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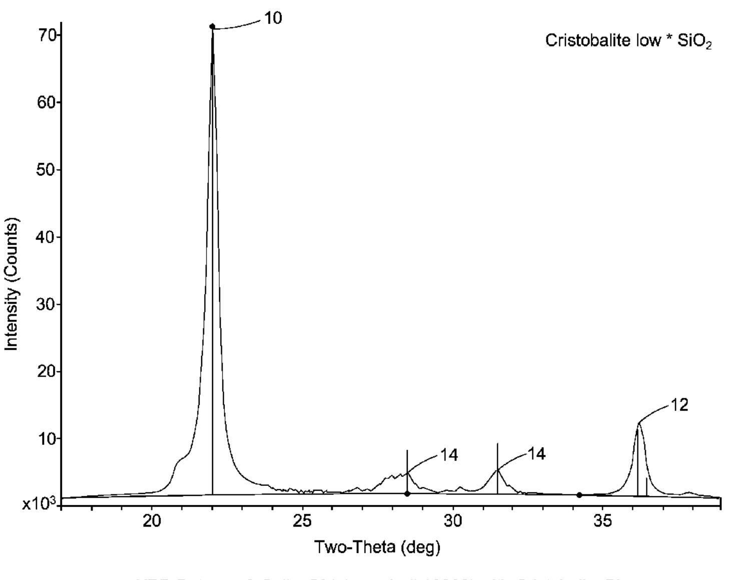
(54) **Title**: OPALINE FLUX-CALCINED DIATOMITE PRODUCTS

(57) **Abstract**: A diatomite product and method of using such is disclosed. The diatomite product may comprise sodium flux-calcined diatomite, wherein the diatomite product has a crystalline silica content of less than about 1 wt%, and the diatomite product has a permeability between 0.8 darcy and about 30 darcy. In some embodiments, the diatomite product may be in particulate or powdered form. This disclosure also concerns flux-calcined silica products containing low or non-detectable levels of crystalline silica. Some of these products can be further characterized by high permeabilities and a measurable content of opal-C, a hydrated form of silicon dioxide.



XRD Pattern of Celite 501 (sample # 18362) with Cristobalite Phase plus minor (1 to 2%) Feldspars

FIG. 1

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SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, KM, ML, MR, NE, SN, TD, TG).

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Opaline Flux-Calcined Diatomite Products

Cross-Reference to Related Patent Applications

[0001] This patent application claims the benefit of U.S. Provisional Patent Application No. 62/245,716, filed October 23, 2015, and claims the benefit of U.S. Provisional Patent Application No. 62/314,005, filed March 28, 2016.

Technical Field

[0002] This disclosure concerns straight-calcined and flux-calcined biogenic silica products, and more specifically straight-calcined and flux-calcined diatomite products comprising low or non-detectable levels of crystalline silica and Silica Documentation (as defined herein), as well as related test methods and formulations. Such diatomite products may comprise a physical component already in the public domain and novel Silica Documentation or a novel physical component and novel Silica Documentation.

Background

[0003] Diatomaceous earth, also called diatomite or kieselgur, is a naturally-occurring sedimentary rock consisting primarily of the skeletal remains (also called frustules) of diatoms, a type of single-celled plant generally found in water, such as lakes and oceans. Diatomite has been used for many years in a variety of manufacturing processes and applications, including use as a filtration media, a carrier, an absorbent and as a functional filler.

[0004] Diatomite, as it naturally occurs, consists of a mixture of the diatom frustules themselves, as well as other minerals, such as clays, volcanic ash, feldspars and quartz, which were deposited through sedimentary processes into the lake or ocean habitats of the living diatoms. The diatom frustules, when formed, are composed of an amorphous, hydrated biogenic silica called opal-A. In the context of this patent, we refer to biogenic silica as silicon dioxide produced by a life form. Common life forms that produce biogenic silica include diatoms, radiolaria, sponges, bamboo, rice plants and horsetails. As formed, diatomite frustules do not contain any crystalline silica, but the other sediments contained within diatomite can include crystalline silica in the form of quartz, the main component of silica sand. Quartz is almost universally found in marine (salt water) deposits of diatomite, but some lacustrine (fresh water) deposits of diatomite are free of quartz or contain quartz grains of sufficient size that they can be removed during processing. Following the death of the diatom, the opal-A can, over time, become partially dehydrated and can, in a series of stages, convert from opal-A to forms of opal with more short-range molecular order and containing less water of hydration, such as opal-CT and opal-C. Over very long periods of time and under suitable conditions, opal-CT can convert to quartz. The natural weathering process of opal-A in the Monterrey diatomite formation in California has been described by Eichhubl and Behl among others.

[0005] Opal-A, opal-CT and opal-C are individually or collectively often referred to as opal, vitreous silica or amorphous silica.

[0006] In its earliest known use, diatomite was employed as a pigment in cave paintings in Europe that date back as far as 40,000 years ago. Modern industrial use of diatomite began in the mid-to-late 1800's and expanded early in the 20th century when it was discovered that the filtration properties of the material could be modified through thermal treatment.

[0007] The earliest uses of thermally modified diatomite occurred around 1913, and in these processes, the material was heated to its softening point in order to agglomerate the diatom frustules to form larger particles and to increase the permeability of the product. Although the main function of this process was to promote the agglomeration of the frustules, and it is therefore perhaps most appropriately called a sintering process, it has been almost exclusively referred to as calcining, perhaps because it partially or fully dehydrates the naturally-occurring mineral.

[0008] About fifteen years after the introduction of calcined diatomite products, it was discovered that the properties of diatomite could be even further modified through the addition of a flux during the calcining process. While various fluxes have been used since the introduction of flux-calcined diatomite, sodium-based fluxes, such as salt (sodium-chloride) or soda ash, have been the most commonly-used fluxes.

[0009] The two sintering processes now in common use in the diatomite industry are almost universally referred to as straight-calcining, for a sintering process in which no flux is used, and flux-calcining, in which a flux is added to the diatomite to promote a lower softening temperature and a greater degree of particle agglomeration. These processes produce different physical and optical changes in the diatomite product.

[0010] Straight-calcining almost always produces a change in the color of natural diatomite, from an off-white color to a pink color. The extent of this color change can be correlated with the iron content of the diatomite. Straight-calcining generally is effective in producing products with low to medium permeabilities in the range of about 0.1 to about 0.6 darcy. In some cases, the permeability of straight-calcined products can be increased beyond these levels, up to about one darcy, through the removal of the fine fraction of particles contained in the calcined product, through separation processes, such as air classification.

[0011] Flux-calcining often changes the color of natural diatomite from off-white to a bright white color or sometimes to a brighter, less pink color. Flux-calcining can lead to much greater agglomeration of particles, and may be used to produce products with permeabilities ranging from about 0.8 darcy to over ten darcy.

[0012] Products comprising straight-calcined or flux-calcined diatomite find wide-spread use in micro-filtration applications. They are primarily used in solid-liquid separations that are difficult due to inherent properties of entrained solids such as sliminess and compressibility. The products are generally used in two modes; as a pre-coat, wherein a layer of the product is established on a supporting surface which then serves as the solid-liquid separation interface, and as body-feed, in which the product is introduced into the pre-filtered suspension to improve and maintain the permeability of separated and captured solids. These products can be used in primary (coarse) filtrations where larger or more numerous particles are removed from suspensions, and in secondary (polish) filtrations, where finer residual particles are removed and captured.

[0013] In addition to filtration applications, the significant improvement in the whiteness and brightness of diatomite through flux-calcining led to the development and widespread use of flux-calcined diatomite in paint and plastic film filler applications.

[0014] Over the course of the development of straight-calcined and flux-calcined products, it became known that the straight-calcination and flux-calcination processes resulted in changes in the composition of the opaline structure of the diatomite. While some of the changes were understood essentially at the time the processes were developed, some aspects of the changes were not completely understood or characterized until recently. As we now understand it, the process of the modification of the diatomite from opal-A, which is the most common form of opal in the diatomite deposits that have been used to produce diatomite filtration and filler products, follows a continuum of dehydration and increase in short-range molecular ordering. Opal-A, which contains about 4 to 6 wt% water of hydration, converts to Opal-C, which contains about 0.2 to 1 wt% water of hydration. Opal-C, if exposed to further high temperatures, can convert to a mineral phase traditionally characterized as cristobalite or, under certain conditions, quartz, which are crystalline forms of silicon dioxide that contain no water of hydration.

[0015] Cristobalite can also be formed during volcanism or through industrial processes such as the thermal processing of quartz. Cristobalite formed through the heating and cooling of quartz does not evolve from the dehydration of opaline raw materials, but rather through a reconstructive crystalline phase change at high temperature.

[0016] During thermal processing, any quartz contained in the diatomite can also undergo a transition to cristobalite. Generally, quartz does not convert to cristobalite when diatomite ores are calcined in the absence of a fluxing agent but may convert to cristobalite when diatomite containing quartz is processed in the presence of a flux.

[0017] In addition to products composed of processed diatomite ores, optionally, with flux additions, a number of products comprising diatomite raw materials and other powdered materials, including ground natural glasses, expanded natural glasses, ground synthetic glasses, thermoplastic polymers, zinc, tin, rice hull ash, precipitated silica, silica gel, cellulose, activated alumina, alumina trihydrate, acid activated bentonite clays or activated carbons have been reported. Natural glasses may be in the form of perlite, pumice, volcanic glass or obsidian. The products comprising diatomite and one or more of these components may be in the form of mixtures or composites and the composites may be formed through thermal sintering, attachment with a binder or precipitation. Products comprising diatomite and optionally one or more of these other components may also contain opal which has been traditionally improperly identified as cristobalite. See for example, Palm et al, US patent Nos. 5,776,353; 6,524,489; 6,712,974; Wang et al, PCT Application No. PCT/US15/65572; and Lu et al., US Patent No. 8,242,050.

[0018] While some straight-calcined and flux-calcined diatomite products and the mixed and blended products comprising them may be known, the understanding of the mineralogy of straight-calcined and flux-calcined diatomite products and the methods for characterizing them are still evolving. In addition to the novel products and novel analytical techniques disclosed by the inventors, they have also identified aspects of the mineralogy of the products, particularly with regard to the stability of the mineralogy, which was previously unknown.

[0019] In particular, in a surprising and wholly unexpected result, the inventors have determined that the various opaline phases of straight-calcined and flux-calcined diatomite and even at least some portion of what appears to be cristobalite, will vitrify (convert into a glass-like amorphous solid) and possibly rehydrate. In other words, the inventors have observed the following: (1) Over weeks and months, a significant portion of the partially dehydrated forms of opal, opal-CT and opal-C, will vitrify and possibly rehydrate to form what appears to be opal-A; and (2) over weeks and months, a significant portion of what appears to be fully dehydrated and de-vitrified opal, which the inventors and the literature would classify as cristobalite, will vitrify and possibly rehydrate to form what appears to be opal-C, opal-CT and opal-A.

[0020] This behavior of vitrification and rehydration over what would be considered the blink of an eye in geologic time is an interesting result that must call into question whether the *biogenic cristobalite* contained in thermally modified diatomite products is actually properly identified as cristobalite, as “cristobalites” formed from the thermal treatment of quartz have not been shown to vitrify and hydrate to form opal. Indeed, from a geological perspective, cristobalite is a metastable phase at ambient conditions and should eventually convert to quartz as that is the stable crystalline silica phase at ambient conditions. This usually takes thousands if not millions of years.

[0021] Over a number of years, it has become accepted within certain scientific and regulatory communities that the chronic inhalation of the crystalline forms of silicon dioxide, quartz, cristobalite and tridymite, may lead to lung disease. While cristobalite can be formed in industrial processes through the thermal conversion of either quartz or biogenic silica, the stages of each conversion process and the intermediate products of conversion differ markedly. These significant differences are not always considered or appreciated in the medical and health literature concerning crystalline silica and have not been completely investigated.

[0022] The inhalation of opaline and most other forms of amorphous silica has not been demonstrated to pose the same health risks as the inhalation of crystalline forms of silicon dioxide may pose. There is therefore a need for the novel analytical techniques that allow the user to distinguish opals from cristobalite for products produced from diatomite.

[0023] Products comprising straight-calcined and flux-calcined diatomite products comprise a number of attributes, including physical and chemical characteristics and regulatory support and hazard communications features. Certain of the physical characteristics which are commonly used to describe or characterize these products include the particle size distribution, the diatom assemblage (species of diatoms from which the frustules are derived), the packed or centrifuged wet density of the material, the brightness and tint of the material and a number of other characteristics which are known to those with a knowledge of the state of the art.

[0024] Products comprising straight-calcined and flux-calcined diatomite products can also be characterized by a number of chemical or compositional attributes, including the mineralogy, crystalline silica content, bulk chemistry and extractable chemistry for a number of substances, including iron, calcium, antimony, lead, chromium, arsenic and others.

[0025] In addition to traditional attributes such as chemical and physical attributes, which we refer to as the physical component of the product, straight-calcined and flux-calcined diatomite products also comprise regulatory or technical support features, such as certificates of analysis and Safety Data Sheets (SDS). Certificates of analysis are documents produced that include certification of certain characteristics agreed-upon by the supplier and the customer which may include almost any characteristic of interest to the customer. Safety Data Sheets, generally required by national governments worldwide and by international agreements, include compositional information about the products and health hazard warnings and are primarily designed to include information about hazards, exposure limits and the safe handling of materials. Safety Data Sheets and their predecessor documents, such as the US Material Safety Data Sheets (MSDS), have, for many years, contained information about hazardous components of materials used in the workplace, such as crystalline silica, as the potential risks of silicosis from chronic inhalation of crystalline silica have been known for many years. Since 1987, when the International Agency for Research on Cancer determined that crystalline silica, in the form of cristobalite, quartz or tridymite, was a probable human carcinogen, many governments have required that warnings about crystalline silica contents above detection limits or certain exposure limits be included on Safety Data Sheets.

[0026] In modern commerce, straight-calcined and flux-calcined diatomite products comprise both a physical component and a data component (the data component including Silica Documentation, as defined below), and, the two components, physical and data are necessary for the sale of the product in essentially all countries. As a result, novel products may be developed through improvements of either the physical component of the product or the associated data component of the product (for example, the Silica Documentation). In this application, the inventors disclose novel products comprising both a physical component that includes low or non-detectable levels of crystalline silica, and corresponding Silica Documentation (the data component). For the purposes of this application, Silica Documentation includes one or more of the following: regulatory support document(s), hazard disclosure(s), Safety Data Sheet(s), label(s), product label(s), product bar code(s), certificates of analysis or other electronic or printed forms of data which document or disclose crystalline silica content, or the absence of crystalline silica in the content, of a product that includes diatomite. The absence of crystalline silica is disclosed in Silica Documentation by either an explicit statement or an absence of crystalline silica (for example, cristobalite, quartz, tridymite) from the product contents identified by the Silica Documentation.

[0027] This disclosure teaches of several types of novel products, including but not limited to:

[0028] 1. Products comprising conventional physical components and novel Silica Documentation. The conventional physical components include straight-calcined or flux-calcined diatomite.

[0029] 2. Products comprising novel physical components and novel Silica Documentation. The novel physical components include flux-calcined diatomite.

[0030] 3. Novel test methods useful in the characterization of products, which include straight-calcined and flux-calcined diatomite, and in the preparation of novel Silica Documentation.

[0031] In each of (1) and (2) above, the physical component may, in some embodiments, be contained in a package. As used herein "package" means a bag, drum, or container. However, in some embodiments, the physical component may be transported or provided in bulk (for example, in a tanker, or the like). Silica Documentation may be associated with an individual package, a shipment of packages or a bulk shipment of the physical component.

[0032] As used herein, the term "about" means plus or minus 20% of the stated value.

Summary of the Disclosure

[0033] In accordance with one aspect of the disclosure, a diatomite product is disclosed. The diatomite product may comprise sodium flux-calcined diatomite, wherein the diatomite product has a crystalline silica content of less than about 1 wt%, and the diatomite product has a permeability between 0.8 darcy and about 30 darcy. In a refinement, the diatomite product may have a permeability between 0.9 darcy and 30 darcy. In a further refinement, the diatomite product may have a permeability between 1.0 darcy and 20 darcy. In a further refinement, the diatomite product may have a permeability between 1.5 darcy and about 9 darcy. In a further refinement, the diatomite product may have a permeability between 1.5 darcy and 4 darcy.

[0034] In an embodiment, the crystalline silica content may be less than about 0.1 wt% of the diatomite product.

[0035] In an embodiment, the diatomite product may have a biogenic silica content of at least 75 wt%. In a refinement, the diatomite product may have a silica content at least 80 wt% silica. In a further refinement, the diatomite product may have a silica content at least 85 wt% silica.

[0036] In an embodiment, the diatomite may have an opal-C content of more than about 1 wt% of the diatomite product. In a refinement, the diatomite product may have an opal-C content of more than about 10 wt% of the diatomite product.

[0037] In an embodiment, the diatomite product may further comprise more than about 4 wt% combined total of aluminum and iron in mineral form, or more than about 7 wt% expressed as oxides. In another embodiment, the diatomite product may further comprise more than about 2.6 wt% aluminum in mineral form, or more than about 5 wt% expressed as aluminum oxide. In another embodiment, the diatomite product may further comprise more than about 1.75 wt% iron in mineral form, or more than about 2.5 wt% expressed as iron oxide. In an embodiment, measurement as oxide(s) may be determined by wave-length dispersive x-ray fluorescence (XRF) analysis.

[0038] In an embodiment, the diatomite product may be a regenerated filtration medium that has been used previously one or more times as a filtration medium and has been regenerated by either a chemical or thermal process. The regenerated filtration medium may be adapted for re-use in filtration processes for at least one of food, beverages, chemicals, fuels, materials, water or biopharmaceuticals. In a refinement, the chemical or thermal process may be pyrolysis, solvent extraction or gasification.

[0039] In an embodiment, the diatomite product may further comprise a soluble calcium content between about 21 ppm and 900 ppm, as measured by the EBC method.

[0040] In an embodiment, the diatomite product may further comprise less than about 160 ppm soluble iron as measured by EBC methods. In a refinement, the diatomite product may further comprise less than about 45ppm soluble iron as measured by EBC methods. In another refinement, the diatomite product may comprise between about 23 ppm and 45 ppm soluble iron, as measured by the EBC method.

[0041] In an embodiment, the diatomite product may further comprise less than about 15 ppm soluble iron as measured by ASBC methods. In a refinement, the diatomite product may further comprise between about 4 ppm and about 14 ppm, beer soluble iron, as measured by the ASBC method.

[0042] In an embodiment. the diatomite product may further comprise a soluble iron content of about 13 to 14 ppm prior to any post-calcining hydration treatments, as measured by the ASBC method.

[0043] In an embodiment, the diatomite product may further comprise less than about 160 ppm soluble aluminum as measured by EBC methods. In a refinement, the diatomite product may further comprise less than about 120 ppm soluble aluminum as measured by EBC methods. In a further refinement, the diatomite product may further comprise less than about 75 ppm soluble aluminum as measured by EBC methods.

[0044] In an embodiment, the diatomite product may further comprise less than about 1 ppm soluble arsenic as measured by EBC methods. In an embodiment, the diatomite product may further comprise less than about 10 ppm soluble arsenic as measured by EBC methods.

[0045] In an embodiment, the diatomite product may optionally have a cristobalite content determined by a method that differentiates between cristobalite and opal-C. In a refinement, the cristobalite content was determined through use of the LH method.

[0046] In any one of the embodiments above, the diatomite product may be a particulate product. In any one of the embodiments above, the sodium flux-calcined diatomite may be in particulate form.

[0047] In any one of the embodiments above, the diatomite product may be in powdered form. In any one of the embodiments above, the sodium flux-calcined diatomite may be in powdered form.

[0048] In any one of the embodiments above, the crystalline silica may be respirable crystalline silica.

[0049] In another embodiment, the diatomite product may have been acid washed and rinsed to reduce soluble impurities.

[0050] In another embodiment, the diatomite product may be a treated product that has undergone a hydration process to reduce beer soluble iron, as measured by the ASBC method.

[0051] In accordance with another aspect of the disclosure, a method of manufacturing a diatomite product is disclosed. The method may comprise selecting a diatomite ore that includes more than about 2.6 wt% aluminum in mineral form or more than about 5 wt% as aluminum oxide, and calcining the diatomite ore with a sodium flux, wherein the diatomite product manufactured comprises sodium flux-calcined diatomite that has a crystalline silica content of less than about 1 wt% and a permeability between 0.8 darcy and about 30 darcy.

[0052] Also disclosed is a method of filtering beer or wine using a composition as a precoat or bodyfeed in primary or secondary filtration, the composition comprising any one of the diatomite products described above. In a refinement of the method, the use may be in secondary filtration and the composition may further comprise one of silica xerogel, silca hydrogel, tannin, or PVPP.

[0053] In accordance with another aspect of the disclosure, a process for using any one of the diatomite products above is disclosed. In an embodiment, the process may comprise using any one of the above diatomite products as a filtration medium. In a refinement, the process may comprise using any one of the diatomite products described above as a filtration medium in filtration applications, in cellular separation, or in blood plasma processing and fractionation.

[0054] In accordance with another aspect of the disclosure, a method of regenerating a composition is disclosed. The method may comprise treating the composition with a liquid characterized by a pH of between about 7 and about 12. In an embodiment, the composition may comprise any one of the diatomite products described above and one of silica xerogel, silca hydrogel, tannin, or PVPP.

[0055] In accordance with another aspect of the disclosure, a method of regenerating a composition is disclosed. The method may comprise applying thermal energy to the composition, the composition may include any one of the diatomite products described above and one of silica xerogel, silica hydrogel, tannin, or PVPP.

[0056] In accordance with another aspect of the disclosure, a process is disclosed for using any one of the diatomite products described above as a component or additive in filter sheets, cartridges or other manufactured filtration products.

