 7789150 B2	07/09/2010
		US 7806183 B2	05/10/2010
		US 7892352 B2	22/02/2011
		US 7927419 B2	19/04/2011
		US 8030253 B2	04/10/2011
		US 8183186 B2	22/05/2012
		US 8261827 B2	11/09/2012
		US 8281859 B2	09/10/2012
		US 8297357 B2	30/10/2012
		US 8307899 B2	13/11/2012
		US 8318642 B2	27/11/2012
		US 8324137 B2	04/12/2012
		US 8327939 B2	11/12/2012
		US 8333240 B2	18/12/2012
		US 8344933 B1	01/01/2013
		US 8399387 B2	19/03/2013
		US 8403045 B2	26/03/2013
		US 8434553 B2	07/05/2013
		US 8440596 B2	14/05/2013
		US 8476203 B2	02/07/2013
		US 8486868 B2	16/07/2013
		US 8486869 B2	16/07/2013
		US 8505629 B2	13/08/2013
		US 8505630 B2	13/08/2013
		US 8522873 B2	03/09/2013
		US 8544543 B2	01/10/2013
		US 8551923 B1	08/10/2013
		US 8555967 B2	15/10/2013
		US 8586512 B2	19/11/2013
		US 8598093 B2	03/12/2013
		US 8603952 B2	10/12/2013
		US 8609595 B2	17/12/2013
		US 8641818 B2	04/02/2014
		US 8672028 B2	18/03/2014
		US 8685903 B2	01/04/2014
		US 8691737 B2	08/04/2014
		US 8733440 B2	27/05/2014
		US 8741818 B2	03/06/2014
		US 8895485 B2	25/11/2014
		US 8895486 B2	25/11/2014
		US 8921284 B2	30/12/2014

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.

PCT/US2017/018930

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
		US 8940670 B2	27/01/2015
		US 8950486 B2	10/02/2015
		US 9006154 B2	14/04/2015
		US 9006155 B2	14/04/2015
		US 9018147 B2	28/04/2015
		US 9051505 B2	09/06/2015
		US 9150773 B2	06/10/2015
		US 9157020 B2	13/10/2015
		US 9199879 B2	01/12/2015
		US 9206344 B2	08/12/2015
		US 9376609 B2	28/06/2016
		US 9512346 B2	06/12/2016
		US 9512351 B2	06/12/2016
		US 9512352 B2	06/12/2016
		US 9644132 B2	09/05/2017
		US 9676989 B2	13/06/2017
		WO 2005-080287 A1	01/09/2005
		WO 2007-028952 A1	15/03/2007
		WO 2007-110591 A1	04/10/2007
		WO 2008-139140 A1	20/11/2008
		WO 2009-103944 A1	27/08/2009
		WO 2009-138747 A1	19/11/2009
		WO 2010-029281 A1	18/03/2010
		WO 2010-061162 A2	03/06/2010
		WO 2010-061162 A3	10/09/2010
		WO 2010-061163 A1	03/06/2010
		WO 2010-061164 A1	03/06/2010
		WO 2010-116143 A1	14/10/2010
		WO 2010-122277 A1	28/10/2010
		WO 2010-136760 A1	02/12/2010
		WO 2011-036462 A1	31/03/2011
		WO 2011-036463 A1	31/03/2011
		WO 2011-051664 A1	05/05/2011
		WO 2011-051684 A1	05/05/2011
		WO 2011-080522 A1	07/07/2011
		WO 2011-161405 A1	29/12/2011
		WO 2012-001343 A1	05/01/2012
		WO 2012-042210 A1	05/04/2012
		WO 2012-085509 A1	28/06/2012
		WO 2012-085509 A8	01/08/2013
		WO 2013-009780 A1	17/01/2013
		WO 2013-123207 A2	22/08/2013
		WO 2013-123207 A3	31/10/2013
		WO 2013-163504 A1	31/10/2013
		WO 2013-177336 A1	28/11/2013
		WO 2014-004773 A1	03/01/2014
		WO 2014-035923 A1	06/03/2014
		WO 2014-036218 A1	06/03/2014
		WO 2014-066737 A1	01/05/2014
		WO 2014-100604 A1	26/06/2014

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.

PCT/US2017/018930

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 2016-0264462 A1	15/09/2016	WO 2014-127334 A1	21/08/2014
		WO 2014-176491 A1	30/10/2014
		WO 2015-017564 A1	05/02/2015
		WO 2015-080977 A1	04/06/2015
US 2016-0264462 A1	15/09/2016	US 2012-0186812 A1	26/07/2012
		US 2014-0345866 A1	27/11/2014
		US 8834624 B2	16/09/2014
		US 9353308 B2	31/05/2016
EP 1900703 A1	19/03/2008	CA 2600959 A1	14/03/2008
		CA 2600959 C	29/11/2011
		NO 20074659 A	17/03/2008
		US 2008-0066652 A1	20/03/2008
US 2004-0112255 A1	17/06/2004	AR 034016 A1	21/01/2004
		BR 0116891 A	09/02/2005
		CA 2438463 A1	22/08/2002
		CN 1500071 A	26/05/2004
		DZ 3497 A1	22/08/2002
		EA 200300887 A1	30/12/2004
		EG 23010 A	31/12/2003
		EP 1236701 A1	04/09/2002
		EP 1362018 A1	19/11/2003
		MX PA03007053 A	02/04/2004
		NO 20033607 A	14/10/2003
		OA 12443 A	22/05/2006
		WO 02-064528 A1	22/08/2002