Brief Description of the Drawings

[0057] FIG. 1 is a graph of the X-ray Diffraction (XRD) pattern of Celite® 501 (sample # 18362) with cristobalite phase plus minor (1 to 2 wt%) feldspars;

[0058] FIG. 2 is a graph of the XRD pattern of FP-4 (2H11B4) showing Opal-C phase plus feldspars and possible hematite;

[0059] FIG. 3 is a graph of the XRD pattern of FP-6 (2B11F1) showing cristobalite phase plus feldspars;

[0060] FIG. 4 is a graph of the XRD pattern of Dicalite® 4500 showing cristobalite phase plus minor feldspars;

[0061] FIG. 5 is a graph of the XRD pattern of sample “FP-2 B12C0”;

[0062] FIG. 6 is a graph of the XRD pattern of sample “Celabrite® 2A20A13F”;

[0063] FIG. 7 is a graph of the XRD patterns of sample “FP-3 B17E2” with and without cristobalite spike;

[0064] FIG. 8 is a graph of the XRD primary peak of sample “FP-3 B17E2” with and without cristobalite spike”;

[0065] FIG. 9 is a graph of the XRD pattern of 18188-4 with 5 wt% cristobalite spike;

[0066] FIG. 10 is a graph of the XRD pattern of sample 18188-9 with 15 wt% cristobalite spike;

[0067] FIG. 11 is a graph of the XRD pattern of sample 18188-9 showing only the primary peak;

[0068] FIG. 12 is a graph of the XRD pattern of sample “S31 15-4-7B”;

[0069] FIG. 13 is a graph of the diffraction pattern of sample HV2BH-E with 5 wt% cristobalite spike (NIST 1879A);

[0070] FIG. 14 is a graph of the diffraction pattern of sample HV2-F with 21 wt% cristobalite spike (NIST 1879A);

[0071] FIG. 15 is a graph of the XRD pattern of sample S3115E with 5 wt% cristobalite spike (NIST 1879A);

[0072] FIG. 16 is a graph of the XRD pattern of sample LCS3-H with 28 wt% cristobalite spike (NIST 1879A);

[0073] FIG. 17 is a graph of the diffraction pattern of sample FEBH showing opal-C plus minor feldspar;

[0074] FIG. 18 is a graph of the diffraction pattern of example 15 (KD 15:30) showing opal-C plus feldspar;

[0075] FIG. 19 is a graph of the XRD scan pattern of soda ash flux-calcined diatomite made from LCS-3, showing the presence of cristobalite;

[0076] FIG. 20 is a graph of the XRD scan patterns of sodium aluminate flux-calcined diatomite made from LCS-3, showing the presence of opal-C and 0.1 wt% quartz;

[0077] FIG. 21 is a graph of the XRD scan patterns of soda ash and 0.3μ alumina flux-calcined diatomite made from LCS-3, showing the presence of opal-C and 0.3 wt% quartz;

[0078] FIG. 22 is a graph of the XRD scan patterns of soda ash and 1.7μ ATH flux-calcined diatomite made from LCS-3, showing the presence of cristobalite and <0.1 wt% quartz;

[0079] FIG. 23 is a graph of the XRD scan patterns of calcined diatomite made from LCS-3, showing the presence of opal-C and 0.2 wt% quartz;

[0080] FIG. 24 is a graph of the XRD scan patterns of calcined diatomite made from LCS-3 with ATH additive, showing the presence of opal-C and 0.25 wt% quartz;

[0081] FIG. 25 is a graph of the diffraction pattern of control sample showing opal-C plus minor feldspar;

[0082] FIG. 26 is a graph of the diffraction pattern of test sample with 5 wt% KASOLV® showing possible cristobalite;

[0083] FIG. 27 is a graph of the XRD Pattern of KD15:30 before and after fine grinding showing no phase change;

[0084] FIG. 28 is a graph of an overlaid XRD pattern of Clarcel DIF-N^{TM} showing partial reversion to amorphous phase;

[0085] FIG. 29 is a graph of an overlaid XRD pattern of HV2-G showing partial reversion of opal-C to amorphous phase;

[0086] FIG. 30 is a graph showing the relationship of b* value to opal-C or cristobalite content in flux-calcined DE samples;

[0087] FIGS. 31a-b illustrate a graph and table showing the Particle Size Distribution (PSD) of sample 18188-4;

[0088] FIGS. 32a-b illustrate a graph and table showing the Particle Size Distribution of sample FP-3 B17E2; and

[0089] FIG. 33 is an illustration of an exemplary product with exemplary Silica Documentation.

Detailed Description

[0090] Historically it has not been possible for producers of straight-calcined and flux-calcined diatomite to distinguish between certain forms of opal (such as opal-CT and opal-C, which are also often found in products comprising straight-calcined and flux-calcined diatomite) and cristobalite and to accurately quantify such components, because test methods to distinguish and accurately quantify mineral phases of silicon dioxide in diatomite products have not existed. As a result, a number of products comprising straight-calcined and flux-calcined diatomite, which have been characterized by traditional analytical techniques, have included Silica Documentation that overstates the actual content of crystalline silica. As a result, it has not been possible to provide products comprising straight-calcined and flux-calcined diatomite with regulatory and technical support features that correctly document that these products may not contain cristobalite above detection limits while also not containing quartz or tridymite above detection limits, i.e. the appropriate Silica Documentation. This is important with regard to the practical application of these products. If the products do not comprise the appropriate Silica Documentation, unneeded restrictions in their use and unnecessary costs of compliance can accrue, limiting their applicability and possibly resulting in substitution by less efficacious products or technologies.

[0091] X-ray Diffraction (XRD) has traditionally been used to identify and quantify crystalline silica phases in diatomite products. This method is well-established, and is generally able to quantify at levels of 0.1 wt% and above except in some cases where interfering crystalline phases exist. The problem with XRD is not in the technique itself, but in the understanding of the results. The diffraction patterns of cristobalite and the opaline phases of diatomite (opal-CT and opal-C) are somewhat similar. Analysts have misidentified opal-C or opal-CT as cristobalite based on the location of the primary diffraction peak, and any discrepancies in the XRD pattern have been either attributed to faults and irregularities in the crystal structure, to small crystallite size, or to instrumental error. A complicating factor related to crystal structure and size is that the XRD pattern of cristobalite formed through thermal treatment of diatomite is always subtly different from that of cristobalite formed through thermal treatment of quartz sand (the defacto ‘standard” cristobalite crystal structure). Whether this difference is due to non-siliceous impurities in diatomite, to the morphology of amorphous diatom frustules, or to other factors is unknown. However, the slight ambiguity it causes adds to the uncertainty of correct phase identification. Another source of confusion is that cristobalite exists in two forms, α-cristobalite and β-cristobalite. β-cristobalite is the high temperature phase and it inverts to the α-cristobalite phase at between 200 and 300°C, thus the α-cristobalite phase is the one that typically exists at ambient conditions. However, through mechanical constraints and chemical impurities, the β-cristobalite phase can sometimes resist complete inversion (see Damby et al). β-cristobalite has an XRD pattern even more closely aligned with opal-C than does α-cristobalite.

[0092] In recent years, a number of studies, including those by Miles et al. and Hillier et al., have shown that the standard analytic techniques used to determine the cristobalite content of mixtures of minerals, such as clays and diatomites, which rely solely on x-ray diffraction (XRD), may not be able to accurately differentiate between certain forms of opal, such as opal-C, and cristobalite. Both Miles and Hillier have proposed new methods of differentiating between cristobalite and opal-C, and these methods have been particularly effective when the opal-C is naturally-occurring, as is the case in certain clay products. However, these methods, which rely on the dissolution of the opaline content of a clay product or ore (the “Dissolution Methods”), are not as effective in the characterization of the opal-C content of certain types of rocks which comprise diatomite, where other mineral constituents may shield the opal-C from exposure to solvents.

[0093] A better method than the Traditional Methods (as defined herein) or the Dissolution Methods is desired to allow for a determination of the opal-C (and/or opal-CT) and cristobalite content of a broad range of compositions of diatomaceous earth. As used herein, "Traditional Methods" means the use of XRD analysis to measure and quantify (using such measurements) crystalline silica phases in a diatomite product(s) without regard to whether opaline phases (opal-C and opal-CT) or cristobalite are actually present, and assuming that said opaline phases are actually cristobalite. Each of cristobalite, quartz, or tridymite can be compared to its respective standard (for example NIST SRM 1878b for quartz) for quantification of the content, or be quantified through the use of an internal standard (such as corundum) and applicable relative intensity ratios. National Institute for Occupational Safety and Health (NIOSH) Method 7500 is an example of a Traditional Method for measuring respirable crystalline silica in dust samples, including dusts comprising diatomaceous earth. Method 7500 references a number of possible interfering phases, including micas, feldspars, and clays, but no mention is made of opal-C or opal-CT, and there is nothing in the test method providing for the quantification of these phases. In Traditional Methods, the quantification of the crystalline silica phases in diatomite product(s) includes the opaline phase (opal-C and opal-CT) content as well. More specifically, such Traditional Methods treat the opaline phases as if they were cristobalite and, as such, quantify the combination of cristobalite plus opaline phases as the "cristobalite content" of a product; this results in an overstatement of the cristobalite content of the product (and an overstatement of the crystalline silica content of the product).

[0094] The inventors have developed a new technique to characterize and quantify the opal-C, and cristobalite content of products. Differentiation between opal-C and opal-CT is not attempted in this disclosure. While it is not likely that both opal-C and opal-CT are present at the same time in the products discussed herein, if both phases are present the opal-C and opal-CT phases are not considered separately. Instead, the total of both phases is identified as opal-C and quantified in total (by wt%) as opal-C. In other words, if both phases are present they are treated collectively as if they were part of one phase. Hence, the term opal-C is used herein to mean opal-C and/or opal-CT, unless indicated otherwise by the context in which it is used.

[0095] They have used their new technique to characterize and quantify the opal-C (and/or opal-CT) and crystalline silica content (for example, cristobalite) of a number of commercial diatomite products that are either straight-calcined or flux-calcined and have determined that certain straight-calcined products and certain flux-calcined products for which the physical components are already in the public domain contain significant levels of opal-C (and/or opal-CT) but no detectable levels of cristobalite. This result, is both surprising and unexpected because these products had previously been determined, using the Traditional X-ray Diffraction technique, to contain detectable levels of cristobalite, and, as a result, the Silica Documentation components of these products is incorrectly overstated.

[0096] Further, in an equally surprising and unexpected result, the inventors have identified diatomite ores of certain compositions which can be flux-calcined using sodium-containing fluxes to produce novel products containing significant levels of opal-

C (and/or opal-CT), but no detectable levels of crystalline silica. These opaline flux-calcined biogenic silica products can also meet other stringent requirements of particulate filtration media, such as low wet bulk density and low extractable iron, calcium, aluminum and arsenic. They can also be combined with other materials such as silica xerogels and hydrogels, tannins, and polyvinylpolypyrrolidone (PVPP) to make them more effective in specialized solid-liquid separations such as those common to wine and beer-making. In addition, these opaline flux-calcined biogenic silica products can be further treated by acid-washing to improve their suitability for use in high purity filtrations such as those related to specialty beverages, specialty chemicals and biopharmaceutical manufacturing. Acid washing improves their suitability because it removes trace impurities present in the products that can be potentially dissolved and transferred to the high purity suspensions being filtered. Due to the concerns associated with the inhalation of crystalline silica, there is a need for straight-calcined and flux-calcined diatomite products that do not contain crystalline silica. Significant effort has been devoted to the development of straight-calcined and flux-calcined diatomite products comprising reduced levels of crystalline silica with limited technical and essentially no commercial success. For flux-calcined products, which have traditionally been produced as white, bright powders that are classified to produce co-product filler and filter aid products, the efforts have concentrated on the development of white flux-calcined products containing low or no crystalline silica because the specifications for flux-calcined diatomite fillers require that the products possess high brightness and whiteness.

[0097] For one of the present inventions, the inventors decided to concentrate on the development of flux-calcined filter aids containing reduced or non-detectable levels of crystalline silica without regard for the color of the product and have been successful. While these novel products, which comprise both novel physical components and novel Silica Documentation, have limited utility as functional additives in many applications, they have outstanding utility when used as filtration media.

[0098] To make crystalline silica-free flux-calcined biogenic silica products requires proper ore selection, defined calcining conditions and post-calcination treatment, and proper characterization of silica phases and documentation thereof. Ore selection not only involves an evaluation of the diatom assemblage present and condition of the frustules, but also characterization of associated detrital and precipitated minerals. Diatom species come in a variety of shapes and sizes, and the species present in any particular diatomite deposit do influence the physical characteristics of finished products made therefrom. For example, some assemblages are more suitable for specific filtration applications than others. Also, the overall condition or integrity of the diatom frustules influences characteristics of the final products. Some diatomite deposits or strata therein contain a plethora of small frustule fragments and very few whole diatom frustules. Products made using such raw materials reflect this starting morphology by, for example, having very low permeability. Any quartz grains (associated detrital mineral) present in the ore must be characterized as to relative quantity and nominal size so that predictions can be made as to the feasibility of removing this phase during processing. Some ores are unsuitable because the quartz grains are too fine (sub-micron) and finely-dispersed within the diatomaceous matrix. In addition to quartz, the non-siliceous materials within the ore are of critical importance. Diatomaceous ores that do not contain extremely fine-grained aluminum and iron-bearing minerals (associated detrital and /or precipitated minerals) in sufficient quantity tend to de-vitrify when flux-calcined and quickly form cristobalite. Processing conditions are also important, although the quantity of flux and temperature of calcination are within the normal range for flux-calcined diatomite products in general. Extremely high temperatures (> 1150°C) and flux amounts (>8 wt% as Na_2CO_3) should be avoided. Finally, these products also comprise proper Silica Documentation. Without this essential element, their utility can be greatly and unnecessarily restricted. Proper Silica Documentation results from the use of the novel test methods/quantification described herein.

Description of the Test Methods

Opal-C (and/or opal-CT) vs. Cristobalite

[0099] There are distinguishing characteristics between opal-C (and/or opal-CT) and cristobalite that can be measured, albeit not always precisely. Opals always contain some water existing as internal or attached silane groups, while cristobalite is anhydrous. Thus, it is possible to perform a “loss on ignition test” to see if water of hydration exists in a sample. Such a test should be carried out at high temperature (for example 980°C - 1200°C, preferably, 982°C - 1000 °C) for a sufficient time (at least 1 hour) so that chemically-bound water has a chance to disassociate and volatilize. Precise measurement of sample mass (to the nearest 0.1mg) before and after this treatment allows quantification of volatiles, including the water of hydration, with a resolution to better than 0.01%. American Society for Testing and Materials (ASTM) method C571 provides a suitable protocol for determination of loss on ignition of samples comprising diatomite. Samples that are determined to contain measurable (generally over 0.1 wt%) loss on ignition have the potential to be opal-C (and/or opal-CT).

[00100] XRD, such as bulk powder XRD, can also be used to differentiate between opal-C and α-cristobalite. The diffraction pattern of cristobalite contains sharp Bragg's peaks, most notably at 22.02°, 36.17°, 31.50°, and 28.49° 2θ. The diffraction pattern of opal-C (and/or opal-CT) is less well-defined as compared to cristobalite, with broader and fewer peaks that may be indicative of radial scattering and not true Bragg's peaks. The locations of the primary and secondary peaks are similar to that of cristobalite, but the peaks at 31.50° and 28.49° 2θ are missing or very poorly developed. To summarize, the opal-C (and/or opal-CT) diffraction pattern differs from that of α-cristobalite in the following ways: the primary peak (22°) and the secondary peak (36°) are at higher d-spacing (lower 2θ angle), there is a broader primary peak for opal-C (and/or opal-CT) as measured using the "Full Width at Half Maximum" (FWHM) statistic, opal-C (and/or opal-CT) has poorly-defined peaks at 31.50° and 28.49° 2θ, and a much more significant amorphous background. For a more complete description of XRD, for example bulk powder XRD, terminology and practice, the volume by Klug and Alexander on XRD practice is hereby referenced.

[00101] Differentiating opal-C from β-cristobalite using XRD is more difficult, however Chao and Lu demonstrated that by grinding samples of β-cristobalite with alumina content less than 10 wt% to fine particle size, most of the β-cristobalite is inverted to the α-cristobalite phase with corresponding XRD pattern peak shifts. This does not occur when diatomite products comprising opal-C (and/or opal-CT) are finely ground and then analyzed using XRD – there is no peak shift. As a matter of standard XRD practice, all samples described herein were milled prior to bulk powder X-ray Diffraction analysis.

[00102] Where differentiation based just on XRD pattern is difficult, Miles et al. advocate a twenty-four hour thermal treatment of the sample at very high temperature (1050 °C). Theoretically, opal-C will de-hydrate and re-crystallize as cristobalite. Diffraction peaks will become sharper, more intense, and will shift. Sharper diffraction peaks are indicative of increasing long-range molecular order (larger crystallite size). Increasing peak intensity indicates an increasing quantity of the crystalline phase represented by the peak. A shift in peak location indicates a change in crystal structure with associated increase or reduction in d-spacing. If cristobalite is present in the original sample, the diffraction pattern will not change significantly. The potential problem with this technique is where a sample is comprised of individual particles, some of which could be opaline and others of which could be composed of cristobalite. Heating of such a sample would convert the opaline phase to cristobalite but not affect the cristobalite, and not much of an argument can subsequently be made that cristobalite was not also present in the original sample.

[00103] Another problem exists with the chemical dissolution techniques of Miles, Hillier and others. Hillier et al. successfully demonstrated the efficacy of a sodium hydroxide digest in determining whether various clay samples contained opaline phases or cristobalite. NaOH is capable of dissolving all forms of silica, but requires more contact time for the crystalline varieties in comparison to the opals. When used on diatomite samples (natural, straight-calcined, and flux-calcined), Hillier's method was not found to entirely remove the opaline phases, including opal-A. This is most likely because diatomite particles are coated with chemically-resistant precipitates in the natural state (such as limonite), iron oxides when straight-calcined, and a sodium-rich vitreous or glass-like phase when flux-calcined. While extending the NaOH contact time does increase the dissolution of the opaline phases, results can be inconsistent between diatomaceous product samples produced using varying processes and from different raw materials.

[00104] One relatively simple way to confirm the absence of cristobalite within a sample is to spike the sample (add a known amount of) with cristobalite standard reference material (i.e. National Institute of Standards and Technology (NIST) Standard Reference Material 1879A), run XRD analysis on the spiked sample and then compare the original un-spiked sample diffraction pattern with the spiked sample pattern. If the spiked sample diffraction pattern simply increases the intensity of the primary and secondary peaks but does not show a position shift or show additional peaks, then the original sample most likely contains cristobalite. If the primary peak shifts and becomes sharper (or resolves into two separate peaks), and secondary peaks appear or become much better defined, then opal-C (and/or opal-CT) and not cristobalite is present in the original sample.

[00105] In summary, to determine whether a sample of a product that includes diatomite contains cristobalite or opal-C (and/or opal-CT) then to quantify the opal-C (and/or opal-CT) and/or crystalline silica content involves a number of steps according to the Improved Method disclosed herein, hereinafter referred to as the "LH Method."

[00106] First, it is determined whether the sample contains water of hydration via high temperature loss on ignition testing. For example, a (representative) first portion of the sample is obtained and loss on ignition testing is performed on such first portion.

[00107] Second, bulk powder X-ray Diffraction is performed, and the resulting (first) diffraction pattern inspected. For example, preferably, a (representative) second portion of the sample is obtained and bulk powder XRD is performed on the second portion. Preferably, the second portion is milled prior to XRD. The resulting (first) diffraction pattern is analyzed for the presence or absence of opal-C (and/or opal-CT) and cristobalite. The resulting (first) diffraction pattern may also be analyzed for the presence or absence of other crystalline silica phases (for example, quartz and tridymite) within the (representative) second portion of the sample. If the (first) diffraction pattern is obviously indicative of opal-C (or opal-CT), then further analysis is not required to determine whether the sample contains cristobalite or opal-C (and/opal-CT). As discussed previously herein, the opal-C (and/or opal-CT) diffraction pattern differs from that of α-cristobalite in the following ways: the primary peak (22°) and the secondary peak (36°) are at higher d-spacing (lower 2θ angle), there is a broader primary peak for opal-C (and/or opal-CT) as measured using the "Full Width at Half Maximum" (FWHM) statistic, opal-C (and/or opal-CT) has poorly-defined peaks at 31.50° and 28.49° 2θ, and a much more significant amorphous background.

[00108] If the (first) diffraction pattern is questionable with regard to whether opal-C (and/or opal-CT) and/or cristobalite is present, then according to the LH Method a second XRD analysis is performed to determine whether opal-C (and/or opal-CT) and/or cristobalite is present. This time the analysis is performed on, preferably, another representative portion of the sample spiked with cristobalite standard reference material (NIST 1879a). For example, a (representative) third portion of the sample is obtained and then spiked with cristobalite standard reference material (NIST 1879a) and XRD is performed on the third portion. The resulting (second) diffraction pattern from the XRD on the third portion is analyzed. Preferably, the third portion is milled prior to XRD. If the original sample (for example, the representative second portion of) comprises opal-C (and/or opal-CT), the cristobalite spike significantly modifies the diffraction pattern (from that of the second portion) with additional peaks identifiable at 22.02° and 36.17° 2θ, along with more prominent peaks at 31.50° and 28.49° 2θ seen in the (second) diffraction pattern of the third portion. If the original sample (more specifically, the second portion of) comprises cristobalite, then addition of the cristobalite spike (to the third portion) only results in increased peak intensity and no other significant change from the (first) diffraction pattern of the second portion (as seen in the (second) diffraction pattern of the third portion).

[00109] Quantifying the opal-C (and/or opal-CT) content of a diatomite sample can be complicated as its diffraction pattern is a combination of broad peaks and amorphous background, and diatomite products often contain other x-ray amorphous phases in addition to opal. According to the LH Method, an estimate of the quantity is obtained by treating the opal-C (and/or opal-CT) peaks (collectively, if both phases are present) of the first diffraction pattern as if they are cristobalite and quantifying against cristobalite standards such as NIST 1879a. This method of quantification of opal-C (and/or opal-CT), which we call the XRD Method, will usually underestimate the opal-C (and/or opal-CT) content but is effective for a number of purposes, such as manufacturing quality control. For clarity, this XRD Method is part of the umbrella LH Method. Alternatively (under the LH Method), a measure may be obtained by heating a representative portion of the sample (for example, a fourth portion) at very high temperature (e.g., 1050 °C) for an extended period (for example 24 to 48 hours) until that heated portion is fully dehydrated. This completely dehydrates opaline phases and forms cristobalite (reduces amorphous background component). XRD analysis is then performed on the fourth portion and the cristobalite in the resulting (third) diffraction pattern of the fourth portion can be quantified against the cristobalite standards to give an estimate of original opal-C (and/or opal-CT) content. Preferably, the fourth portion is milled prior to XRD. As long as additional flux is not added prior to heating the fourth portion, and the temperature kept below 1400 °C, any quartz present in the fourth portion will not be converted to cristobalite.

[00110] To obtain the total crystalline silica content wt% of the sample according to the LH Method, the weight percentage of the identified cristobalite (if any), the weight percentage of the quartz (if any) and the weight percentage of tridymite (if any) are added together to calculate the total weight percentage of the crystalline silica content in the sample. To obtain the weight percentage of quartz or tridymite found to be present during the analysis of the (first) diffraction pattern of the second portion of the sample, each of quartz or tridymite may be compared to its respective standard (for example, NIST SRM 1878b for quartz) for quantification of the content, or be quantified through the use of an internal standard (such as corundum) and applicable relative intensity ratios. If it is determined by the LH Method that cristobalite is present, the cristobalite seen in the (first) diffraction pattern of the second portion of the sample, may be compared to its respective standard (for example NIST 1879a) for quantification of the content, or be quantified through the use of an internal standard (such as corundum) and applicable relative intensity ratios. In the unusual case where there is both opal-C (or opal-CT) and cristobalite present and the primary peak of the opal-C (or opal-CT) cannot be differentiated or de-convoluted from that of cristobalite, the opal-C (or opal-CT) and cristobalite are quantified as one phase and reported as cristobalite. The quantity of cristobalite thus reported will be higher than the actual quantity in the sample. Because the sample is a representative sample of the product, the total weight percentage of the crystalline silica content in the sample is considered to accurately represent the total weight percentage of the crystalline silica content in the product from which the sample was taken.

[00111] All of the bulk powder XRD work detailed herein was performed using a Siemens® D5000 diffractometer controlled with MDI^{TM} Datascan5 software, with CuKα radiation, sample spinning, graphite monochromator, and scintillation detector. Power settings were at 50KV and 36mA, with step size at 0.04° and 4 seconds per step. JADE™ (2010) software was used for analyses of XRD scans. Sample preparation included SPEX® milling in zirconia vials with zirconia grinding media.

Permeability and Wet Bulk Density

[00112] Permeability and bulk density of diatomite filter media are determined using various established methods. These parameters are useful in characterizing how diatomite products perform in filtration applications. The samples described herein were analyzed for these properties using a Celatom Permeameter (U.S. Patent No. 5,878,374), which is an automated instrument that forms a "filter cake" from a diatomite sample of known mass and then measures all required parameters needed to calculate permeability and wet bulk density. The equations for calculating wet bulk density (WBD) and permeability are listed below:

[00113] Wet Bulk Density (g/ml) = $m / (h * A)$

[00114] Permeability (Darcy) = $(V * u * h) / (A * dP * t)$

Where:

A = cross-sectional area of the cake (cm^2)

dP = pressure drop across the cake (atm)

t = time of flow (s)

m = dry sample mass (g)

u = filtrate viscosity (cp)

V = filtrate volume (ml)

h = cake height (cm)

EBC Soluble Metals (Iron, Calcium, Aluminum, Arsenic)

[00115] The European Brewery Convention (EBC) has established a compendium of accepted test methods, including one designed to determine the soluble metal contribution of filter media to filtrate (i.e. beer). The EBC soluble metals test consists of suspending the sample (2.5% slurry concentration) for two hours at ambient temperature in a 1% solution of potassium hydrogen phthalate (pH of 4), filtering the suspension, and then analyzing the filtrate for metals content using AA or ICP spectrophotometers.

ASBC Iron

[00116] The American Society of Brewing Chemists (ASBC) also has established a set of test methods related to the manufacture of beer, and it includes one used to determine the soluble iron contribution to beer from filter media. This method is widely used in North America. The test calls for suspending the filter aid in de-gassed, room temperature beer (2.5% slurry concentration) for 6 minutes, filtering the suspension, and analyzing the filtrate for iron pickup using either a colorimetric method or atomic adsorption instrumental analysis.

Optical Properties

[00117] The optical properties of products may be characterized using the color space defined by the Commission Internationale de I'Eclairage (CIE), as the L*a*b* color space. The “L*” coordinate is a measure of reflected light intensity (0 to 100). The “a*” coordinate is the degree of redness (positive value) or greenness (negative value). The “b*” coordinate is the degree of yellowness (positive value) or blueness (negative value). A Konica Minolta® Chroma-meter CR-400 was used to measure the optical properties of samples described herein.

[00118] It has been observed that under the same calcining conditions (same flux amount and calcination temperature), flux-calcined products from diatomaceous ores of differing chemistry will have different color and brightness as expressed in terms of the L*a*b* color space. It has also been observed that the color of a flux-calcined product, especially the b* value inversely correlates well with the quantity of opal-C (and/or opal-CT) (as measured using the XRD Method) contained therein.

Respirable Cristobalite and Quartz

[00119] In order to address the issue of “how much respirable crystalline silica (RCS) is contained in a bulk material,” the IMA Metrology Working Group developed a standardized methodology called the SWeRF – Size-Weighted Respirable Fraction (since changed to SWeFF, or Size-Weighted Fine Fraction). This approach quantifies the content of respirable particles in a bulk product which, if inhaled when made airborne, might reach the alveoli. It takes into account the particle size distribution (PSD) fractions as defined in the CEN EN481 Standard of the European Committee for Standardization (which includes a particle density factor), and the crystalline silica content of these particles, and is called the Size-weighted Fine Fraction – crystalline silica (SWeFFcs). This methodology was used with regard to the sample results reported herein. Bulk sample XRD was performed on the minus 500 mesh (25*u*m) fraction of each sample to determine the crystalline silica content of the fine fraction. Particle size distribution of each original sample was determined using a Microtrac® S3500 (ultrasonic dispersion, particle Refractive Index (RI) of 1.48, fluid RI of 1.333, irregular particle shape, transparent particles). An average particle density of 1.15 was also used in the SWeFF calculations.

Crystalline Silica Contents of Natural, Straight-Calcined and Flux-Calcined Diatomite Products Comprising Physical Components Already in the Public Domain

[00120] Tables 1, 2 and 3 show the crystalline silica contents of a large number of natural, calcined and flux-calcined diatomite products, as reported in the crystalline silica data section of Safety Data Sheets (SDS) of EP Minerals, Imerys Filtration Minerals, Ceca, Dicalite Corp., and Showa Chemical. EP Minerals, Imerys Filtration Minerals, Ceca, Dicalite Corp. and Showa Chemicals are manufacturers of natural, calcined and flux-calcined diatomite products. “Celatom” is a trademark of EP Minerals. “Celite”, “Kenite”, and “Celpure” are trademarks of Imerys Filtration Minerals, “Clarcel” is a trademark of Ceca, “Radiolite” is a trademark of Showa Chemicals, and “Dicalite” is a trademark of Dicalite Corp. The table also shows the approximate permeability ranges of the diatomite products corresponding to the Silica Documentation.

[00121] As the tables show, the natural products, which are diatomite products that are processed thermally at temperatures sufficient to dry the material but low enough to prevent significant dehydration of the Opal-A component of the diatomite and also significant agglomeration of the diatomite, are available in permeability ranges of less than 0.01 to slightly over 0.1 darcy. Due to the lower processing temperatures, natural diatomite products have generally been reported as containing low or no measurable levels of crystalline silica, although some products contain up to about 4 wt% crystalline silica, generally in the form of quartz.

[00122] The tables also show that, based on Traditional Methods employed by the companies that supply the products listed therein, all commercial straight-calcined and flux-calcined diatomite products contain detectable levels of crystalline silica. The ranges of permeability and crystalline silica contents for these products are 0.01 to over 20 darcy and less than 5 wt% to over 90 wt% crystalline silica content.

[00123] Table 1. SDS Documentation and Permeability Range for Natural Diatomite Products Comprising Physical Components Already in the Public Domain

Producer	Product			Safety Data Sheet Information					
	Grades	Perm. Darcy	Made in	Quartz wt%	Crist. wt%	For	Doc.#	Rev.	Year
EP	Celatom MN-2, FN-1, FN-2, FN-6	0.01-0.12	US			US		9	2015
EP	Celatom MN-3, MN-4, MN-4HT, MN-23, LCS-3	n/a	US			US		9	2015
EP	Celatom MN-47, MN-51, MN-53, MN-74, MN-84, Drill-n-Dry™, Natural Crude Ore	n/a	US			US		9	2015
EP	Celatom MP77, MP78, MP79	n/a	US			US		9	2015
EP	Natural DE AFA	n/a	US			US		9	2015
Imerys	Celite for Concrete	n/a	Fernley, NV, US			US	2213	5	2015
Imerys	Diafil -all grades	n/a	Fernley, NV, US			US	2800	7	2015
Imerys	Celpure S25, C25, C25i	0.025	Lompoc, CA, US			US	3105	10	2015
Imerys	Celpure S65, C65, P65, NP, 65i	0.065	Lompoc, CA, US			US	3110	13	2015
Imerys	C206, C209, C209C, C230, C266, C266C, C292, C321, C392, C410, C441, C500, FC, Snow Floss, Snow Floss C, Celite for Concrete, Sil-O-Cel	n/a	Lompoc, CA, US	<4	<3	US, Asia	2200	12	2015
Imerys	Celite S, Kenite 100, Filter Cel,	n/a	Zacoalco, Mexico			US, Lat.	3225	5	2015

	Filter Cel LV					Am.			
Imerys	C209, C221, C221M, C221C, C280, C289, C400, C400A, C400D, C400TC, C490, C MNPP, Diactiv 21, Snow Floss	n/a	Zacoalco, Mexico			US, Lat. Am.	2209	10	2015
Imerys	CelTiX, CelTiX-P	n/a	Zacoalco, Mexico			US	2214	7	2015
Imerys	Diactiv 17, Diactiv 117, Diactiv 18C, Diactiv 18D, Ultrafiltracion	n/a	Arica, Chile	<1	<1	Lat. Am.	3520	6	2010
Dicalite	Dicalite 104, 143, 153, 183, BP3, BP5, BP8, CC1, CA3, SA3, D4A, D4C, D4R, IG3, IG33.	n/a	US	<3	<5	Europe	0011	3	2003
Dicalite	Dicalite 104, 183, BP-3, BP-5, CA-3, CA-5, D4A, D4C, D4R, D4AFA, 677, 677S, SA3	n/a	US	<2			002	0	2014

[00124] Table 2. SDS Documentation and Permeability Range for Calcined Diatomite Products Comprising Physical Components Already in the Public Domain

Producer	Product			Safety Data Sheet Information					
	Grades	Perm. Darcy	Made in	Quartz wt%	Crist. wt%	For	Doc.#	Rev.	Year
EP	Celatom® FP-1, FP-2, FP-22	0.01-0.15	US		<5	US		14	2014
EP	Celatom® FP-3, FP-4, FP-6, FP-12	0.14-1.2	US		10-40	US		13	2014
Imerys	Celpure S100, C100, P100	0.1	Lompoc, CA, US	<1	<10	US	3113	8	2015
Imerys	Celpure S300, C300, P300	0.3	Lompoc, CA, US	<1	<15	US	3115	12	2015
Imerys	C350, C507	<0.02	Lompoc, CA, US	<3	<35	US, Asia	2303	2	2015
Imerys	C577, C577 NF, Filter Cell, Filter Cell NF, Celite BPP	0.1 - 0.2	Lompoc, CA, US	<3.5	<5.5	US, Asia	2320	8	2015
Imerys	Std Super Cel, SSC, Std Super Cel BP	0.2 - 0.3	Lompoc, CA, US	<3	<20	US, Asia	2310	6	2015
Imerys	C3Z, C201, C270, C271, C350, C505, C507, C512, C512 Z, C520, Hyflo PZ, CR, X-3	<0.9	Lompoc, CA, US	<3	<35	US, Asia	2300	11	2015
Imerys	C315, C350, C505, C512, C512Z, C520, C520-CB, C577, Celite CM-7, Kenite 101, Kenite 200, Filter Cel M, Diactiv 14, Standard Super Cel	<0.45	Zacoalco, Mexico	<1	<53	US, Lat. Am.	3230	12	2015
Dicalite	PS, Dicalite 215, Superaid, UF, SA-UF, Speedflow, 231	<0.5	US	<5	<20		005	0	2014
Ceca	Clarcel CBL	0.025-	France	<20	<20		893169	2.01	2003

		0.05					01		
Ceca	Clarcel CBR	0.08-0.2	France	<20	<60		89346901	2.02	2005

[00125] Table 3. SDS Documentation and Permeability Range for Flux-Calcined Products Comprising Physical Components Already in the Public Domain

Producer	Product			Safety Data Sheet Information					
	Grades	Darcy	Location	Quartz wt%	Crist. wt%	For	Doc. #	Rev.	Year
EP	Celatom® FW-6,FW-12, FW-14, FW-18, FW-20, FW-40, FW-50, FW-60, FW-70, FW-80, SP	0.4-7.5	US		35-50	US		12	2014
EP	Celatom® MW-25, MW-27, MW-31, Celabrite®, Celabloc®	n/a	US		40-70	US		13	2014
Imerys	Celpure S1000, C1000, P1000	1	Lompoc, CA, US	<1	<85	US	3125	11	2015
Imerys	C110, C224, C226, C319, C501, C513, C522, FA for cooking oil, C HSC, Hyflo, HSC, X-4, X-5	<1.3	Lompoc, CA, US	<4	<40	US, Asia	2400	12	2015
Imerys	Aqual-Cel, C269, C503, C535, C545, C560, C566, C578P, C580, X-6, X-7	<25	Lompoc, CA, US	<4	<50	US, Asia	2410	8	2015
Imerys	C219, C233, C263, C281, C388, C427A, C499, SFSF, SF, White Mist, CWPP8	n/a	Lompoc, CA, US	<2.5	<70	US, Asia	2420	8	2015
Imerys	C281, C535, C545, C555, C555R, C580, CPC, K300, K700, K1000, K2500, K3000, K5200, K5500, K5800, K7.5, Hyflo, Swimming Pools, X-4, X-5,	<25	Quincy, WA, US	<1	<60	US, Asia	3040	15	2015

	X-6, X-7								
Imerys	Micro-Ken 118, 140, 800, 801, 805, 811, 900	n/a	Quincy, WA, US	<1	<93	US, Asia	3045	3	2015
Imerys	C281, C281D, C281 USA, C499, Super Floss, Super Floss MX, Super Floss Q	n/a	Zacoalco, Mexico	<1	<77	US, Lat. Am.	3242	4	2015
Imerys	C281, C499, C501, C501-F, C503, C508, C535, C545, Diactiv 12, Diactive 34, Hyflo AN, Hyflo Z, Hyflo ZS, Hyflo SC, Kenite 700, Kenite 300	<1.1	Zacoalco, Mexico	<1	<77	US, Lat. Am.	3240	16	2015
Imerys	C110, C281, C281-A, C281-M, C388, C427, C501, C501-A, C503, C508, C513, C535, C535-QM, C545, C545-D, Celite BP-1, Celite FCFA, Celite SW, Diactiv 34, Hyflo AN, Hyflo Z, Hyflo ZS, Hyflo Super Cel, Kenite 700, Kenite 1000, Kenite 2500, Kenite 3000, Super Floss, Super Floss-P, Super Floss-MX, Super Floss-Q, QP-HSC,C564	<4	Arica, Chile	<1	<77	Lat. Am.	3580	2	2010
Imerys	C503, C520A, C535, C545, Diactiv 7, Diactiv	<4	Arica, Chile	<1	<67	Lat. Am.	3540	6	2009

	8, Diactiv 9, Diactiv 10, Diactiv 11, Diactiv 12, Diactiv 13, Diactiv 14, Diactiv 14F, Diactiv 15F, Hyflo Super Cel, QS								
Imerys	Diactiv 16, Microfiltrcion		Arica, Chile	<1	<51	Lat. Am.	3560	6	2010
Dicalite	Dicalite 341, Speedplus, 375, Speedex, 2500, Swimpool, 4200, 4500, 4500C, 5000, 6000, 7000, WB-6, WB-6A	<12	US	<5	<70		001	0	2014
Ceca	Clarcel DIC, DICB, DICH, DIFB, DIFBO, DIFD, DIFN, DIFR, FD		France		65		891 509-001	2.1	2011
Showa	Radiolite #600, 700, 900, 900S, 1100, Ace II, F, Deluxe W-50		Japan, China	Amorphous silica may crystalize			SW-1		2011

[00126] As can be seen in Tables 1, 2 and 3, it is a common practice in the industry for companies to report ranges of the crystalline silica content in their Safety Data Sheets. These ranges are sometimes expressed as "less than" a certain level of content. When this reporting format is used, it indicates that the product(s) contain detectable levels of either quartz or cristobalite, as the case may be, up to the numerical amount indicated. When there is no quartz or cristobalite present, the suppliers do not report a range for the level of content.

[00127] While the reporting methods, if understood, indicate which commercial products contain, based on the Traditional Methods, measureable amounts of quartz or cristobalite, the reporting methods do not provide a clear indication of the average or typical crystalline silica contents of these products. As a result, the inventors have included actual measurements of selected products in Table 4 (measured using the Traditional Methods).

[00128] Table 4 shows the permeabilities and crystalline silica contents (as determined using Traditional Methods) of a number of commercial diatomite products comprising physical components already in the public domain, as characterized in EP Minerals' Research and Development laboratories. The data in this table are consistent with the data of Tables 1, 2 and 3, and show that diatomite products characterized using traditional X-ray Diffraction techniques for crystalline silica content with permeabilities between 0.03 and 10 darcy all contain levels of crystalline silica above the detection limit, with the lowest percentage content of crystalline silica at a level of 0.1 wt% and the highest above 80 wt%. This table also shows that, when measured by using Traditional Methods, all straight-calcined and flux-calcined products contain measurable levels of crystalline silica and that some natural diatomite products do not contain measurable levels of crystalline silica.

[00129] **Table 4. Estimates of Quartz and Cristobalite Contents Prepared through Traditional Methods for Commercial Diatomite Products Comprising Physical Components Already in the Public Domain**

Product	Sample ID	Permeability (Darcy)	Quartz (wt%)	Cristobalite (wt%)

Ceca Clarcel 78	23139	0.02	0.8	0.0
Imerys Celite S	20633	0.03	0.2	0.0
Ceca Clarcel Dif N	17956	n/a	0.0	80.4
EP Minerals FN-2	25037	0.06	0.1	0.0
EP Minerals MN-4	25061	0.01	0.0	0.0
Dicalite Superaid	19918	0.05	0.7	3.9
Ceca CBL	22602	0.06	11.0	15.0
Ceca CBL-3	22603	0.03	3.0	7.0
Ceca Clarcel CBR	3234	0.14	8.1	n/a
Imerys Celite 505	19154	0.04	0.7	4.2
Imerys Celite 512	24081	0.43	3.0	12.0
Imerys Celite 512	21881	0.79	11.4	25.2
Imerys Celite Std. Supercel	27115	0.20	4.4	4.7
Imerys Celite 577	27116	0.10	1.9	3.3
Showa Radiolite 200	27117	0.10	2.1	7.9
Showa Radiolite 300	27118	0.20	3.5	14.7
Imerys Cynergy 200	27121	0.20	2.1	3.4
EP Minerals FP-2	B12C0	0.20	0.0	16.0
EP Minerals FP-3	B17E2	0.24	0.0	18.6
EP Minerals FP-4	2H11B4	0.37	0.0	38.1
EP Minerals FP-6	2B11F1	0.70	0.0	71.1
Imerys Celite 501	18362	1.50	0.0	74.0
EP Minerals FW-6	1D17B14	0.72	0.0	17.7
EP Minerals FW-14	2E16I14	1.55	0.0	41.2
Imerys Celite 501	18362	1.50	0.0	45.9
Imerys Celite 508	22813	1.00	0.0	64.0
Imerys Celite Hyflo	22814	1.40	0.0	55.0
Imerys Celite 535	22800	2.80	0.0	58.0
Imerys Celite 545	27113	3.50	1.5	35.4
Chuo H-600	21196	2.60	3.0	23.0
Dicalite Speedex	21164	3.20	0.0	68.7
Dicalite Speedflow	19917	1.72	0.0	80.8
Dicalite 4500	24541	7.30	0.0	50.8
[1]Showa Radiolite 500	21195	1.60	3.0	18.8
Showa Radiolite 700	27119	2.20	1.2	50.5
[1]Showa Radiolite 800	15291	1.11	1.3	10.1
Showa Radiolite 900S	27120	4.10	1.9	35.6
Showa Radiolite 1100	24340	4.50	1.2	58.0
EP Minerals FW-80	E19A1XR	9.89	0.0	47.9
Ceca Clarcel AK Starch	25084	9.40	0.0	38.7
Ceca Clarcel DIF BO	19894	0.90	0.1	41.0

Imerys Celite Superfloss	19638	n/a	0.0	85.2
Imerys Celite 281	19559	n/a	0.1	42.2
Imerys Kenite 2500	21838	5.27	0.0	45.2

[1] Showa Radiolite 500 and 800 are straight-calcined products.

[00130] Some straight-calcined and flux-calcined products, when analyzed by Traditional Methods have been reported to contain very low or non-detectable levels of crystalline silica. These products have been reported in the patent literature, but have not to date been commercialized. See for, example, U.S. Patent No. 8,084,392 (Lenz, et al), U.S. Patent No. 5,179,062 (Dufour), and U.S. Patent No. 9,095,842 (Nannini et al).

Examples

Example 1 – Products Comprising Physical Components in the Public Domain and Novel Silica Documentation

[00131] Table 5 shows the results of using the LH Method for differentiating opal-C from cristobalite on the samples listed in Table 4. Almost half of the samples have been re-classified from comprising cristobalite to comprising opal-C. However only a few of these are completely free of crystalline silica as quartz is still present in the majority. Still, through use of the LH Method, the Silica Documentation associated with these would be revised to reflect the absence of cristobalite and a reduced or non-detectable level of crystalline silica.

[00132] Table 5. Products Comprising Physical Components in the Public Domain and Novel Silica Documentation

Product	Sample ID	Opal-C(wt%)[1]	Quartz (wt%)	Cristobalite (wt%)
Ceca Clarcel 78	23139	0.0	0.8	0.0
Imerys Celite S	20633	0.0	0.2	0.0
Ceca Clarcel Dif N	17956	0.0	0.0	80.4
EP Minerals FN-2	25037	0.0	0.1	0.0
EP Minerals MN-4	25061	0.0	0.0	0.0
Dicalite Superaid	19918	3.9	0.7	0.0
Ceca CBL	22602	13.9	11.0	0.0
Ceca CBL-3	22603	6.6	3.0	0.0
Ceca Clarcel CBR	3234	0.0	8.1	22.9
Imerys Celite 505	19154	4.2	0.7	0.0
Imerys Celite 512	24081	12.0	3.0	0.0
Imerys Celite 512	21881	0.0	11.4	25.2
Imerys Celite Std. Supercel	27115	3.6	4.4	0.0
Imerys Celite 577	27116	1.3	1.9	0.0
Showa Radiolite 200	27117	5.6	2.1	0.0
Showa Radiolite 300	27118	11.3	3.5	0.0
Imerys Cynergy 200	27121	2.1	2.1	0.0
EP Minerals FP-2	B12C0	16.0	0.0	0.0
EP Minerals FP-3	B17E2	18.6	0.0	0.0
EP Minerals FP-4	2H11B4	38.1	0.0	0.0
EP Minerals FP-6	2B11F1	0.0	0.0	71.1
Imerys Celite 501	18362	0.0	0.0	58.0
EP Minerals FW-6	1D17B14	17.7	0.0	0.0
EP Minerals FW-14	2E16I14	0.0	0.0	41.2
Imerys Celite 501	18362	0.0	0.0	45.9
Imerys Celite 508	22813	0.0	0.0	64.0
Imerys Celite Hyflo	22814	0.0	0.0	55.0
Imerys Celite 535	22800	0.0	0.0	58.0
Imerys Celite 545	27113	0.0	1.5	35.4
Chuo H-600	21196	0.0	3.0	23.0
Dicalite Speedex	21164	0.0	0.0	68.7
Dicalite Speedflow	19917	0.0	0.0	80.8
Dicalite 4500	24541	0.0	0.0	50.8
[2]Showa Radiolite 500	21195	18.8	3.0	0.0

Showa Radiolite 700	27119	0.0	1.2	50.5
[2]Showa Radiolite 800	15291	10.1	1.3	0.0
Showa Radiolite 900S	27120	0.0	1.9	35.6
Showa Radiolite 1100	24340	0.0	1.2	58.0
EP Minerals FW-80	E19A1XR	0.0	0.0	47.9
Ceca AK Starch	25084	0.0	0.0	38.7
Ceca Clarcel DIF BO	19894	0.0	0.1	41.0
Imerys Celite Superfloss	19638	0.0	0.0	85.2
Imerys Celite 281	19559	0.0	0.1	42.2
Imerys Kenite 2500	21838	0.0	0.0	45.2

[1] Opal-C quantification is based on the XRD Method

[2] Showa Radiolite 500 and 800 are straight-calcined products

[00133] FIGS. 1 through 4 are X-ray Diffraction patterns of four of the samples listed in Table 5 with the standard stick pattern of low cristobalite super-imposed. FIG. 1 shows the pattern for a sample of Celite 501. This flux-calcined filter aid comprises cristobalite but does not contain either quartz or opal-C. The current SDS accurately reflects this information. FIG. 2 shows the XRD pattern for a sample of FP-4, a straight-calcined filter aid. Reference number 10 identifies the primary peak and reference number 12 identifies the secondary peak on the FIGS. This sample was found to comprise opal-C along with minor amounts of feldspars and possibly hematite. The Silica Documentation for this product should be modified to reflect the lack of cristobalite. FIG. 3 is the diffraction pattern of another straight-calcined filter aid, FP-6. In this case, the principal crystalline phase is cristobalite and no change needs to be made to the SDS. FIG. 4 is the diffraction pattern of Dicalite 4500, a flux-calcined filter aid. This sample also comprises cristobalite, and the current SDS reflects this.

[00134] Tables 6 and 7 present physical and chemical data obtained on many of the samples listed in table 5.

[00135] Table 6: Physical and Chemical Data for Selected Diatomite Products Comprising Physical Components in the Public Domain

Sample	FP-2 B12C0	FP-3 B17E2	FW-6 1D17B14	FW-14 2E16I14	Radiolite 800	Celabrite 2A20A13F
Type	Straight-calcined	Straight-calcined	Flux-calcined	Flux-calcined	Straight-calcined	Flux-calcined
Total Chemistry (XRF expressed as oxides)						
SiO_2 (wt%)	94.3	94.5	90.8	91.2	85.6	94.5
Al_2O_3 (wt%)	2.5	2.4	2.9	2.7	7.9	1.6
CaO (wt%)	0.6	0.6	0.4	0.7	1.0	0.4
MgO (wt%)	0.3	0.2	0.2	0.3	0.4	0.2
Na_2O (wt%)	0.4	0.4	3.8	3.1	1.6	2.1
K_2O (wt%)	0.2	0.3	0.3	0.3	0.7	0.1
Fe_2O_3 (wt%)	1.5	1.4	1.4	1.6	2.5	0.9
TiO_2 (wt%)	0.1	0.1	0.1	0.1	0.2	0.1
Permeability (darcy)	0.20	0.24	0.72	1.55	1.11	
Wet Bulk Density (g/ml)	0.37	0.36	0.32	0.33	0.33	
EBC Soluble Metals						
Fe (ppm)					75	
As (ppm)	3.3	3.2	5.8	1.3	1.2	
Loss on Ignition (wt%)	0.2	0.2	0.1	0.1	0.2	< 0.1
Opal-C/Cristobalite Analysis						
Primary Peak centroid(Å)	4.09	4.08	4.08	4.07	4.08	4.06
FWHM ($^\circ 2\theta$)	0.35	0.34	0.44	0.33	0.41	0.30
Peaks between 10° – $37^\circ 2\theta$	2 of 4	2 of 4	2 of 4	4 of 4	3 of 4	4 of 4
Opal-C (wt%)[1]	16.0%	18.6%	17.7%	0.0%	10.1%	0.0%
Cristobalite (wt%)	0.0%	0.0%	0.0%	41.2%	0.0%	56.8%
Quartz (wt%)	0.0%	0.0%	0.0%	0.0%	1.3%	0.0%

[1] Opal-C quantification is based on the XRD Method

Note: FP-2, FP-3, FW-6, FW-14 and Celabrite are products of EP Minerals LLC; Radiolite 800 is a product of Showa Chemical.

[00136] Table 7: Physical and Chemical Data for Additional Selected Diatomite Products Comprising Physical Components in the Public Domain

Sample	Dicalite 4500	Kenite 2500	Celite 512	Celite Std. Supercel	FP-6 2B11F1
Type	Flux-calcined	Flux-calcined	Straight-calcined	Straight-calcined	Straight-calcined
Total Chemistry (XRF expressed as oxides)					
SiO_2 (wt%)	91.7	90.1	90.0	89.0	91.9
Al_2O_3 (wt%)	2.3	2.0	5.0	5.4	4.7
CaO (wt%)	0.2	3.4	0.5	0.6	0.5
MgO (wt%)	0.1	0.3	0.7	0.9	0.3
Na_2O (wt%)	4.4	2.3	0.7	0.7	0.2
K_2O (wt%)	0.1	0.4	0.7	0.9	0.1
Fe_2O_3 (wt%)	0.9	0.9	1.6	1.9	2.0
TiO_2 (wt%)	0.1	0.1	0.2	0.3	0.3
Permeability (darcy)	7.30	5.27	0.30	0.25	0.70
Wet Bulk Density (g/ml)	0.31	0.36	0.40	0.33	0.42
EBC Soluble Metals					
Fe (ppm)	34	35	146	73	
As (ppm)	0.5	0.5	2.3	6.4	1.0
Loss on Ignition (wt%)	< 0.1	0.5	0.4	0.2	0.1
Opal-C/Cristobalite Analysis					
Primary Peak centroid(Å)	4.06	4.06	4.07	4.08	4.06
FWHM ($^{\circ}$ 2θ)	0.32	0.31	0.37	0.44	0.31
Peaks between 10° – 37° 2θ	4 of 4	4 of 4	3 of 4	2 of 4	4 of 4
Opal-C (wt%)[1]	0.0%	0.0%	13.4%	1.3%	0.0%
Cristobalite (wt%)	52.1%	39.2%	0.0%	0.0%	71.1%
Quartz (wt%)	0.0%	0.0%	3.1%	3.5%	0.0%

[1] Opal-C quantification is based on the XRD Method

Note: Dicalite 4500 is a product of Dicalite Minerals; Kenite 2500, Celite 512 and Celite Standard Super-Cel are products of Imerys Filtration Minerals; FP-6 is a product of EP Minerals LLC.

[00137] FIG. 5 shows the XRD pattern of sample FP-2 (B12C0) (see Tables 4, 5, and 6) with the standard stick pattern of α-cristobalite super-imposed. As can be seen, the FP-2 primary peak (reference no. 10 on FIG. 5) and secondary peak (reference no. 12 on FIG. 5) are offset (higher d-spacing) and the peaks at 31.50° and 28.49° 2θ are very poorly developed. These factors along with a relatively broad FWHM indicate that the silica phase represented is opal-C. Minor peaks attributable to feldspars are also evident.

[00138] FIG. 6 shows the XRD pattern of the “Celabrite 2A20A13F” sample with the standard stick pattern of α-cristobalite super-imposed. This product is a flux-calcined fine filler, and the XRD pattern matches that of “standard” cristobalite fairly well.

[00139] FIGS. 7 and 8 show XRD patterns of sample “FP-3 B17E2” before and after spike addition of cristobalite standard. FIG. 8 is an enlarged view of the primary peaks in the XRD patterns for sample “FP-3 B17E2.” The standard stick pattern of α-cristobalite is super-imposed in FIGS. 7 – 8. As compared to the XRD pattern of the non-spiked sample, the cristobalite spike resulted in a well-defined secondary peak (see reference number 12), well-defined tertiary peaks (see reference number 14) at 31.50° and 28.49° 2θ and a visible “hump” on the shoulder of the primary peak (see reference number 10). This is fairly clear evidence that the original sample comprises opal-C and not cristobalite.

Examples 2 through 6: Flux-calcined Diatomite Products Comprising Novel Physical Components and Novel Silica Documentation

[00140] A number of samples of opaline flux-calcined biogenic silica products have been prepared in the EP Minerals Research and Development laboratory from selected ores of unusual chemical composition. While there is evidence that opal-C and not cristobalite can form from standard ores when flux-calcined at relatively low temperatures (i.e. FW-6 1D17B14), that is not usually the case with flux-calcined products. However with these selected ores, opal-C (and/or opal-CT) forms even when flux-calcined at high temperatures, for example 920°C to 1150°C. Without being bound by theory, it is theorized that unusually high levels of finely-divided aluminum and iron compounds in these ores inhibit the formation of cristobalite during flux-calcination, although other factors could also be of influence. Table 8 presents information regarding processing conditions, physical and chemical characteristics, and silica phase determination for several opaline flux-calcined biogenic silica products.

Table 8: Five Examples of Novel Flux-calcined Diatomite Products

Sample	18184-3	18188-2	18188-4	18188-7	18188-9
Type	Flux-calcined	Flux-calcined	Flux-calcined	Flux-calcined	Flux-calcined
Soda Ash Addition level (wt%)	2.0	2.0	2.0	5.0	8.0
Calcination Temperature (°C)	1038	954	1038	1104	1104
Calcination Time (min.)	40	40	40	40	40
Total Chemistry (XRF expressed as oxides)					
SiO_2 (wt%)	88.7	87.3	87.8	87.7	86.4

Al_2O_3 (wt%)	5.6	6.9	6.5	5.4	5.3
CaO (wt%)	0.6	0.6	0.6	0.6	0.6
MgO (wt%)	0.3	0.4	0.4	0.3	0.3
Na_2O (wt%)	1.4	1.5	1.5	2.6	4.0
K_2O (wt%)	0.2	0.2	0.2	0.2	0.2
Fe_2O_3 (wt%)	2.8	2.7	2.8	2.8	2.8
TiO_2 (wt%)	0.3	0.4	0.4	0.4	0.4
Permeability (darcy)	1.27	1.16	1.66	4.43	8.91
Wet Bulk Density (g/ml)	0.28	0.29	0.28	0.28	0.26
EBC Soluble Metals					
Fe (ppm)	31	39	23	29	45
Ca (ppm)	54	90	43	39	41
Al (ppm)	69	116	54	29	21
As (ppm)	1.4	0.3	0.6	0.4	0.2
ASBC Beer Soluble Iron (ppm)	13		14		
Loss on Ignition (wt%)	0.2	0.5	0.3	0.1	0.1
Opal-C/Cristobalite Analysis					
Primary Peak centroid(Å)	4.08	4.08	4.10	4.08	4.07
FWHM (° 2θ)	0.39	0.43	0.39	0.46	0.50
Peaks between 10° – 37° 2θ	2 of 4	2 of 4	2 of 4	2 of 4	3 of 4
Opal-C (wt%)[1]	10.9%	2.6%	9.0%	16.1%	22.4%
Cristobalite (wt%)	0.0%	0.0%	0.0%	0.0%	0.0%
Quartz (wt%)	0.0%	0.0%	0.0%	0.0%	0.0%

[1] Opal-C quantification is based on XRD Method

[00141] All of the samples listed in Table 8 were prepared from crude ore by the following steps: drying at 120 °C for 24 hours; crushing (jaw crusher) to minus 1.25cm; milling (with a hammer-mill) until 99% passes 70 mesh (210 *u*m); classifying using a Federal Equipment Company cyclonic classifier with coarse fraction discarded (average of 10%); soda ash addition and mixing using a paint shaker; calcination in a muffle furnace in ceramic crucibles; and sieving at 70 mesh with overs brushed through the sieve.

[00142] FIG. 9 shows the XRD pattern of sample 18188-4 with and without a 5 wt% cristobalite spike. The standard stick pattern of α-cristobalite is super-imposed in FIG. 9. As can be seen in FIG. 9, the cristobalite spike is easily distinguished from the original opal-C phase through use of the LH Method. This presents solid proof that the identification of the opal-C phase is correct when the LH Method is used. There would not be the need to include warnings about crystalline silica in the Silica Documentation for these five flux-calcined products, even though analysis using Traditional Methods and traditional interpretation of XRD patterns would indicate that all of these samples would have been considered to comprise cristobalite at roughly the same percentages as are listed for opal-C and, as such, crystalline silica warnings would be needed. As a result, both the compositions of these products and their Silica Documentation are novel.

[00143] FIG. 10 is the X-ray diffraction pattern of sample 18188-9 overlaying the same sample with a 15 wt% cristobalite spike. The standard stick pattern of α-cristobalite is super-imposed in FIG. 10. While the cristobalite primary peak (10b) in this case still overlaps the opal-C primary peak (10a), the addition of the spike shows a significant change in the pattern and not just an increase in intensity. FIG. 11 is an enlarged view of the same diffraction pattern but centered only on the primary peak area.

[00144] Splits of samples 18184-3 and 18188-4 were subjected to post-calcination hydration treatments to reduce beer soluble iron as measured via the ASBC protocol. The hydration treatment consisted of adding 6% deionized water to each sample, heating at 90°C for 5 hours in a sealed container, and then drying at 105°C in an open container to remove any remaining free moisture. ASBC beer soluble iron was reduced from 13ppm to 7ppm in sample 18184-3, and from 14ppm to 4ppm in sample 18188-4.

Example 7 Flux-Calcined Diatomite Product Comprising Novel Physical Component and Novel Silica Documentation

[00145] A diatomite ore (S31 15-4-7B 35-40) was hammer milled, dried and classified using the Federal Equipment Company cyclonic classifier to obtain two size fractions. The coarse fraction had a mass yield of 27% and a particle size distribution of d10 = 30, d50 = 73 and d90 = 141 micrometers. A high permeability product was made from the coarse fraction by mixing with 7 wt% soda ash as the fluxing agent, calcining in a muffle furnace at 1038 °C for 40 minutes and brushing through a 70 mesh screen for dispersion. The product had 30.5 darcy permeability and 0.33 g/ml wet bulk density. FIG. 12 shows the XRD diffraction pattern for this sample. The standard stick pattern of α-cristobalite is super-imposed in FIG. 12. The primary peak (10) offset, FWHM, and lack of developed tertiary peaks 31.50° and 28.49° 2θ indicate that the phase present is opal-C. The relative quantity of opal-C, calculated using the XRD Method, is 31.3 wt%. Once again, through use of the LH Method, the correct Silica Documentation would show that the crystalline silica content of the product is non-detectable, whereas traditional Silica Documentation comprising data developed through Traditional Methods would improperly show that the sample contains about 31 wt% crystalline silica.

Example 8 Flux-Calcined Diatomite Product Comprising Novel Physical Component and Novel Silica Documentation

[00146] A sample of ore from another deposit (SIS B-7) was dried, crushed, hammer-milled, then sieved at 80 mesh (177*u*m). Soda ash (5% by weight) was blended with the minus 80 mesh portion, and the mixture calcined in an electric muffle furnace at 927 °C for 40 minutes. Table 9 presents the data on the resultant product. In this case, the Silica Documentation when prepared with information developed from the LH Method would show 0.1 wt% as quartz, but Silica Documentation when prepared using Traditional Methods would show about 3 wt% combined quartz and cristobalite.

Table 9: Example 8 - Product Data on Sample SIS B-7

Total Chemistry (XRF expressed as oxides)	
SiO_2 (wt%)	85.7
Al_2O_3 (wt%)	6.2
CaO (wt%)	0.9
MgO (wt%)	1.0
Na_2O (wt%)	2.7
K_2O (wt%)	0.2
Fe_2O_3 (wt%)	2.6
TiO_2 (wt%)	0.4
Permeability (darcy)	2.61
Wet Bulk Density (g/ml)	0.26
EBC Soluble Metals	
Fe (ppm)	53
Ca (ppm)	903
Al (ppm)	59
As (ppm)	2.2
Loss on Ignition (%)	0.4
Opal-C/Cristobalite Analysis	
Primary Peak centroid (Å)	4.08
FWHM ($^{\circ}$ 2^{θ})	0.45

Peaks between $10^{\circ} - 37^{\circ}$ 2θ	1 of 4
Opal-C (wt%)[1]	2.8
Cristobalite (wt%)	0.0
Quartz (wt%)	0.1

[1] Opal-C quantification is based on XRD Method

Examples 9 through 13: Flux-Calcined Diatomite Products Comprising Novel Physical Components and Novel Silica Documentation

[00147] Table 10 presents information regarding processing conditions, physical and chemical characteristics, and silica phase determination for several more flux-calcined and one straight-calcined diatomite products produced in the lab, and not yet commercially available. Most, but not all of these comprise opal-C. Processing conditions include flux composition, flux quantity, calcination or sintering temperature, calcination time, sintering time or the like. All of the samples listed in Table 10 were prepared from different crude ores by the following steps:

drying at 120 °C for 24 hours;

crushing (jaw crusher) to minus 1.25cm;

milling (hammer-mill) until 99% passes 70 mesh (210 *u*m);

classifying using Federal Equipment Company cyclonic classifier with coarse fraction discarded (typically 10%);

soda ash addition and mixing using a paint shaker;

calcination in muffle furnace in ceramic crucibles; and

sieving at 70 mesh with overs brushed through the sieve.

Table 10: Five Additional Examples of Novel Diatomite Products.

Sample	**9** HV2BH-E	**10** HV2-F	**11** S3115-C	**12** S3115-E	**13** LCS3-H
Type	Flux-calcined	Flux-calcined	Straight-Calcined	Flux-calcined	Flux-calcined
Soda Ash Addition level (wt%)	3.0	3.0	0.0	3.0	7.0
Calcination Temperature (^{O}C)	1020	1140	1140	1020	1020
Calcination Time (min.)	40	40	40	40	40
Total Chemistry (XRF expressed as oxides)					
SiO_2 (wt%)	84.7	85.6	82.6	80.7	88.3
Al_2O_3 (wt%)	6.5	6.6	8.3	8.2	3.3
CaO (wt%)	0.8	0.8	2.3	2.3	0.9
MgO (wt%)	0.4	0.4	0.7	0.8	0.3
Na_2O (wt%)	2.3	2.1	0.7	2.3	4.2
K_2O (wt%)	0.2	0.2	0.3	0.3	0.4
Fe_2O_3 (wt%)	2.9	3.2	4.2	4.2	1.8
TiO_2 (wt%)	0.4	0.4	0.6	0.6	0.1
Permeability (darcy)	0.86	4.09	0.77	1.26	2.42
Wet Bulk Density (g/ml)	0.30	0.28	0.47	0.44	0.32
EBC Soluble Metals					
Fe (ppm)	36	36	49	29	76
Ca (ppm)	152	95	460	541	253
Al (ppm)	70	72	152	64	25
As (ppm)	3.3	3.9	9.3	6.4	6.2
Loss on Ignition (wt%)	1.8	0.6	0.1	0.5	0.3
Opal-C/Cristobalite Analysis					
Primary Peak centroid(Å)	4.09	4.09	4.09	4.09	4.06
FWHM (^{O} 2$^{\theta}$)	0.42	0.38	0.46	0.42	0.44
Peaks between 10^{O} – 37^{O} 2 $^{\theta}$	2 of 4	3 of 4	3 of 4	2 of 4	4 of 4
Opal-C (wt%)[1]	8.5%	27.1%	23.8%	7.6%	0.0%

Cristobalite (wt%)	0.0%	0.0%	0.0%	0.0%	46.7%
Quartz (wt%)	0.1%	0.0%	0.0%	0.5%	0.0%

[1] Opal-C quantification is based on XRD Method

[00148] FIG. 13 shows the diffraction pattern of sample HV2BH-E (Table 10) with a 5 wt% cristobalite spike added. The standard stick pattern of α-cristobalite is super-imposed in FIG. 13. Once again, the primary peak (10a) of opal-C is easily distinguished from the primary peak (10b) of cristobalite. FIG. 14 shows a similar pattern for sample HV2-F. Both of these samples also comprise minor quantities of feldspar and possible hematite. FIG. 15 presents the diffraction pattern of sample S3115-E with a 5 wt% cristobalite spike and the standard stick pattern of α-cristobalite super-imposed. This sample also comprises significant feldspars, 0.5 wt% quartz, and other crystalline phases, but contains no cristobalite. FIG. 16 shows the XRD pattern of sample LCS3-H, spiked with 28 wt% cristobalite spike and the standard stick pattern of α-cristobalite super-imposed. In this case, the added cristobalite primary peak (10b) is not distinguishable from the original primary peak (10). Thus it is most likely that the original sample comprises cristobalite, albeit somewhat poorly-ordered. This sample contains a relatively low percentage of aluminum and iron. When characterized using the LH Method, the Silica Documentation for the first four samples would show non-detectable levels of cristobalite, but two of the four would show low levels of quartz (0.1 wt% and 0.5 wt% respectively). When characterized using Traditional Methods, the Silica Documentation of the first four samples would show 9 wt%, 27 wt%, 24 wt%, and 8wt% total crystalline silica, respectively. Example 13 (LCS3-H) when characterized by either the LH Method or Traditional Methods would show about 47 wt% cristobalite before addition of the spike.

Examples 14 through 18: Flux-Calcined Diatomite Products Comprising Novel Physical Components and Novel Silica Documentation

[00149] Table 11 contains data related to samples collected from a production-scale trial conducted in December, 2015 in EP Minerals' Vale, Oregon facility. All samples were flux-calcined with soda ash. Example 14 is a sample of a finished product from the production-scale trial. Examples 15 and 16 are samples of kiln discharge that were classified in the laboratory. Examples 17 and 18 are samples of kiln feed that were flux-calcined in the laboratory under controlled conditions.

[00150] **Table 11: Sample Data from Plant Trial, December 2015**

Sample	**14** FEBH 15:15	**15** KD 11:30	**16** KD 15:30	**17** 2-31 10:15	**18** 2-31 13:15
Type	Flux-calcined	Flux-calcined	Flux-calcined	Flux-calcined	Flux-calcined
Calcination Temperature (^{O}C)	n/a	n/a	n/a	927	1020
Calcination Time (min.)	n/a	n/a	n/a	40	40
Total Chemistry (XRF expressed as oxides)					
SiO_2 (wt%)	89.7	85.6	85.6	86.0	83.4
Al_2O_3 (wt%)	3.9	5.8	5.4	5.5	6.0
CaO (wt%)	0.5	0.7	0.7	0.7	0.8
MgO (wt%)	0.3	0.4	0.4	0.4	0.4
Na_2O (wt%)	2.9	3.9	4.2	3.8	5.2
K_2O (wt%)	0.1	0.1	0.1	0.2	0.2
Fe_2O_3 (wt%)	1.6	2.8	3.0	2.7	3.2
TiO_2 (wt%)	0.2	0.3	0.4	0.3	0.4

Permeability (darcy)	0.09	0.78	2.72	0.61	1.60
Wet Bulk Density (g/ml)	0.42	0.30	0.35	0.32	0.31
EBC Soluble Metals					
Fe (ppm)	126	158	63	93	55
Ca (ppm)	106	184	107	197	226
Al (ppm)	43	53	33	46	37
As (ppm)	1.5	0.9	1.7	1.0	0.6
Loss on Ignition (wt%)	0.8	0.3	0.1	0.3	0.3
Opal-C/Cristobalite Analysis					
Primary Peak centroid(Å)	4.08	4.08	4.08	4.07	4.09
FWHM (^{O} 2^{θ})	0.50	0.46	0.49	0.48	0.52
Peaks between 10^{O} – 37^{O} 2^{θ}	2 of 4	3 of 4	3 of 4	3 of 4	2 of 4
Opal-C (wt%)[1]	18.5%	6.4%	31.9%	6.9%	6.7%
Cristobalite (wt%)	0.0%	0.0%	0.0%	0.0%	0.0%
Quartz (wt%)	0.0%	0.0%	0.1%	0.0%	0.0%

[1] Opal-C quantification is based on XRD Method

[00151] FIG. 17 shows the XRD pattern for example 14 (FEBH). This sample comprises opal-C plus minor feldspar. FIG. 18 shows the XRD pattern associated with example 16 (KD 15:30). Once again, it exhibits characteristics of opal-C. These two patterns are typical of all those associated with the trial. The standard stick pattern of α-cristobalite is super-imposed in FIGS. 17 – 18.

[00152] For four of these five samples, the Silica Documentation would show non-detectable levels of crystalline silica when characterized using the LH Method, while example 16 (KD 15:30) would show no cristobalite but 0.1 wt% quartz. Using the Traditional Method for characterization, the five samples would show about 18 wt%, 6 wt%, 32 wt%, 7 wt%, and 7 wt% crystalline silica respectively.

Example 19: Diatomite Products Comprising Alkali Metal Aluminates and Novel, Silica Documentation

[00153] US Patent Publication 2014/0,035,243A1 by Wang et al. teaches a method of producing reduced content of soluble iron in diatomite filter aids by using an alkali metal aluminate as a fluxing agent. In this example, the impact of the fluxing agent on crystalline silica formation during flux-calcination of diatomite is examined by comparing a sodium aluminate ($NaAlO_2 \cdot xH_2O$) fluxed sample against a soda ash fluxed sample. A natural diatomite product of EP Minerals, LCS-3, made from an ore mined from the Horseshoe Basin deposit in northern Nevada, was used as the starting material. The major elemental composition of the diatomite, as determined by wave-length dispersive x-ray fluorescence (XRF) analysis and presented on the ignited basis, is listed in Table 12. It had a relatively low content of Al_2O_3. The soda ash used was of -325 mesh (-44 μm) and, before use, was brushed through a 100-mesh sieve on to the diatomite in a desired ratio. The sodium aluminate used was a moist powder and contained 24.6 wt% total free and bound water. A desired amount of sodium aluminate was premixed and co-milled with 0.5 g of the same diatomite by hand in a mortar and pestle set and then brushed through a 100-mesh sieve on to the rest of diatomite to be calcined. Each of the flux-added diatomite samples were mixed in a jar in a paint shaker. Flux-calcination was carried out in a ceramic crucible by heating in a muffle furnace at 649°C for 40 minutes. After cooling, the flux-calcined samples were dispersed through a 70-mesh screen by ro-tapping. Both 4 wt% soda ash and 8 wt% sodium aluminate fluxed samples had similar permeability (about 1.3-1.5 darcy) and similar wet bulk density (about 0.28 g/cc). Analytical results (using the LH Method and the XRD Method) of the flux-calcined products are shown in Table 13 and FIGS. 19 – 20. FIG. 19 illustrates the results for the soda ash flux-calcined diatomite sample, and FIG. 20 illustrates the results for the sodium aluminate flux-calcined diatomite sample. The standard stick patterns of α-cristobalite (16), albite (18) and quartz (20) are super-imposed on FIGS. 19 – 20. Both samples had about the same X-ray diffraction counts at the 22° primary peak (10), however, their silica crystallinities are significantly different: the soda ash fluxed sample (FIG. 19) shows an XRD scan pattern of cristobalite but the sodium aluminate fluxed sample (FIG. 20) is clearly opal-C, as demonstrated by the shifts of the primary (10) and secondary (12) peaks and absence of the tertiary peaks (14) at 31.50° and 28.49° 2θ (see also, Table 13). The formation of opal-C instead of cristobalite in the sodium aluminate fluxed product negates the need to list cristobalite in its Safety Data Sheet as a health hazard. It is conceivable that a diatomite feed material containing less than 0.1 wt% or non-detectable level of quartz would result in less than 0.1 wt% or non-detectable level of quartz in the product which enables non-listing quartz in the safety data sheet as well.

[00154] In Example 19, the Silica Documentation would show about 35 wt% and 0.1 wt% crystalline silica for the two samples respectively when prepared through use of the LH Method, but about 35 wt% and about 32 wt% crystalline silica respectively when prepared through use of Traditional Methods.

[00155] Table 12. Major Oxide Composition of Natural Diatomite LCS-3 used in this Study (Ignited Basis)

	SiO_2	Al_2O_3	CaO	MgO	Na_2O	K_2O	Fe_2O_3	TiO_2	LOI
wt%	92.7	3.23	0.87	0.35	0.46	0.36	1.73	0.13	7.4

[00156] **Table 13. XRD analysis Using the LH Method and the XRD Method on flux-calcined LCS-3 based DE samples with or without Al-additive**

Fluxing Agent or Additive* (wt%)	22° peak		Secondary and tertiary cristobalite peaks			4Å phase determination		Quartz wt %	Total crystal. silica wt%
	Centroid Å	FWHM °	36.2°	31.5°	28.5°	Phase	wt %		
4.0% Na_2CO_3	4.02	0.378	Yes	Yes	Yes	Cristobalite	34.5	ND	34.5
8.0% $NaAlO_2$	4.06	0.385	Shifted	Poor	Poor	Opal-C	32.4	0.1	0.1
5.1% Na_2CO_3 + 4.2% 0.3μ Al_2O_3	4.07	0.432	Shifted	Poor	Poor	Opal-C	24.0	0.3	0.3
5.0% Na_2CO_3 + 6.2% 1.7μ $Al(OH)_3$	4.06	0.436	Yes	Poor	Poor	Cristobalite	28.5	<0.1	28.6
6.2% 18μ $Al(OH)_3$	4.07	0.311	Shifted	Poor	no	Opal-C	9.0	0.2	0.2
None	4.08	0.334	Shifted	Poor	no	Opal-C	8.5	0.25	0.25

* As-is basis.

Example 20: Diatomite Products Comprising Alumina Additives and Novel Silica Documentation

[00157] US Patent Publication 2015/0129490A1 by Wang et al. teaches a method of producing reduced content of soluble iron in diatomite filter aids by using fine powder of alumina (Al_2O_3) or aluminum hydroxide ($Al(OH)_3$) as an additive. Aluminum hydroxide is otherwise called aluminum tri-hydrate or ATH. In one of the embodiments described in the application, an alumina or ATH additive is used in conjunction with soda ash in diatomite flux-calcination. In this example, the effect of the alumina or aluminum hydroxide on crystalline silica formation of soda ash flux-calcined diatomite is examined. The aluminum additives tested include a 0.3-µ α-alumina powder from Electron Microscopy Sciences, Hatfield, PA, USA (cat. #50361-05) and an aluminum hydroxide powder of Huber Engineered Materials, Atlanta, GA, USA, Hydral® 710. Analyses on the samples show the former having a free moisture of <0.2 wt% and a specific surface area of 24.2 m^2/g and the latter a free moisture of 12.9 wt%, a specific surface area of 4.0 m^2/g and a median particle size of 1.7 µm. The same natural diatomite LCS-3 and soda ash and the same experimental procedures and conditions used in Example 19 were used in the current examples. The sample made with 5.1 wt% soda ash and 4.2 wt% 0.3µ-alumina had 0.88 darcy permeability and 0.33 g/cc wet bulk density while the one made with 5.0 wt% soda ash and 6.2 wt% of the 1.7µ aluminum hydroxide (Hydral 710) had 1.2 darcy permeability and 0.29 g/cc wet bulk density.

[00158] FIG. 21 illustrates the results for the soda ash and 0.3µ-alumina flux-calcined diatomite sample, and FIG. 22 illustrates the results for the soda ash and 1.7µ ATH flux-calcined diatomite sample. The standard stick patterns of α-cristobalite (16), albite (18) and quartz (20) are super-imposed on FIGS. 21 – 22. Analysis on the products show that while the soda ash fluxed sample of FIG. 19 has an XRD scan pattern of cristobalite, the addition of 3µ alumina changed the phase to that of opal-C (see FIG. 21), as demonstrated by the shifts of the primary and secondary peaks (10, 12) and the absence of the tertiary peaks (see also Table 13). However, the addition of 1.7μ ATH to flux-calcination of diatomite did not inhibit cristobalite formation (Table 13, FIG. 22). More than 0.1 wt% quartz remained in the product in which 0.3μ alumina was added which can be avoided if a non-quartz containing diatomite is used as the feedstock.

[00159] In Example 20, the Silica Documentation would show that the products contain about 0.3 wt% and 29 wt% crystalline silica respectively when characterized through use of the LH Method, but would contain about 24 wt% and about 29 wt% crystalline silica respectively when characterized through use of the Traditional Method.

Example 21: Diatomite Products Comprising Alumina Additives and Novel Silica Documentation

[00160] Patent Publication WO 2015/0,069,432A1 by Wang et al. teaches a method of producing reduced content of soluble arsenic in diatomite filter aids by using aluminum hydroxide or tri-hydrate (ATH) as an additive. In one of the embodiments described in the application, ATH powder is used as an additive in straight-calcination of diatomite. In this example, the impact of ATH on crystalline silica formation in straight-calcined diatomite is examined. The ATH additive tested was a powder from R.J. Marshall Co., Southfield, MI, USA, having a 18 μm median particle size, 1.0 m^2/g specific surface area and <1 wt% free moisture. Straight-calcinations of the same natural diatomite LCS-3, with or without the ATH additive, were carried out with the same experimental procedures and under the same conditions used in Example 19. The straight-calcined samples, with 6.2 wt% ATH and without, had 0.16 and 0.15 darcy permeability and 0.25 and 0.34 g/cc wet bulk density, respectively.

[00161] FIG. 23 illustrates the results for the straight-calcined diatomite sample, and FIG. 24 illustrates the results for the straight-calcined diatomite sample with ATH additive. The standard stick patterns of α-cristobalite (16), albite (18) and quartz (20) are super-imposed on FIGS. 23 – 24. Cristobalite did not form in either product as demonstrated by their XRD scan patterns in which both primary and secondary peaks (10, 12) were disposed at respective lower angles than that of of cristobalite and the tertiary peaks were absent (FIGS. 23 – 24 and Table 13). More than 0.1 wt% quartz remained in both products which can be avoided if a non-quartz diatomite is used as the feedstock.

[00162] In Example 21, the Silica Documentation would show that the products contain about 0.2 wt% and about 0.3 wt% crystalline silica when characterized through use of the LH Method , but about 9 wt% crystalline silica in each when characterized through use of the Traditional Method.

Example 22: Diatomite Products Comprising a Potassium Silicate binder and Novel Silica Documentation

[00163] US Patent No. 9,095,842 by Nannini et al. teaches a method of producing low crystalline silica diatomite products with a large permeability range by adding potassium silicate to the natural diatomite and calcining. A sample was prepared using this technique, and compared with a sample of the same material straight-calcined without the potassium silicate additive, ie the control sample. A natural diatomite product called Celawhite^{TM} was used as the starting material. Five (5) wt% of potassium silicate (KASOLV® 16 potassium silicate) was added to one representative portion of the Celawhite, and then it and another representative portion of the Celawhite without the additive were placed in ceramic crucibles and straight-calcined in a laboratory muffle furnace at 1038° C for 45 minutes. After cooling, the two samples were dispersed through a 70-mesh sieve and analyzed. Use of the additive increased the permeability of the product to 0.29 darcy in comparison to a permeability of 0.13 darcy with the control sample (the sample without potassium silicate additive). The primary diffraction peak also decreased about 80% from that of the control (from 6.2% to 1.3%, quantified using the XRD method). The primary peak (10) of the control sample (FIG. 25) is indicative of opal-C. Interestingly, the primary peak (10) of the test sample with 5wt% KASOLV®,as compared to that of the control sample, is shifted toward a peak indicative of cristobalite (see FIG. 26). FIGS. 25 and 26 show the diffraction patterns of the control and test sample respectively. The standard stick pattern of α-cristobalite is superimposed on FIGS. 25 – 26.

[00164] In Example 22, the Silica Documentation would show that the straight-calcined control product contains no crystalline silica when characterized through use of the LH Method , but 6.2 wt% crystalline silica when characterized through use of the Traditional Method. The straight-calcined sample with potassium silicate additive would have Silica Documentation that shows 1.3 wt% cristobalite via either method.

Example 23: Composite Filtration Media Comprising Novel Silica Documentation

[00165] PCT Patent Application No. PCT/US15/65572 by Wang et al. teach a method of producing composite filtration media of diatomite and expanded perlite, with or without the presence of a fluxing agent. In certain embodiments of the invention, the composite filtration media may contain neither more than 0.1 wt% of any phase of crystalline silica nor opal-C or opal-CT. In other embodiments of the invention, the composite filter media may contain opal-C or opal-CT quantified according to the LH Method, phases that might be characterized as cristobalite by the Traditional Method. In further other embodiments, the composite filter media may contain a small amount of cristobalite as determined by either method. A few examples of these composite filter media products are listed in Table 14. All of these products contain either less than 0.1 wt% or non-detectable amount of quartz.

[00166] **Table 14. Example 23 - XRD analysis on selected diatomite-perlite composite products**

Examp. 23-	Feed and process parameters				Composite product crystallinity					
	DE/ Perlite wt ratio	Fluxing agent		Temp. °C	22° 2θ Peak		28.5° 2θ Peak	LOI wt%	4-Å phase	
		Type	wt%		d Å	FWHM ° 2θ			Phase	wt%
1	75/25	None	0	982	4.08	0.33	no	0.43	Opal-C/CT	<0.1
2	50/50	Na_2CO_3	1.0	982	4.06	0.30	no	0.80	Opal-C/CT	0.5
3	50/50	Na_2CO_3	2.0	927	4.03	0.34	poor	1.1	Cristobalite	1.2
4	25/75	Na_2CO_3	2.0	927	4.05	0.29	poor	1.2	Opal-C/CT	0.5
5	75/25	Na_2CO_3	5.0	871	4.06	0.42	poor	0.17	Opal-C/CT	17.5
6	50/50	Na_2CO_3	5.0	871	4.06	0.40	poor	0.19	Opal-C/CT	13.3
7	25/75	Na_2CO_3	5.0	871	4.08	0.40	poor	0.29	Opal-C/CT	5.8
8	50/50	Na_2CO_3	7.0	704	4.06	0.31	poor	1.2	Opal-C/CT	2.3
9	50/50	Na_2CO_3	7.0	760	4.02	0.35	poor	0.63	Cristobalite	2.9

10	25/75	Na_2CO_3	7.0	760	4.06	0.34	no	0.64	Opal-C/CT	1.3
11	50/50	H_3BO_3	3.0	816	4.06	0.29	no	0.99	Opal-C/CT	0.1
12	50/50	K_2CO_3	5.0	816	4.05	0.33	no	1.4	Opal-C/CT	1.2
13	50/50	K_2SiO_3	5.0	816	4.06	0.29	poor	1.5	Opal-C/CT	1.3
14	25/75	K_2SiO_3	6.8	816	4.06	0.27	poor	1.2	Opal-C/CT	1.4

Example 24: Grinding to Differentiate Opal-C from β-cristobalite

[00167] To confirm that the silica phase identified as opal-C in products comprising diatomaceous earth is not poorly-ordered β-cristobalite, the sample described in Example 16 was analyzed before and after grinding in accordance with the evidence presented by Chao and Lu. They found that grinding of a sample containing β-cristobalite that comprises less than 10 wt% alumina will result in a change of phase from β-cristobalite to α-cristobalite. Therefore, a significant peak shift and additional peaks should be apparent in the XRD pattern after grinding if in fact the original sample comprises β-cristobalite. FIG. 27 shows the XRD patterns of sample KD 15:30 before grinding (KD 1530 NO SPEX in FIG. 27) and after grinding (K2 disch 1530 in FIG. 27). The standard stick pattern of α-cristobalite is super-imposed on FIG. 27. A split of the sample was ground using a Spex® mill with ceramic media. The d90 of the material before milling was 122 *u*m, and the d90 after milling was 43*u*m. As can be seen in FIG. 27, milling of the sample did not result in a significant peak shift nor did additional peaks appear in the pattern. The milled sample did have somewhat lower peak intensity, but this is most likely due to non-uniform distribution of the opal-C phase in the coarser original sample.

Example 25: Phase Reversion

[00168] FIG. 28 shows two XRD patterns of a sample of Ceca Clarcel DIF-N® (sample # 17956). The standard stick pattern of α-cristobalite is super-imposed on FIG. 28. The sample was first analyzed in November 2012 (17956 2012-11-12 in FIG. 28), and then stored in a sealed plastic container. It was re-analyzed in January 2016 (17956 CECA CLARCEL DIFN_2016-01-15 in FIG. 28), just over three years later. After accounting for differences in x-ray tube intensity via the periodic monitoring of control standards, the difference in patterns still suggests a net loss in cristobalite content of about 25%, dropping from 80% cristobalite to 60% cristobalite. This sample also contains a minor amount of feldspar, and the quantity of feldspar did not change over the three year period.

[00169] FIG. 29 shows a similar result for a sample prepared in the lab in November 2015. The standard stick pattern of α-cristobalite is super-imposed on FIG. 29. This flux-calcined sample (HV2-G) was analyzed using XRD then re-hydrated under pressure (HV2-G pressure hydrated_2015-12-03 in FIG. 29). It was re-analyzed just over two months later (HV2-G PRESS HYD RUN #3_2016-02-05 in FIG. 29). Once again, the silica phase (this time opal-C) was reduced by about 25%, from 6.2% to 4.7%. A minor amount of quartz and more significant feldspars contained in this sample were unaffected by the two month aging period and pressure re-hydration.

Example 26: Use of Optical Method to Estimate Silica Phase Quantity

[00170] Table 15 shows data on flux-calcined samples from diatomite ores with differing bulk chemistry, flux-calcined under the exact same process conditions (7 wt%

soda ash, flux-calcined at 927°C for 40 minutes). The data show a definite inverse relationship between the b* value of the L*a*b* color space and the quantity of opal-C (and/or opal-CT) or cristobalite contained in the sample. FIG. 30 graphically shows this relationship. As the third step (spiking a split with cristobalite standard) of the LH Method for characterization of opal-C (and/or opal-CT) and cristobalite was not carried out with these samples, it was not possible to definitively determine the silica phase on some of the samples. However, it appears that the relationship between the hue of the flux-calcined samples and the quantity of specific silica phase present extends through opal-C and into cristobalite. While not absolute, b* values of less than 3 under these calcination conditions indicate that the silica phase present in the samples is probably cristobalite. Conversely, b* values equal to or greater than 3 indicate that the phase present is most likely opal-C (and/or opal-CT).

[00171] Disclosed is a process control method for products that comprise straight or flux-calcined diatomite, and more specifically for particulate products that comprise straight or flux-calcined diatomite. The opal-C (and/or opal-CT) or cristobalite content of such products may change depending on the mineral composition of the starting diatomite ore that is sourced for use in the straight or flux-calcination manufacturing process. To ensure that the content of the finished product remains consistent (and to ensure accurate content disclosure), samples of the products may be tested before shipment to customers/distributors. XRD testing can be time consuming. Below describes an efficient method to control product quality and to confirm the continuing accuracy of content disclosure.

[00172] The method estimates the cristobalite or collective opal-C and opal-CT wt% content of a product (that contains diatomite) using optical properties of the product. The method comprises selecting a representative first test sample of the product for testing. The method further comprises determining the process parameters used in the production of the first test sample of the product for which the cristobalite wt% content or the (collective) opal-C and opal-CT wt% content is to be estimated. The process parameters may include, but are not limited to, one or more of the following: flux composition and quantity, calcination temperature, sintering temperature, calcination time, sintering time, kiln residence time, or kiln atmosphere composition.

[00173] The method further comprises determining the optical properties of such first test sample of the product. Optical properties include, but are not limited to, one or more of the following: color space values: b* value, a* value or L* value. For example, color space values b* value, a* value or L* value may be determined using a Konica Minolta® Chroma-meter CR-400, or the like to sense the values of the first test sample.

[00174] The method further comprises applying a model to estimate the cristobalite wt% content or the (collective) opal-C and opal-CT wt% content of the first test sample of the product based on the process parameters and the optical properties of (the first test sample of) the product.

[00175] In one embodiment, the model may be used to estimate whether the cristobalite wt% content of the first test sample is above an acceptable cristobalite threshold value for the product being tested. For example, if a first test sample having a given set of process parameters is determined to have a sensed optical b* value of less than 3, the model may be configured to estimate that cristobalite is present in such first test sample (and by extension the product) at a level above a desired acceptable cristobalite threshold value of, for example, 0 wt% of the first test sample. In other embodiments, the desired acceptable cristobalite threshold value (for the same or a different product) may be different. In some embodiments, the model may be used to estimate the collective opal-C and opal-CT wt% of the first test sample and compare such to another threshold or to an acceptable threshold range.

[00176] In yet another embodiment, the model may be used to estimate a specific cristobalite wt% content and/or a collective opal-C and opal-CT wt% content of the first test sample based on the process parameters and the measured optical properties of the first test sample. In this embodiment, a specific value is determined/estimated by the model for cristobalite wt% content and/or a collective opal-C and opal-CT wt% content, as opposed to an estimation of whether the content is greater than a desired threshold value for wt%. Similar to the above, the estimated wt% content may be compared to a desired threshold value or range. In either case, the method may use a controller that includes a processor and a memory component to estimate the cristobalite or collective opal-C and opal-CT wt% content of the first test sample.

[00177] Such processor may be a microprocessor or other processor as known in the art. The processor may be configured to execute instructions and generate control signals for estimating/determining the wt% cristobalite content or the collective wt% opal-C and opal-CT content of the first test sample of the product (resulting from a set of process parameters) as a function of the measured optical properties of the first test sample of the product. Such instructions may be read into or incorporated into a computer readable medium, such as the memory component or provided external to the processor. In alternative embodiments, hard wired circuitry may be used in place of, or in combination with, software instructions to implement a control method. The term "computer readable medium" as used herein refers to any non-transitory medium or combination of media that participates in providing instructions to the processor for execution. Such a medium may comprise all computer readable media except for a transitory, propagating signal. Common forms of computer-readable media include, for example, a memory stick, or any magnetic medium, optical medium, or any other medium from which a computer processor can read. The controller is not limited to one processor and memory component. The controller may be several processors and memory components.

[00178] The model is configured to estimate the cristobalite or collective opal-C and opal-CT wt% content of the product based on one or more relationships identified through a linear regression (and/or another mathematical relationship) of the cristobalite wt% content (as determined by the LH Method) or the collective opal-C and opal-CT wt% content (as determined by the LH Method) as a function of the optical properties of a plurality of test products manufactured under the same or similar process parameters as the first test sample of the product. It is preferable if it is the same process parameters.

[00179] The method may further comprise conducting an XRD analysis on the first test sample of the product, or a representative second test sample from the same product, if the cristobalite wt% content estimated by the model fails the threshold comparison (for example, is above an acceptable threshold value). In some embodiments the method may comprise conducting an XRD analysis on the first test sample of the product, or a representative second test sample from the same product, if the collective opal-C and opal-CT wt% estimated by the model fails a threshold comparison for opal-C and opal-CT (for example is greater than a threshold value, outside of an anticipated or acceptable range of threshold values, or in some embodiments, less than a threshold value).

[00180] The method may further comprise removing from sales inventory, or the like, the product or the lot/batch of products from which the first (and second) test sample(s) was/were obtained, if the result of the XRD analysis also indicates that the cristobalite wt% content is above an acceptable threshold. Sales inventory means inventory available for shipment to distributors or customers.

[00181] The method may further comprise adjusting one or more process parameters (for example, calcination time or temperature, wt% of flux added, etc.) and/or the diatomite ore source used in manufacturing the product and repeating some or all of the method steps described above until any cristobalite present is estimated by the model or determined by XRD analysis to be at or below an acceptable threshold (wt% content) level (passes the threshold comparison). In some embodiments, the method may further comprise adjusting one or more process parameters (for example, calcination time or temperature, wt% of flux added, etc.) and/or the diatomite ore source used in manufacturing the product and repeating some or all of the method steps described above until the collective opal-C and opal-CT wt% estimated by the model or determined by

XRD analysis passes the desired threshold comparison for opal-C and opal-CT, collectively.

[00182] To build the model, a plurality of test products are selected for a set of process parameters (for example, flux composition and quantity, calcination temperature, and calcination time). The optical properties of each of the test products is measured (for example, the color space values: b* value, a* value or L* value). The cristobalite wt% content according to the LH Method is measured for each test product. The collective opal-C and opal-CT wt% content is measured for each test product according to the LH Method (preferably quantified according to the XRD Method). A linear regression analysis is then conducted (for example, see FIG. 30) to determine the best relationship between the wt% cristobalite content or the (collective) wt% opal-C and opal-CT content of the test products (resulting from the set of process parameters) as a function of the optical properties the test products. Alternatively, or in addition to, other appropriate mathematical analysis may be used to determine a suitable mathematical relationship between the wt% cristobalite content or the collective wt% opal-C and opal-CT content of the test products (resulting from the set of process parameters) as a function of the optical properties the test products. (Preferably this analysis is repeated for a plurality of sets of different process parameters (and their respective test products) to provide for a robust model to estimate the wt% cristobalite content or the collective wt% of opal-C and opal-CT content for a variety of products having different processing parameters. Similar to above, building the model may be accomplished using a controller that includes a processor and a memory component. The processor may be a microprocessor or other processor as known in the art. The processor may be configured to execute instructions and generate control signals for determining a relationship between the wt% cristobalite content or the wt% opal-C (and/or opal-CT) content of the test products (resulting from the set of process parameters) as a function of the optical properties the test products. Such instructions may be read into or incorporated into a computer readable medium, such as the memory component or provided external to the processor. In alternative embodiments, hard wired circuitry may be used in place of, or in combination with, software instructions to implement a control method. The controller is not limited to one processor and memory component. The controller may be several processors and memory components.

[00183] Table 15: Color Space and Silica Phase Data on Flux-Calcined Samples of Different Diatomite Ores

Sample	L*	a*	b*	Primary Peak d (Å)	FWHM (Å)	Phase	Quantity (%)
W18184	67.8	14.1	22.1	4.067	0.43	opal-C	18.1%
W18203	70.5	13.7	26.7	4.088	0.42	opal-C	9.6%
W18206	66.1	16.2	27.7	4.088	0.39	opal-C	9.5%
W18208	64.0	15.3	26.6	4.095	0.41	opal-C	10.0%
W18213	72.1	12.2	23.8	4.081	0.41	opal-C	12.4%
W18222	94.0	-0.2	1.1	4.059	0.37	cristobalite	50.4%
W18225	93.4	0.1	1.5	4.060	0.40	cristobalite	48.9%
W18228	91.3	1.2	4.3	4.067	0.40	opal-C	44.2%
W18241	93.4	-0.3	2.0	4.060	0.36	undetermined	49.6%
W18251	89.4	1.4	4.4	4.067	0.40	opal-C	40.8%
W18252	84.6	4.3	8.1	4.066	0.42	undetermined	35.9%
W18253	93.8	-0.3	1.8	4.060	0.37	cristobalite	49.0%
W18254	83.0	4.9	9.6	4.074	0.41	opal-C	38.0%
W18258	90.3	1.0	3.9	4.060	0.39	undetermined	43.9%

Opal-C quantification is based on XRD Method

Example 27: Respirable Silica Phases

[00184] As discussed previously, the respirable content (and silica phases therein) of a bulk powder sample can be determined by calculation. After obtaining silica phase information on the fine fraction of a sample via XRD, the particle size distribution of the entire sample is measured. CEN EN481 provides a statistical calculation on the likelihood of particles being respirable based on their size and particle density, thus it is applied to the measured distribution to determine the respirable fraction. The respirable fraction is then multiplied by the silica phase quantity to determine the respirable quantity of that particular silica phase.

[00185] Two samples were analyzed using this methodology. FIGS. 31 and 32 present their particle size distributions, and Table 16 includes the results of the respirable analysis.

Table 16: Results of Respirable Analysis (SWeFF)

Sample	18188-4	FP-3 B17E2
Opal-Cin minus 25*u*m Fraction (wt%)	9.1	17.2
Cristobalite and Quartz Content (wt%)	0.0	0.0
Respirable Fraction -EN481 (wt%)	0.1	1.8
Respirable Opal-C (wt%)	0.0	0.3
Respirable Cristobalite and Quartz (wt%)	0.0	0.0

Example 28: Improved Silica Documentation – Flux-calcined Sample

[00186] Silica Documentation was prepared for sample 18188-9, both using the Traditional Method (incorrectly identifying opal-C as cristobalite) and the LH Method. Table 17 is the SDS information for sales within the United States prepared using data generated via the Traditional Method for determining the cristobalite content in flux-calcined diatomite products. Table 18 is the corrected SDS information using data generated with the LH Method. Significant changes were made in sections 2 (hazards), 3 (composition), 8 (exposure controls), 11 (toxicological information), and 15 (regulatory information), in comparison with the SDS information shown in Table 17.

Table 17: SDS Information for Sample 18188-9 with Data based on Traditional Methods

SECTION 1: PRODUCT AND COMPANY IDENTIFICATION	
PRODUCT IDENTIFIER	18188-9 with Traditional Crystalline Silica Quantification
CHEMICAL NAME	Diatomaceous Earth, Flux-Calcined
CHEMICAL	Silica
MATERIAL USE	Filter Aid
RESTRICTION ON	None Known
MANUFACTURER	EP Minerals, LLC., 9875 Gateway Dr., Reno, NV 89521
TELEPHONE NO.	(775) 824 7600 (Monday – Friday 8:00 am PST – 5:00 pm PST)
EMERGENCY	(775) 824 7600 (Monday – Friday 8:00 am PST – 5:00 pm PST)
SDS DATE OF	January 31, 2014
SECTION 2: HAZARDS IDENTIFICATION	
OSHA GHS HAZARD CLASSIFICATION	Carcinogen Category 1A Specific Target Organ Toxicity, Repeated Exposure Category 1

HAZARDS NOT OTHERWISE CLASSIFIED	None
LABEL ELEMENTS	DANGER May cause cancer by inhalation. Causes damage to lungs through prolonged or repeated exposure. **Obtain special instructions before use.** **Do not handle until all safety precautions have been read and understood.** Do not breathe dust. Wear eye protection. If exposed or concerned: Get medical advice. **Dispose of contents in accordance with local, state and federal regulations.**

SECTION 3: COMPOSITION / INFORMATION ON INGREDIENTS

INGREDIENT IDENTIFICATION	APPROXIMATE CONCENTRATION (%)	C.A.S. NUMBERS
Diatomaceous Earth, Flux-Calcined (kieselguhr) (contains 35-50% Crystalline Silica - Cristobalite)	100%	68855-54-9 14464-46-1

SECTION 4: FIRST AID MEASURES

EYE	Flush eyes with generous quantities of water or eye rinse solution. Consult physician if irritation persists.
SKIN	Use moisture renewing lotions if dryness occurs.
INGESTION	Drink generous amounts of water to reduce bulk and drying effects.
INHALATION	Remove to fresh air. Blow nose to evacuate dust.
Most important symptoms/effects, acute and delayed	Dust may cause abrasive irritation to eyes. Prolonged skin contact may cause dryness. Dust may cause nose, throat and upper respiratory tract irritation. Prolonged inhalation of respirable dust containing silica may cause a progressive lung disease, silicosis and lung cancer. See Section 11 for additional information.

Indication of immediate medical attention and special treatment, if necessary	Immediate medical attention is not normally required. If dust irritates the eyes, seek medical attention.	
MATERIAL NAME	18188-9 with Traditional Crystalline Silica	Page 2 of 4
SECTION 5: FIRE FIGHTING MEASURES		
EXTINGUISHING MEDIA	Not applicable, the material is not combustible.	
SPECIFIC HAZARDS ARISING FROM THE CHEMICAL	Not applicable, the material is not combustible.	
SPECIAL PROTECTIVE EQUIPMENT AND PRECAUTIONS FOR FIRE-FIGHTERS	Not applicable, the material is not combustible.	
SECTION 6: ACCIDENTAL RELEASE MEASURES		
PERSONAL PRECAUTIONS	If dust is present, use respirator fitted with particulate filter as specified in Section 8. Protect eyes with goggles. Do not breathe dust.	
ENVIRONMENTAL PRECAUTIONS	This material is not a significant environmental concern.	
METHODS AND MATERIALS FOR CONTAINMENT AND CLEANING UP	Vacuum clean spillage or wet sweep. Avoid creating airborne dust. Place in a container for use or disposal.	
SECTION 7: HANDLING AND STORAGE		
PRECAUTIONS FOR SAFE HANDLING	Minimize dust generation. Avoid contact with eyes. Do not breathe dust. Repair or dispose of broken bags. Observe all label precautions and warnings.	
CONDITIONS FOR SAFE STORAGE	Store in a dry place to maintain packaging integrity and product quality. Do not store near hydrofluoric acid or concentrated caustic solutions.	
SECTION 8: EXPOSURE CONTROLS / PERSONAL PROTECTION		

EXPOSURE GUIDELINES:				
Component	OSHA PEL	ACGIH TLV	MSHA PEL	NIOSH REL
Diatomaceous Earth, Flux-Calcined (kieselguhr)	5 mg/m^3 respirable dust 15 mg/m^3 total dust	None Established	5 mg/m^3 respirable dust 15 mg/m^3 total dust	None Established
Crystalline Silica (Cristobalite)	$\frac{1}{2} \times \frac{30\ mg/m^3}{\%\ SiO_2+2}$ total dust $\frac{1}{2} \times \frac{10\ mg/m^3}{\%\ SiO_2+2}$ Respirable dust	0.025 mg/m^3 Respirable dust	$\frac{1}{2} \times \frac{30\ mg/m^3}{\%\ SiO_2+2}$ total dust $\frac{1}{2} \times \frac{10\ mg/m^3}{\%\ SiO_2+2}$ Respirable dust	0.05 mg/m^3 Respir-able dust
ENGINEERING CONTROLS	Use general or local exhaust ventilation to control dust within recommended exposure limits. Refer to ACGIH publication “Industrial Ventilation” or similar publications for design of ventilation systems.			
PERSONAL PROTECTIVE EQUIPMENT:				
EYE / FACE PROTECTION	Goggles to protect from dust			
SKIN PROTECTION	No special equipment is needed.			
RESPIRATORY PROTECTION	Respirators fitted with filters certified to standard 42CFR84 under series N95 should be worn when dust is present. If the dust concentration is less than ten (10) times the Permissible Exposure Limit (PEL) use a quarter or half-mask respirator with a N95 dust filter or a single use dust mask rated N95. If dust concentration is greater than ten (10) times and less than fifty (50) times the PEL, a full-face piece respirator fitted with replaceable N95 filters is recommended. If dust concentration is greater than fifty (50) and less than two hundred (200) times the PEL use a power air-purifying (positive pressure) respirator with a replaceable N95 filter. If dust concentration is greater than two hundred (200) times the PEL use a type C, supplied air respirator (continuous flow, positive pressure), with full face piece, hood or helmet.			

GENERAL HYGIENE	Avoid breathing dust. Avoid contact with eyes. Wash hands after handling and before eating or drinking.	
MATERIAL NAME	18188-9 with Traditional Crystalline Silica Quantification	Page 3 of 4

SECTION 9: PHYSICAL AND CHEMICAL PROPERTIES

APPEARANCE, COLOR	Dark pink to off-white powder	**ODOR**	Odorless
PHYSICAL STATE	Solid	**ODOR THRESHOLD**	Not applicable
VAPOR PRESSURE	Not applicable	**VAPOR DENSITY**	Not applicable
BOILING POINT	Not applicable	**MELTING POINT**	> 1300° C
FLASH POINT	Not applicable	**pH (10% SUSPENSION)**	10
FLAMMABILITY LIMITS	Not applicable	**EVAPORATION RATE**	Not applicable
DECOMPOSITION TEMPERATURE	> 1300° C	**SPEC. GRAVITY / RELATIVE DENSITY**	2.3
AUTOIGNITION TEMPERATURE	Not applicable	**PARTITION COEFFICIENT – n-OCTANOL/WATER**	Not applicable
FLAMMABILITY (solid/gas)	Not applicable	**SOLUBILITY – WATER**	< 1%
		VISCOSITY	Not applicable

SECTION 10: STABILITY AND REACTIVITY

REACTIVITY	Material is not reactive.
CHEMICAL STABILITY	Material is stable.
POSSIBILITY OF HAZARDOUS REACTIONS	Material is not reactive under normal conditions of handling unless mixed with incompatible substances below.
CONDITIONS TO AVOID	Not applicable
INCOMPATIBLE MATERIALS	Hydrofluoric acid and concentrated caustic solutions may react violently with the product.
HAZARDOUS DECOMPOSITION PRODUCTS	Not applicable

SECTION 11: TOXICOLOGICAL INFORMATION	
POTENTIAL HEALTH	
Likely Routes of	See below
EYE	May cause irritation (tear formation and redness) if dust gets in eyes.
SKIN	Not absorbed by the skin, but may cause dryness if prolonged exposure.
INGESTION	Ingestion of small quantities is not considered harmful, but may cause irritation of the mouth, throat and stomach.
INHALATION	Acute inhalation can cause dryness of the nasal passage and lung congestion, coughing and general throat irritation. Acute inhalation of high concentrations of respirable crystalline silica may cause acute silicosis.
CHRONIC EFFECTS	This product contains crystalline silica. Respirable crystalline silica may cause lung cancer and lung disease (silicosis) if inhaled for prolonged periods. Symptoms of silicosis include wheezing, cough and shortness of breath.
CARCINOGENICITY	Flux-calcined diatomaceous earth (Kieselguhr) is composed of amorphous and crystalline silica. Respirable crystalline silica (cristobalite) is classified by IARC and NTP as a known human carcinogen. Crystalline silica is only known to cause cancer when inhaled in a respirable form. It is not known to cause cancer by any other route of exposure.
NTP	Respirable crystalline silica (cristobalite) is classified as a known human carcinogen.
IARC	Respirable crystalline silica (cristobalite) is classified as a known human carcinogen.
NUMERICAL MEASURES OF TOXICITY	No data available
CORROSIVENESS, SENSITIZATION, IRRITANCY	Not applicable

MATERIAL NAME	18188-9 with Traditional Crystalline Silica Quantification	Page 4 of 4

REPRODUCTIVE TOXICITY	Not available
TERATOGENICITY, MUTAGENICITY	Not available

SECTION 12: ECOLOGICAL INFORMATION	
ECOTOXICITY:	Diatomaceous earth products have shown some efficacy as a natural insecticide, but otherwise have no demonstrated toxicity in regards to aquatic or terrestrial life.
PERSISTENCE AND DEGRADABILITY	Non-biodegradable, inert.
BIOACCUMULATIVE POTENTIAL	Little potential for bioaccumulation
MOBILITY IN SOIL	No mobility
OTHER ADVERSE EFFECTS	None known
SECTION 13: DISPOSAL CONSIDERATIONS	
WASTE DISPOSAL	If this material as supplied becomes a waste, use solid waste disposal common to landfill type operations or in slurry to sumps. Not considered a hazardous waste under RCRA (4OCFR Part 261).
PACKAGING DISPOSAL	Dispose of in accordance with applicable laws and regulations, typically solid waste disposal common to landfill type operations.
SECTION 14: TRANSPORT INFORMATION	
BASIC SHIPPING INFORMATION	DOT shipping classification 55 (no restrictions). Technical name is “Diatomaceous Earth”.
ADDITIONAL INFORMATION	No special requirements or placarding necessary.
SECTION 15: REGULATORY INFORMATION	
U.S. FEDERAL:	
TSCA	Diatomaceous Earth and Cristobalite appear on the EPA TSCA inventory list.
CERCLA	Diatomaceous Earth is not classified as a hazardous substance under regulations of the Comprehensive Environmental Response Compensation and Liability Act (CERCLA), 40 CFR 302.
SARA TITLE III	Not listed.
California Proposition 65:	This product contains crystalline silica, a chemical known to the State of California to cause cancer.
INTERNATIONAL:	
WHMIS Classification	Class D-2-A
WHMIS Ingredient Disclosure List	Silica, crystalline, cristobalite
SECTION 16: OTHER INFORMATION	

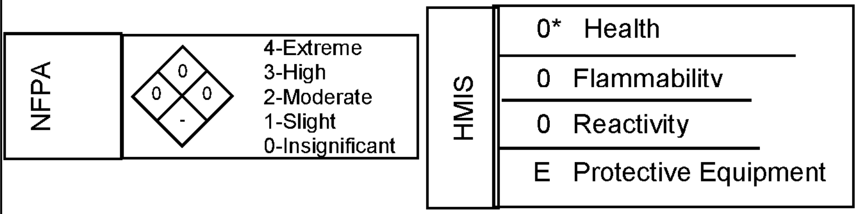
	
ORIGINAL ISSUE DATE	Not applicable
REVISION DATE	Not applicable
REVISION NO.	Example

Table 18: SDS Information for Sample 18188-9 with Data from LH Method

SECTION 1: PRODUCT AND COMPANY IDENTIFICATION	
PRODUCT IDENTIFIER	18188-9 with Silica Content Quantification according to the LH Method
CHEMICAL NAME	Diatomaceous Earth, Flux-Calcined
CHEMICAL FAMILY	Silica
MATERIAL USE	Filter Aid
RESTRICTION ON	None Known
MANUFACTURER	EP Minerals, LLC., 9875 Gateway Dr., Reno, NV 89521
TELEPHONE NO.	(775) 824 7600 (Monday – Friday 8:00 am PST – 5:00 pm
EMERGENCY	(775) 824 7600 (Monday – Friday 8:00 am PST – 5:00 pm
SDS DATE OF	January 31, 2014
SECTION 2: HAZARDS IDENTIFICATION	
OSHA GHS HAZARD CLASSIFICATION	Not classified as hazardous
HAZARDS NOT OTHERWISE CLASSIFIED	None

<table>
<tr><td>LABEL ELEMENTS</td><td colspan="3">No GHS labeling required</td></tr>
<tr><td></td><td colspan="3"></td></tr>
<tr><td colspan="4">SECTION 3: COMPOSITION / INFORMATION ON INGREDIENTS</td></tr>
<tr><td colspan="2">INGREDIENT IDENTIFICATION</td><td>APPROXIMATE CONCENTRATION (%)</td><td>C.A.S. NUMBERS</td></tr>
<tr><td colspan="2">Diatomaceous Earth, Flux-Calcined (kieselguhr)</td><td>100%</td><td>68855-54-9</td></tr>
<tr><td colspan="4">SECTION 4: FIRST AID MEASURES</td></tr>
<tr><td>EYE</td><td colspan="3">Flush eyes with generous quantities of water or eye rinse solution. Consult physician if irritation persists.</td></tr>
<tr><td>SKIN</td><td colspan="3">Use moisture renewing lotions if dryness occurs.</td></tr>
<tr><td>INGESTION</td><td colspan="3">Drink generous amounts of water to reduce bulk and drying effects.</td></tr>
<tr><td>INHALATION</td><td colspan="3">Remove to fresh air. Blow nose to evacuate dust.</td></tr>
<tr><td>Most important symptoms/effects, acute and delayed</td><td colspan="3">Dust may cause abrasive irritation to eyes. Prolonged skin contact may cause dryness. Dust may cause nose, throat and upper respiratory tract irritation. Prolonged inhalation of high concentration of dust may cause lung effects.</td></tr>
<tr><td>Indication of immediate medical attention and special treatment, if necessary</td><td colspan="3">Immediate medical attention is not normally required. If dust irritates the eyes, seek medical attention.</td></tr>
<tr><td>MATERIAL NAME</td><td colspan="2">18188-9 with Silica Content Quantification</td><td>Page 2 of 4</td></tr>
<tr><td colspan="4">SECTION 5: FIRE FIGHTING MEASURES</td></tr>
<tr><td>EXTINGUISHING MEDIA</td><td colspan="3">Not applicable, the material is not combustible.</td></tr>
<tr><td>SPECIFIC HAZARDS ARISING FROM THE CHEMICAL</td><td colspan="3">Not applicable, the material is not combustible.</td></tr>
<tr><td>SPECIAL PROTECTIVE EQUIPMENT AND PRECAUTIONS FOR FIRE-FIGHTERS</td><td colspan="3">Not applicable, the material is not combustible.</td></tr>
</table>

SECTION 6: ACCIDENTAL RELEASE MEASURES	
PERSONAL PRECAUTIONS	If dust is present, use respirator fitted with particulate filter as specified in Section 8. Protect eyes with goggles. Do not breathe dust.
ENVIRONMENTAL PRECAUTIONS	This material is not a significant environmental concern.
METHODS AND MATERIALS FOR CONTAINMENT AND CLEANING UP	Vacuum clean spillage or wet sweep. Avoid creating airborne dust. Place in a container for use or disposal.
SECTION 7: HANDLING AND STORAGE	
PRECAUTIONS FOR SAFE HANDLING	Minimize dust generation. Avoid contact with eyes. Do not breathe dust. Repair or dispose of broken bags. Observe all label precautions and warnings.
CONDITIONS FOR SAFE STORAGE	Store in a dry place to maintain packaging integrity and product quality. Do not store near hydrofluoric acid or concentrated caustic solutions.
SECTION 8: EXPOSURE CONTROLS / PERSONAL PROTECTION	

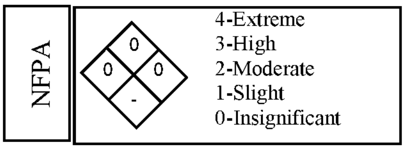
EXPOSURE GUIDELINES:				
Component	OSHA PEL	ACGIH TLV	MSHA PEL	NIOSH REL
Diatomaceous Earth, Flux-Calcined (kieselguhr)	5 mg/m^3 respirable dust 15 mg/m^3 total dust	None Established	5 mg/m^3 respirable dust 15 mg/m^3 total dust	None Established

ENGINEERING CONTROLS	Use general or local exhaust ventilation to control dust within recommended exposure limits. Refer to ACGIH publication “Industrial Ventilation” or similar publications for design of ventilation systems.
PERSONAL PROTECTIVE EQUIPMENT:	
EYE / FACE PROTECTION	Goggles to protect from dust
SKIN PROTECTION	No special equipment is needed.

<table>
<tr><td>RESPIRATORY PROTECTION</td><td colspan="3">Respirators fitted with filters certified to standard 42CFR84 under series N95 should be worn when dust is present. If the dust concentration is less than ten (10) times the Permissible Exposure Limit (PEL) use a quarter or half-mask respirator with a N95 dust filter or a single use dust mask rated N95. If dust concentration is greater than ten (10) times and less than fifty (50) times the PEL, a full-face piece respirator fitted with replaceable N95 filters is recommended. Selection and use of respiratory equipment must be in accordance with OSHA 1910.134 and good industrial hygiene practice.</td></tr>
<tr><td>GENERAL HYGIENE</td><td colspan="3">Avoid breathing dust. Avoid contact with eyes. Wash hands after handling and before eating or drinking.</td></tr>
<tr><td>MATERIAL NAME</td><td colspan="2">18188-9 with Silica Content Quantification according to the LH Method</td><td>Page 3 of 4</td></tr>
<tr><td colspan="4">SECTION 9: PHYSICAL AND CHEMICAL PROPERTIES</td></tr>
<tr><td>APPEARANCE, COLOR</td><td>Dark pink to off-white powder</td><td>ODOR</td><td>Odorless</td></tr>
<tr><td>PHYSICAL STATE</td><td>Solid</td><td>ODOR THRESHOLD</td><td>Not applicable</td></tr>
<tr><td>VAPOR PRESSURE</td><td>Not applicable</td><td>VAPOR DENSITY</td><td>Not applicable</td></tr>
<tr><td>BOILING POINT</td><td>Not applicable</td><td>MELTING POINT</td><td>> 1300° C</td></tr>
<tr><td>FLASH POINT</td><td>Not applicable</td><td>pH (10% SUSPENSION)</td><td>10</td></tr>
<tr><td>FLAMMABILITY LIMITS</td><td>Not applicable</td><td>EVAPORATION RATE</td><td>Not applicable</td></tr>
<tr><td>DECOMPOSITION TEMPERATURE</td><td>> 1300° C</td><td>SPEC. GRAVITY / RELATIVE DENSITY</td><td>2.3</td></tr>
<tr><td>AUTOIGNITION TEMPERATURE</td><td>Not applicable</td><td>PARTITION COEFFICIENT – n-OCTANOL/WATER</td><td>Not applicable</td></tr>
<tr><td>FLAMMABILITY (solid/gas)</td><td>Not applicable</td><td>SOLUBILITY – WATER</td><td>< 1%</td></tr>
<tr><td></td><td></td><td>VISCOSITY</td><td>Not applicable</td></tr>
<tr><td colspan="4">SECTION 10: STABILITY AND REACTIVITY</td></tr>
<tr><td>REACTIVITY</td><td colspan="3">Material is not reactive.</td></tr>
<tr><td>CHEMICAL STABILITY</td><td colspan="3">Material is stable.</td></tr>
</table>

POSSIBILITY OF HAZARDOUS REACTIONS	Material is not reactive under normal conditions of handling unless mixed with incompatible substances below.	
CONDITIONS TO AVOID	Not applicable	
INCOMPATIBLE MATERIALS	Hydrofluoric acid and concentrated caustic solutions may react violently with the product.	
HAZARDOUS DECOMPOSITION PRODUCTS	Not applicable	
SECTION 11: TOXICOLOGICAL INFORMATION		
POTENTIAL		
Likely Routes of	See below	
EYE	May cause irritation (tear formation and redness) if dust gets in eyes.	
SKIN	Not absorbed by the skin, but may cause dryness if prolonged exposure.	
INGESTION	Ingestion of small quantities is not considered harmful, but may cause irritation of the mouth, throat and stomach.	
INHALATION	Acute inhalation can cause dryness of the nasal passage and lung congestion, coughing and general throat irritation. Chronic inhalation of dust should be avoided.	
CHRONIC EFFECTS	Chronic inhalation of dust in excess of the Permissible Exposure Limit (PEL) established by OSHA over a prolonged number of years may cause lung changes.	
NTP	Diatomaceous earth without crystalline silica is not classified as a carcinogen.	
IARC	Diatomaceous earth without crystalline silica is not classifiable as to carcinogenicity in humans (Group 3)	
NUMERICAL MEASURES OF TOXICITY	No data available	
CORROSIVENESS, SENSITIZATION, IRRITANCY	Not applicable	
MATERIAL NAME	18188-9 with Silica Content Quantification according to the LH Method	Page 4 of 4

REPRODUCTIVE TOXICITY	Not available
TERATOGENICITY, MUTAGENICITY	Not available
SECTION 12: ECOLOGICAL INFORMATION	
ECOTOXICITY:	Diatomaceous earth products have shown some efficacy as a natural insecticide, but otherwise have no demonstrated toxicity in regards to aquatic or terrestrial life.
PERSISTENCE AND DEGRADABILITY	Non-biodegradable, inert.
BIOACCUMULATIVE POTENTIAL	Little potential for bioaccumulation
MOBILITY IN SOIL	No mobility
OTHER ADVERSE EFFECTS	None known
SECTION 13: DISPOSAL CONSIDERATIONS	
WASTE DISPOSAL	If this material as supplied becomes a waste, use solid waste disposal common to landfill type operations or in slurry to sumps. Not considered a hazardous waste under RCRA (4OCFR Part 261).
PACKAGING DISPOSAL	Dispose of in accordance with applicable laws and regulations, typically solid waste disposal common to landfill type operations.
SECTION 14: TRANSPORT INFORMATION	
BASIC SHIPPING INFORMATION	DOT shipping classification 55 (no restrictions). Technical name is “Diatomaceous Earth”.
ADDITIONAL INFORMATION	No special requirements or placarding necessary.
SECTION 15: REGULATORY INFORMATION	
U.S. FEDERAL:	
TSCA	Diatomaceous Earth appears on the EPA TSCA inventory list.
CERCLA	Diatomaceous Earth is not classified as a hazardous substance under regulations of the Comprehensive Environmental Response Compensation and Liability Act (CERCLA), 40 CFR 302.
SARA TITLE III	Not listed.
INTERNATIONAL:	
WHMIS Classification	This product is not regulated by WHMIS

WHMIS Ingredient Disclosure List	No reportable ingredients are present.
SECTION 16: OTHER INFORMATION	
	 HMIS 0* Health 0 Flammability 0 Reactivity E Protective
ORIGINAL ISSUE DATE	Not applicable
REVISION DATE	Not applicable
REVISION NO.	Example

Example 29: Improved Silica Documentation – Straight-Calcined Sample

[00187] Silica Documentation information was also prepared for straight-calcined products similar to some of those described in Tables 6 and 7. Table 19 is the SDS information for sales within the United States prepared using data generated via the Traditional Method for determining the crystalline silica content in such straight-calcined diatomite products (those containing some quartz plus opal-C misidentified as cristobalite). Table 20 is the corrected SDS information using data generated with the LH Method. In this case, the changes to the Silica Documentation are not as significant as in Example 28. However, meaningful changes have been made in sections 3, 8, and 11.

Table 19: SDS Information for Straight-Calcined Products Containing Quartz with Data based on Traditional Methods

SECTION 1: PRODUCT AND COMPANY IDENTIFICATION	
PRODUCT IDENTIFIER	Straight-calcined – Traditional Crystalline Silica Content Determination
CHEMICAL NAME	Diatomaceous Earth, Calcined
CHEMICAL FAMILY	Silica
MATERIAL USE	Filter Aid, Functional Filler
RESTRICTION ON USE	None Known
MANUFACTURER	EP Minerals, LLC., 9875 Gateway Dr., Reno, NV 89521
TELEPHONE NO.	(775) 824 7600 (Monday – Friday 8:00 am PST – 5:00 pm
EMERGENCY	(775) 824 7600 (Monday – Friday 8:00 am PST – 5:00 pm
SDS DATE OF	2016
SECTION 2: HAZARDS IDENTIFICATION	
OSHA GHS HAZARD CLASSIFICATION	Carcinogen Category 1A Specific Target Organ Toxicity, Repeated Exposure Category
HAZARDS NOT OTHERWISE CLASSIFIED	None
LABEL ELEMENTS	DANGER May cause cancer by inhalation. Causes damage to lungs through prolonged or repeated exposure. **Obtain special instructions before use.** **Do not handle until all safety precautions have been read and understood.** Do not breathe dust. Wear eye protection. If exposed or concerned: Get medical advice. **Dispose of contents in accordance with local, state and federal regulations.**

SECTION 3: COMPOSITION / INFORMATION ON INGREDIENTS		
INGREDIENT IDENTIFICATION	APPROXIMATE CONCENTRATION (%)	C.A.S. NUMBERS

Diatomaceous Earth, Calcined (kieselguhr) (contains 2-30% Crystalline Silica – Cristobalite and 0.1 to 5% Crystalline Silica - Quartz)	100%	91053-39-3 14464-46-1 14808-60-7
SECTION 4: FIRST AID MEASURES		
EYE	Flush eyes with generous quantities of water or eye rinse solution. Consult physician if irritation persists.	
SKIN	Use moisture renewing lotions if dryness occurs.	
INGESTION	Drink generous amounts of water to reduce bulk and drying effects.	
INHALATION	Remove to fresh air. Blow nose to evacuate dust.	
Most important symptoms/effects, acute and delayed	Dust may cause abrasive irritation to eyes. Prolonged skin contact may cause dryness. Dust may cause nose, throat and upper respiratory tract irritation. Prolonged inhalation of respirable dust containing silica may cause a progressive lung disease, silicosis and lung cancer. See Section 11 for additional information.	
Indication of immediate medical attention and special treatment, if necessary	Immediate medical attention is not normally required. If dust irritates the eyes, seek medical attention.	
MATERIAL NAME	Straight-calcined – Traditional Crystalline Silica Content Determination	Page 2 of 4
SECTION 5: FIRE FIGHTING MEASURES		
EXTINGUISHING MEDIA	Not applicable, the material is not combustible.	
SPECIFIC HAZARDS ARISING FROM THE CHEMICAL	Not applicable, the material is not combustible.	
SPECIAL PROTECTIVE EQUIPMENT AND PRECAUTIONS FOR FIRE-FIGHTERS	Not applicable, the material is not combustible.	
SECTION 6: ACCIDENTAL RELEASE MEASURES		

PERSONAL PRECAUTIONS	If dust is present, use respirator fitted with particulate filter as specified in Section 8. Protect eyes with goggles. Do not breathe dust.
ENVIRONMENTAL PRECAUTIONS	This material is not a significant environmental concern.
METHODS AND MATERIALS FOR CONTAINMENT AND CLEANING UP	Vacuum clean spillage or wet sweep. Avoid creating airborne dust. Place in a container for use or disposal.
SECTION 7: HANDLING AND STORAGE	
PRECAUTIONS FOR SAFE HANDLING	Minimize dust generation. Avoid contact with eyes. Do not breathe dust. Repair or dispose of broken bags. Observe all label precautions and warnings.
CONDITIONS FOR SAFE STORAGE	Store in a dry place to maintain packaging integrity and product quality. Do not store near hydrofluoric acid or concentrated caustic solutions.

SECTION 8: EXPOSURE CONTROLS / PERSONAL PROTECTION				
EXPOSURE GUIDELINES:				
Component	OSHA PEL	ACGIH TLV	MSHA PEL	NIOSH REL
Diatomaceous Earth, Calcined (kieselguhr)	5 mg/m^3 respirable dust 15 mg/m^3 total dust	None Established	5 mg/m^3 respirable dust 15 mg/m^3 total dust	None Established
Crystalline Silica (Cristobalite)	$\frac{1}{2} \times \frac{30\ mg/m^3}{\%\ SiO_2+2}$ total dust $\frac{1}{2} \times \frac{10\ mg/m^3}{\%\ SiO_2+2}$ Respirable dust	0.025 mg/m^3 Respirable dust	$\frac{1}{2} \times \frac{30\ mg/m^3}{\%\ SiO_2+2}$ total dust $\frac{1}{2} \times \frac{10\ mg/m^3}{\%\ SiO_2+2}$ Respirable dust	0.05 mg/m^3 Respirable dust

Crystalline Silica (Quartz)	$\frac{30\ mg/m^3}{\%\ SiO_2+2}$ total dust $\frac{10\ mg/m^3}{\%\ SiO_2+2}$ Respirable dust	0.025 mg/m^3 Respirable dust	$\frac{30\ mg/m^3}{\%\ SiO_2+2}$ total dust $\frac{10\ mg/m^3}{\%\ SiO_2+2}$ Respirable dust	0.05 mg/m^3 Respirable dust

ENGINEERING CONTROLS	Use general or local exhaust ventilation to control dust within recommended exposure limits. Refer to ACGIH publication “Industrial Ventilation” or similar publications for design of ventilation systems.
PERSONAL PROTECTIVE EQUIPMENT:	
EYE / FACE PROTECTION	Goggles to protect from dust
SKIN PROTECTION	No special equipment is needed.
RESPIRATORY PROTECTION	Respirators fitted with filters certified to standard 42CFR84 under series N95 should be worn when dust is present. If the dust concentration is less than ten (10) times the Permissible Exposure Limit (PEL) use a quarter or half-mask respirator with a N95 dust filter or a single use dust mask rated N95. If dust concentration is greater than ten (10) times and less than fifty (50) times the PEL, a full-face piece respirator fitted with replaceable N95 filters is recommended. If dust concentration is greater than fifty (50) and less than two hundred (200) times the PEL use a power air-purifying (positive pressure) respirator with a replaceable N95 filter. If dust concentration is greater than two hundred (200) times the PEL use a type C, supplied air respirator (continuous flow, positive pressure), with full face piece, hood or helmet.
GENERAL HYGIENE	Avoid breathing dust. Avoid contact with eyes. Wash hands after handling and before eating or drinking.

MATERIAL NAME	Straight-calcined – Traditional Crystalline Silica Content Determination	Page 3 of 4

SECTION 9: PHYSICAL AND CHEMICAL PROPERTIES

APPEARANCE, COLOR	Buff to pink powder	**ODOR**	Odorless
PHYSICAL STATE	Solid	**ODOR THRESHOLD**	Not applicable

VAPOR PRESSURE	Not applicable	**VAPOR DENSITY**	Not applicable
BOILING POINT	Not applicable	**MELTING POINT**	> 1300° C
FLASH POINT	Not applicable	**pH (10% SUSPENSION)**	7
FLAMMABILITY LIMITS	Not applicable	**EVAPORATION RATE**	Not applicable
DECOMPOSITION TEMPERATURE	> 1300° C	**SPEC. GRAVITY / RELATIVE DENSITY**	2.2
AUTOIGNITION TEMPERATURE	Not applicable	**PARTITION COEFFICIENT – n-OCTANOL/WATER**	Not applicable
FLAMMABILITY (solid/gas)	Not applicable	**SOLUBILITY – WATER**	< 1%
		VISCOSITY	Not applicable

SECTION 10: STABILITY AND REACTIVITY	
REACTIVITY	Material is not reactive.
CHEMICAL STABILITY	Material is stable.
POSSIBILITY OF HAZARDOUS REACTIONS	Material is not reactive under normal conditions of handling unless mixed with incompatible substances below.
CONDITIONS TO AVOID	Not applicable
INCOMPATIBLE MATERIALS	Hydrofluoric acid and concentrated caustic solutions may react violently with the product.
HAZARDOUS DECOMPOSITION PRODUCTS	Not applicable
SECTION 11: TOXICOLOGICAL INFORMATION	
POTENTIAL HEALTH	
Likely Routes of Exposure	See below
EYE	May cause irritation (tear formation and redness) if dust gets in eyes.
SKIN	Not absorbed by the skin, but may cause dryness if prolonged exposure.

INGESTION	Ingestion of small quantities is not considered harmful, but may cause irritation of the mouth, throat and stomach.	
INHALATION	Acute inhalation can cause dryness of the nasal passage and lung congestion, coughing and general throat irritation. Acute inhalation of high concentrations of respirable crystalline silica may cause acute silicosis.	
CHRONIC EFFECTS	This product contains crystalline silica. Respirable crystalline silica may cause lung cancer and lung disease (silicosis) if inhaled for prolonged periods. Symptoms of silicosis include wheezing, cough and shortness of breath.	
CARCINOGENICITY	Calcined diatomaceous earth (Kieselguhr) is composed of amorphous and crystalline silica. Respirable crystalline silica (quartz and cristobalite) is classified by IARC and NTP as a known human carcinogen. Crystalline silica is only known to cause cancer when inhaled in a respirable form. It is not known to cause cancer by any other route of exposure.	
NTP	Respirable crystalline silica (quartz and cristobalite) is classified as a known human carcinogen.	
IARC	Respirable crystalline silica (quartz and cristobalite) is classified as a known human carcinogen.	
NUMERICAL MEASURES OF TOXICITY	No data available	
CORROSIVENESS, SENSITIZATION, IRRITANCY	Not applicable	
MATERIAL NAME	Straight-calcined – Traditional Crystalline Silica Content Determination	Page 4 of 4
REPRODUCTIVE TOXICITY	Not available	
TERATOGENICITY, MUTAGENICITY	Not available	
SECTION 12: ECOLOGICAL INFORMATION		
ECOTOXICITY:	Diatomaceous earth products have shown some efficacy as a natural insecticide, but otherwise have no demonstrated toxicity in regards to aquatic or terrestrial life.	
PERSISTENCE AND DEGRADABILITY	Non-biodegradable, inert.	

BIOACCUMULATIVE POTENTIAL	Little potential for bioaccumulation
MOBILITY IN SOIL	No mobility
OTHER ADVERSE EFFECTS	None known
SECTION 13: DISPOSAL CONSIDERATIONS	
WASTE DISPOSAL	If this material as supplied becomes a waste, use solid waste disposal common to landfill type operations or in slurry to sumps. Not considered a hazardous waste under RCRA (4OCFR Part 261).
PACKAGING DISPOSAL	Dispose of in accordance with applicable laws and regulations, typically solid waste disposal common to landfill type operations.
SECTION 14: TRANSPORT INFORMATION	
BASIC SHIPPING INFORMATION	DOT shipping classification 55 (no restrictions). Technical name is “Diatomaceous Earth”.
ADDITIONAL INFORMATION	No special requirements or placarding necessary.
SECTION 15: REGULATORY INFORMATION	
U.S. FEDERAL:	
TSCA	Diatomaceous Earth, Quartz, and Cristobalite appear on the EPA TSCA inventory list.
CERCLA	Diatomaceous Earth is not classified as a hazardous substance under regulations of the Comprehensive Environmental Response Compensation and Liability Act (CERCLA), 40 CFR 302.
SARA TITLE III	Not listed.
California Proposition 65:	This product contains crystalline silica, a chemical known to the State of California to cause cancer.
INTERNATIONAL:	
WHMIS Classification	Class D-2-A
WHMIS Ingredient Disclosure List	Silica, crystalline, cristobalite , and Silica, crystalline, quartz
SECTION 16: OTHER INFORMATION	

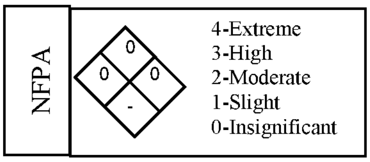
	 HMIS 0* Health 0 Flammability 0 Reactivity E Protective Equipment
ORIGINAL ISSUE DATE	Not applicable
REVISION DATE	Not applicable
REVISION NO.	

Table 20: SDS Information for Straight-Calcined Products Containing Quartz with Data from LH Method

SECTION 1: PRODUCT AND COMPANY IDENTIFICATION	
PRODUCT IDENTIFIER	Straight-calcined –Silica Content Determination according to the LH Method
CHEMICAL NAME	Diatomaceous Earth, Calcined
CHEMICAL FAMILY	Silica
MATERIAL USE	Filter Aid, Functional Filler
RESTRICTION ON	None Known
MANUFACTURER	EP Minerals, LLC., 9875 Gateway Dr., Reno, NV 89521
TELEPHONE NO.	(775) 824 7600 (Monday – Friday 8:00 am PST – 5:00 pm
EMERGENCY	(775) 824 7600 (Monday – Friday 8:00 am PST – 5:00 pm
SDS DATE OF	2016
SECTION 2: HAZARDS IDENTIFICATION	
OSHA GHS HAZARD CLASSIFICATION	Carcinogen Category 1A Specific Target Organ Toxicity, Repeated Exposure Category 1

HAZARDS NOT OTHERWISE CLASSIFIED	None
LABEL ELEMENTS	DANGER May cause cancer by inhalation. Causes damage to lungs through prolonged or repeated exposure. **Obtain special instructions before use.** **Do not handle until all safety precautions have been read and understood.** Do not breathe dust. Wear eye protection. If exposed or concerned: Get medical advice. **Dispose of contents in accordance with local, state and federal regulations.**

SECTION 3: COMPOSITION / INFORMATION ON INGREDIENTS

INGREDIENT IDENTIFICATION	APPROXIMATE CONCENTRATION (%)	C.A.S. NUMBERS
Diatomaceous Earth, Calcined (kieselguhr) (contains 0.1% to 5% Crystalline Silica - Quartz)	100%	91053-39-3 14808-60-7

SECTION 4: FIRST AID MEASURES

EYE	Flush eyes with generous quantities of water or eye rinse solution. Consult physician if irritation persists.
SKIN	Use moisture renewing lotions if dryness occurs.
INGESTION	Drink generous amounts of water to reduce bulk and drying effects.
INHALATION	Remove to fresh air. Blow nose to evacuate dust.

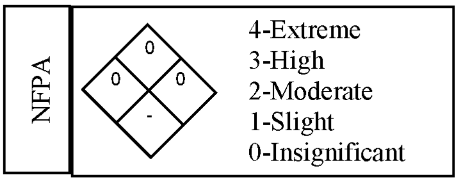
Most important symptoms/effects, acute and delayed	Dust may cause abrasive irritation to eyes. Prolonged skin contact may cause dryness. Dust may cause nose, throat and upper respiratory tract irritation. Prolonged inhalation of respirable dust containing silica may cause a progressive lung disease, silicosis and lung cancer. See Section 11 for additional information.	
Indication of immediate medical attention and special treatment, if necessary	Immediate medical attention is not normally required. If dust irritates the eyes, seek medical attention.	
MATERIAL NAME	Straight-calcined –Silica Content Determination according to the LH Method	Page 2 of 4
SECTION 5: FIRE FIGHTING MEASURES		
EXTINGUISHING MEDIA	Not applicable, the material is not combustible.	
SPECIFIC HAZARDS ARISING FROM THE CHEMICAL	Not applicable, the material is not combustible.	
SPECIAL PROTECTIVE EQUIPMENT AND PRECAUTIONS FOR FIRE-FIGHTERS	Not applicable, the material is not combustible.	
SECTION 6: ACCIDENTAL RELEASE MEASURES		
PERSONAL PRECAUTIONS	If dust is present, use respirator fitted with particulate filter as specified in Section 8. Protect eyes with goggles. Do not breathe dust.	
ENVIRONMENTAL PRECAUTIONS	This material is not a significant environmental concern.	
METHODS AND MATERIALS FOR CONTAINMENT AND CLEANING UP	Vacuum clean spillage or wet sweep. Avoid creating airborne dust. Place in a container for use or disposal.	
SECTION 7: HANDLING AND STORAGE		
PRECAUTIONS FOR SAFE HANDLING	Minimize dust generation. Avoid contact with eyes. Do not breathe dust. Repair or dispose of broken bags. Observe all label precautions and warnings.	

CONDITIONS FOR SAFE STORAGE	Store in a dry place to maintain packaging integrity and product quality. Do not store near hydrofluoric acid or concentrated caustic solutions.			
SECTION 8: EXPOSURE CONTROLS / PERSONAL PROTECTION				
EXPOSURE GUIDELINES:				
Component	OSHA PEL	ACGIH TLV	MSHA PEL	NIOSH REL
Diatomaceous Earth, Calcined (kieselguhr)	5 mg/m^3 respirable dust 15 mg/m^3 total dust	None Established	5 mg/m^3 respirable dust 15 mg/m^3 total dust	None Established
Crystalline Silica (Quartz)	$\frac{30\ mg/m^3}{\%\ SiO_2+2}$ total dust $\frac{10\ mg/m^3}{\%\ SiO_2+2}$ Respirable dust	0.025 $mg/\ m^3$ Respirable dust	$\frac{30\ mg/m^3}{\%\ SiO_2+2}$ total dust $\frac{10\ mg/m^3}{\%\ SiO_2+2}$ Respirable dust	0.05 mg/m^3 Respirable dust
ENGINEERING CONTROLS	Use general or local exhaust ventilation to control dust within recommended exposure limits. Refer to ACGIH publication "Industrial Ventilation" or similar publications for design of ventilation systems.			
PERSONAL PROTECTIVE EQUIPMENT:				
EYE / FACE PROTECTION	Goggles to protect from dust			
SKIN PROTECTION	No special equipment is needed.			

RESPIRATORY PROTECTION	Respirators fitted with filters certified to standard 42CFR84 under series N95 should be worn when dust is present. If the dust concentration is less than ten (10) times the Permissible Exposure Limit (PEL) use a quarter or half-mask respirator with a N95 dust filter or a single use dust mask rated N95. If dust concentration is greater than ten (10) times and less than fifty (50) times the PEL, a full-face piece respirator fitted with replaceable N95 filters is recommended. If dust concentration is greater than fifty (50) and less than two hundred (200) times the PEL use a power air-purifying (positive pressure) respirator with a replaceable N95 filter. If dust concentration is greater than two hundred (200) times the PEL use a type C, supplied air respirator (continuous flow, positive pressure), with full face piece, hood or helmet.		
GENERAL HYGIENE	Avoid breathing dust. Avoid contact with eyes. Wash hands after handling and before eating or drinking.		
MATERIAL NAME	Straight-calcined –Silica Content Determination according to the LH Method		Page 3 of 4
SECTION 9: PHYSICAL AND CHEMICAL PROPERTIES			
APPEARANCE, COLOR	Buff to pink powder	**ODOR**	Odorless
PHYSICAL STATE	Solid	**ODOR THRESHOLD**	Not applicable
VAPOR PRESSURE	Not applicable	**VAPOR DENSITY**	Not applicable
BOILING POINT	Not applicable	**MELTING POINT**	> 1300° C
FLASH POINT	Not applicable	**pH (10% SUSPENSION)**	7
FLAMMABILITY LIMITS	Not applicable	**EVAPORATION RATE**	Not applicable
DECOMPOSITION TEMPERATURE	> 1300° C	**SPEC. GRAVITY / RELATIVE DENSITY**	2.2
AUTOIGNITION TEMPERATURE	Not applicable	**PARTITION COEFFICIENT – n-OCTANOL/WATER**	Not applicable
FLAMMABILITY (solid/gas)	Not applicable	**SOLUBILITY – WATER**	< 1%
		VISCOSITY	Not applicable

SECTION 10: STABILITY AND REACTIVITY	
REACTIVITY	Material is not reactive.
CHEMICAL STABILITY	Material is stable.
POSSIBILITY OF HAZARDOUS REACTIONS	Material is not reactive under normal conditions of handling unless mixed with incompatible substances below.
CONDITIONS TO AVOID	Not applicable
INCOMPATIBLE MATERIALS	Hydrofluoric acid and concentrated caustic solutions may react violently with the product.
HAZARDOUS DECOMPOSITION PRODUCTS	Not applicable
SECTION 11: TOXICOLOGICAL INFORMATION	
POTENTIAL	
Likely Routes of	See below
EYE	May cause irritation (tear formation and redness) if dust gets in eyes.
SKIN	Not absorbed by the skin, but may cause dryness if prolonged exposure.
INGESTION	Ingestion of small quantities is not considered harmful, but may cause irritation of the mouth, throat and stomach.
INHALATION	Acute inhalation can cause dryness of the nasal passage and lung congestion, coughing and general throat irritation. Acute inhalation of high concentrations of respirable crystalline silica may cause acute silicosis.
CHRONIC EFFECTS	This product contains a natural form of crystalline silica (quartz). Respirable crystalline silica may cause lung cancer and lung disease (silicosis) if inhaled for prolonged periods. Symptoms of silicosis include wheezing, cough and shortness of breath.

CARCINOGENICITY	Calcined diatomaceous earth (Kieselguhr) is composed primarily of amorphous silica, but can also contain crystalline silica in the form of quartz. Respirable crystalline silica (quartz) is classified by IARC and NTP as a known human carcinogen. Crystalline silica is only known to cause cancer when inhaled in a respirable form. It is not known to cause cancer by any other route of exposure.	
NTP	Respirable crystalline silica (quartz) is classified as a known human carcinogen.	
IARC	Respirable crystalline silica (quartz) is classified as a known human carcinogen.	
NUMERICAL MEASURES OF TOXICITY	No data available	
CORROSIVENESS, SENSITIZATION, IRRITANCY	Not applicable	
MATERIAL NAME	Straight-calcined –Silica Content Determination according to the LH Method	Page 4 of 4
REPRODUCTIVE TOXICITY	Not available	
TERATOGENICITY, MUTAGENICITY	Not available	
SECTION 12: ECOLOGICAL INFORMATION		
ECOTOXICITY:	Diatomaceous earth products have shown some efficacy as a natural insecticide, but otherwise have no demonstrated toxicity in regards to aquatic or terrestrial life.	
PERSISTENCE AND DEGRADABILITY	Non-biodegradable, inert.	
BIOACCUMULATIVE POTENTIAL	Little potential for bioaccumulation	
MOBILITY IN SOIL	No mobility	
OTHER ADVERSE EFFECTS	None known	
SECTION 13: DISPOSAL CONSIDERATIONS		
WASTE DISPOSAL	If this material as supplied becomes a waste, use solid waste disposal common to landfill type operations or in slurry to sumps. Not considered a hazardous waste under RCRA (4OCFR Part 261).	

PACKAGING DISPOSAL	Dispose of in accordance with applicable laws and regulations, typically solid waste disposal common to landfill type operations.
SECTION 14: TRANSPORT INFORMATION	
BASIC SHIPPING INFORMATION	DOT shipping classification 55 (no restrictions). Technical name is "Diatomaceous Earth".
ADDITIONAL INFORMATION	No special requirements or placarding necessary.
SECTION 15: REGULATORY INFORMATION	
U.S. FEDERAL:	
TSCA	Diatomaceous Earth and Quartz appear on the EPA TSCA inventory list.
CERCLA	Diatomaceous Earth is not classified as a hazardous substance under regulations of the Comprehensive Environmental Response Compensation and Liability Act (CERCLA), 40 CFR 302.
SARA TITLE III	Not listed.
California Proposition 65:	This product contains crystalline silica, a chemical known to the State of California to cause cancer.
INTERNATIONAL:	
WHMIS Classification	Class D-2-A
WHMIS Ingredient Disclosure List	Silica, crystalline, quartz
SECTION 16: OTHER INFORMATION	
	 HMIS 0* Health 0 Flammability 0 Reactivity E Protective Equipment

ORIGINAL ISSUE DATE	Not applicable
REVISION DATE	Not applicable
REVISION NO.	

[00188] FIG. 33 illustrates an exemplary embodiment of the product 4. The product 4 includes a physical component 6 (of the product 4) and a data component 9. The data component 9 includes the novel Silica Documentation 8. In the example shown in FIG. 33, the Silica Documentation 8 includes a product label 8a, a bar code 8b and an SDS 8c. This is not to imply that all three of these types of Silica Documentation 8 must be associated with a given product 4. FIG. 33 is for exemplary purposes only. In other embodiments, the Silica Documentation 8 may include, as discussed earlier, one or more of a regulatory support document(s), hazard disclosure(s), Safety Data Sheet(s), label(s), product label(s), product bar code(s), certificates of analysis or other electronic or printed forms of data which document or disclose crystalline silica content, or the absence of crystalline silica in the content, of the product 4. In the example illustrated in FIG. 33, the Silica Documentation 8 (associated with the product 4) discloses crystalline silica content present (or the absence of crystalline silica) in the physical component 6 as determined, measured or quantified by the LH Method. As noted previously, the absence of crystalline silica (for example, cristobalite, quartz, tridymite) is disclosed either by an explicit statement or an absence of crystalline silica from the product contents identified by the Silica Documentation 8.

[00189] The disclosures of the publications referenced below are hereby incorporated by reference into the present disclosure in their entirety. Eichhubl, P, and R.J. Behl, 1998. “Diagenesis, Deformation, and Fluid Flow in the Miocene Monterey Formation”: Special Publication, Pacific Section, SEPM, V83, p.5-13. J.M. Elzea, I.E. Odom, W.J. Miles, “Distinguishing well-ordered opal-CT and opal-C from high temperature cristobalite by x-ray diffraction”, Anal. Chim. Acta 286 (1994) 107-116. Hillier, S., and D.G. Lumsdon. “Distinguishing opaline silica from cristobalite in bentonites: a practical procedure and perspective based on NaOH dissolution”, Clay Minerals (2008) 43, 477-486. Damby, David E., Llewellin, Edward W., Horwell, Claire J., Williamson, Ben J., Najorka, Jens, Cressey, Gordon, Carpenter, Michael, 2014, “The α-β phase transition in volcanic cristobalite”, Journal of Applied Crystallography, 47, 1205-1215. Chao, Chin-Hsiao, Lu, Hong-Yang, 2002, “Stress-induced β to α-cristobalite phase transformation in ($Na_2O + Al_2O_3$)-codoped silica”, Materials Science and Engineering, A328, 267-276. Klug, H.P., & Alexander, L.E., 1974, “X-ray Diffraction Procedures”, John Wiley and Sons, Inc. Silica, Crystalline, by XRD 7500, NIOSH Manual of Analytical Methods, Fourth Edition, 2003.

Industrial Applicability

[00190] The teachings of this disclosure include products comprising powdered diatomite and novel Silica Documentation, and the associated novel LH Method for determination and quantification of the silica content of such products (for example, the opal-C (and/or opal-CT), cristobalite, quartz or tridymite content). Such products, properly characterized by Silica Documentation based on the LH Method, provide benefits in the analysis of potential product hazards, appropriate incentives for the producers of products that include diatomite to develop and introduce new products comprising reduced levels of crystalline silica and improved information regarding the potential exposures of both workers and consumers to crystalline silica, and respirable crystalline silica. Further the novel LH Method disclosed herein for determining and quantifying the opal-C (and/or opal-CT) and crystalline silica (cristobalite, quartz, tridymite) content of products that include diatomite and method of process control disclosed herein provide effective and novel quality control during manufacturing of such products.

[00191] Moreover, the teachings of the present disclosure may be practiced on the industrial scale for providing novel filtration media, carriers, absorbents, functional fillers and the like that include low or non-detectable levels of crystalline silica. Such novel products, and methods of producing such products, benefit users, handlers, and manufacturers by reducing exposure to crystalline silica.

[00192] Recitation of ranges of values herein are merely intended to serve as a shorthand method of referring individually to each separate value falling within the range, unless otherwise indicated herein, and each separate value is incorporated into the specification as if it were individually recited herein. All methods described herein can be performed in any suitable order unless otherwise indicated herein or otherwise clearly contradicted by context.

[00193] Accordingly, this disclosure includes all modifications and equivalents of the subject matter recited in the claims appended hereto as permitted by applicable law. Moreover, any combination of the above-described elements in all possible variations thereof is encompassed by the disclosure unless otherwise indicated herein or otherwise clearly contradicted by context.

Claims

We claim:

1. A diatomite product comprising:

sodium flux-calcined diatomite,

wherein the diatomite product has a crystalline silica content of less than about 1 wt%,

wherein the diatomite product has a permeability between 0.8 darcy and about 30 darcy.

2. The diatomite product of claim 1, wherein the diatomite product has a permeability between 0.9 darcy and 30 darcy.

3. The diatomite product of claim 1, wherein the crystalline silica content is less than about 0.1 wt% of the diatomite product.

4. The diatomite product of claim 1, wherein the diatomite product has a biogenic silica content of at least 80 wt%.

5. The diatomite product of claim 1, wherein the diatomite product has a permeability between about 1.5 darcy and about 9 darcy.

6. The diatomite product of claim 1, wherein the diatomite product has an opal-C content of more than about 1 wt% of the diatomite product.

7. The diatomite product of claim 1, wherein the diatomite product has an opal-C content of more than about 10 wt% of the diatomite product.

8. The diatomite product of claim 1, wherein the diatomite product is a particulate product.

9. The diatomite product of claim 1 further comprising more than about 4 wt % combined total of aluminum and iron in mineral form or more than about 7 wt % expressed as oxides.

10. The diatomite product of claim 1, wherein the diatomite product is a regenerated filtration medium that has been used previously one or more times as a filtration medium and has been regenerated by either a chemical or thermal process, the regenerated filtration medium adapted for re-use in filtration processes for at least one of food, beverages, chemicals, fuels, materials, water or biopharmaceuticals.

11. The diatomite product of claim 1 further comprising a soluble calcium content between about 21 ppm and 900 ppm, as measured by the EBC method.

12. The diatomite product of claim 1 further comprising between about 23 ppm and 45 ppm soluble iron, as measured by the EBC method.

13. The diatomite product of claim 1 further comprising between about 4 ppm and about 14 ppm, beer soluble iron, as measured by the ASBC method.

14. The diatomite product of claim 1, wherein the diatomite product optionally has a cristobalite content, wherein further the cristobalite content was determined by a method that differentiates between cristobalite and opal-C.

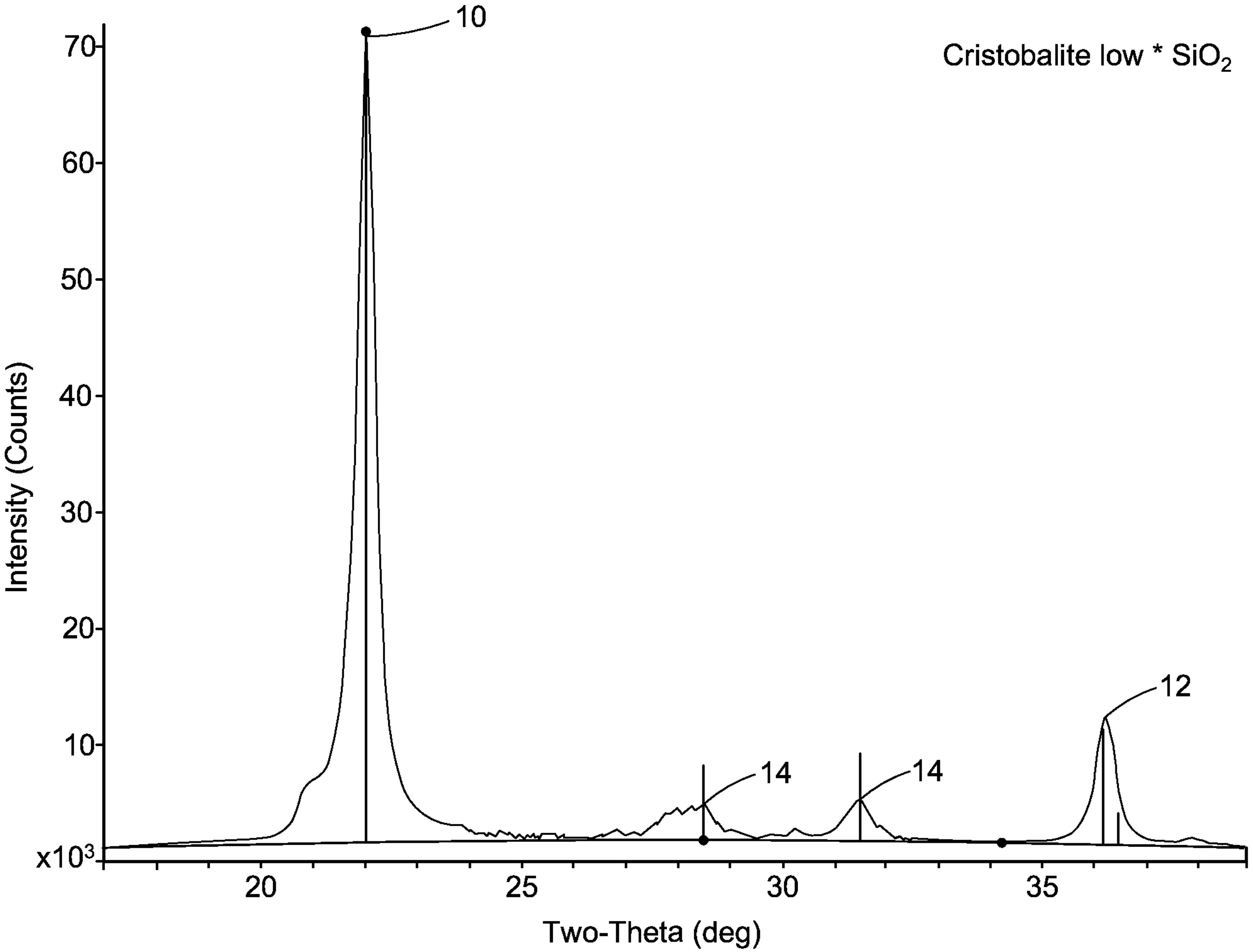
15. The diatomite product of claim 14, wherein the cristobalite content was determined through use of the LH method.

16. A method of manufacturing a diatomite product, the method comprising:

selecting a diatomite ore that includes more than about 2.6 wt% aluminum in mineral form or more than about 5 wt% as aluminum oxide; and

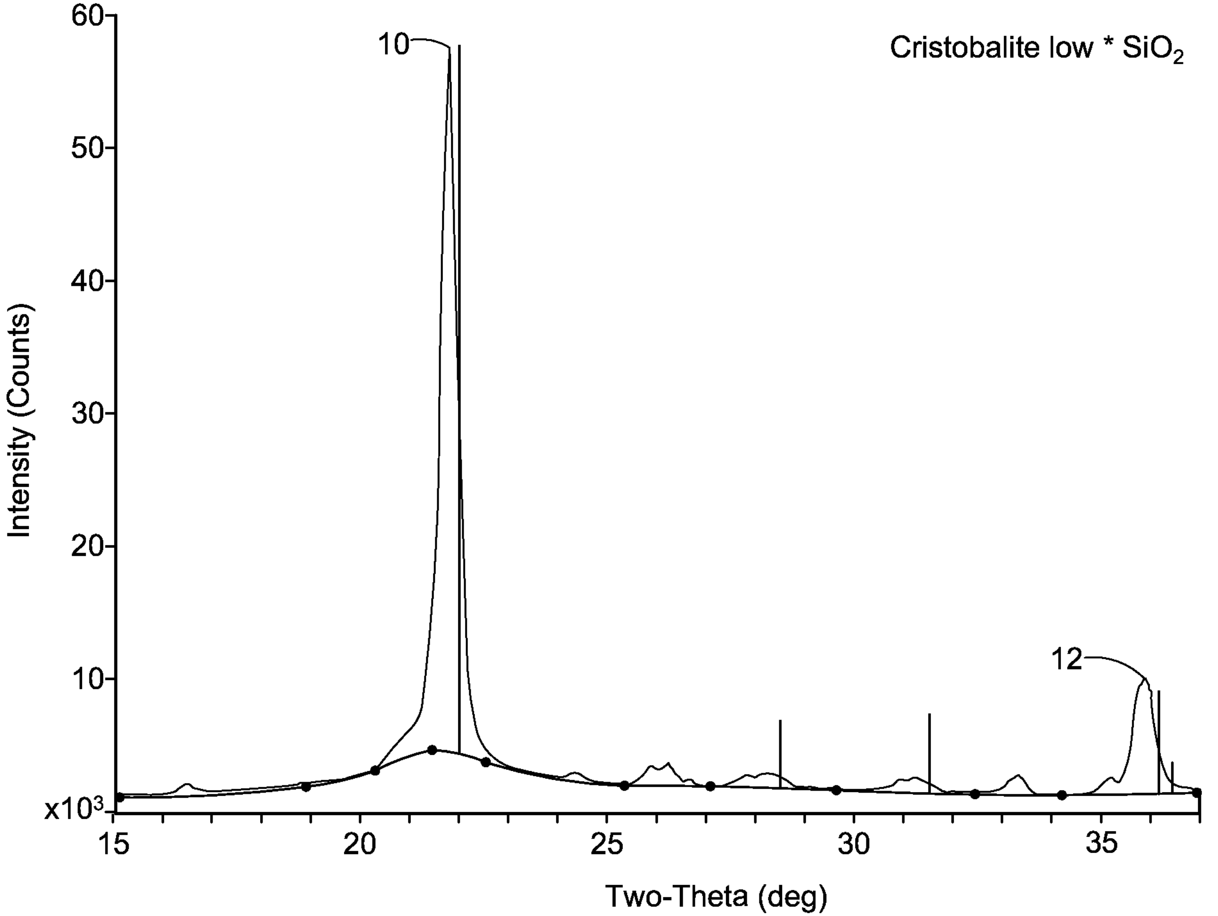
calcining the diatomite ore with a sodium flux,

wherein the diatomite product manufactured comprises sodium flux-calcined diatomite that has a crystalline silica content of less than about 1 wt% and a permeability between 0.8 darcy and about 30 darcy.



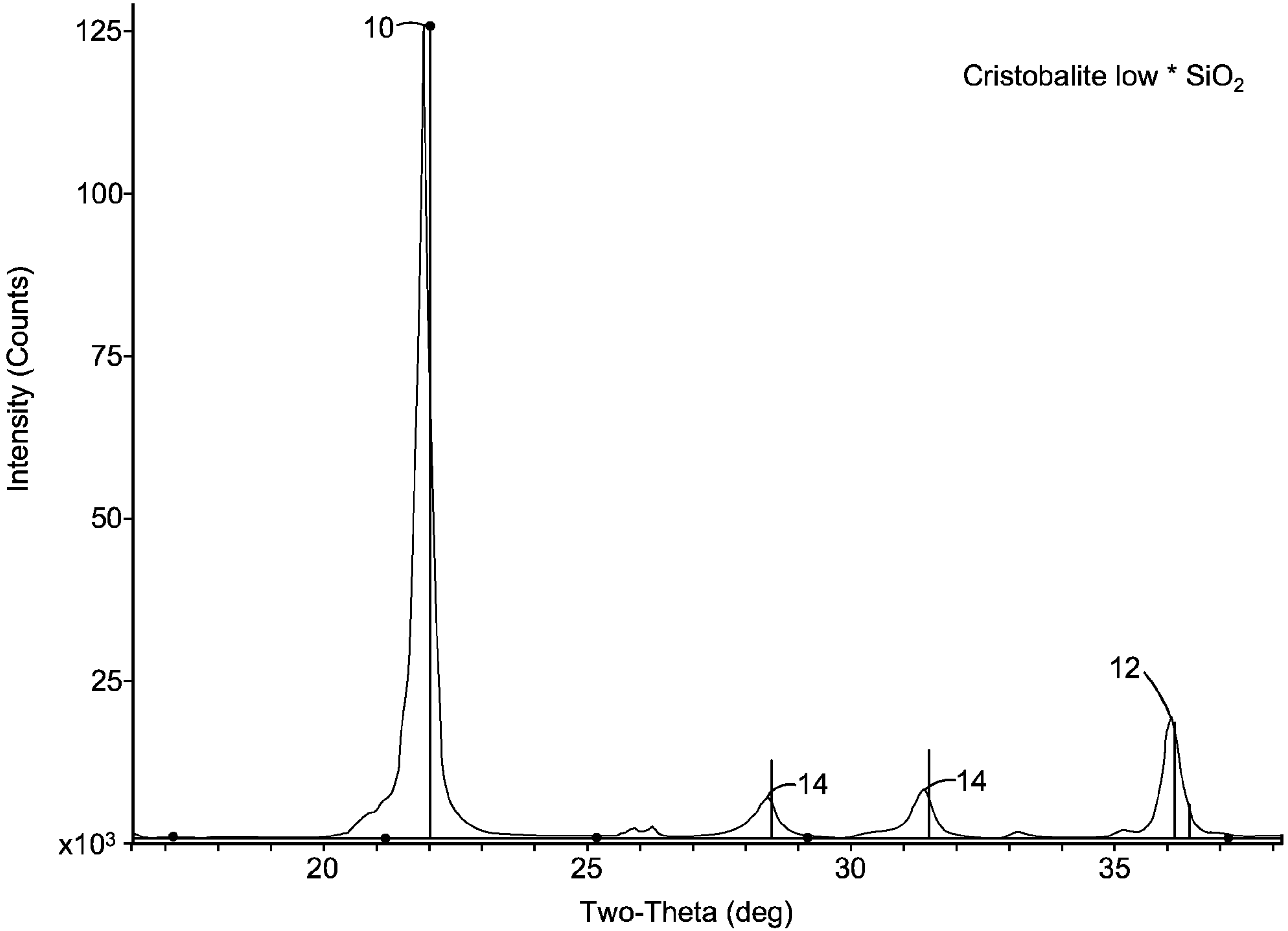
XRD Pattern of Celite 501 (sample # 18362) with Cristobalite Phase plus minor (1 to 2%) Feldspars

FIG. 1



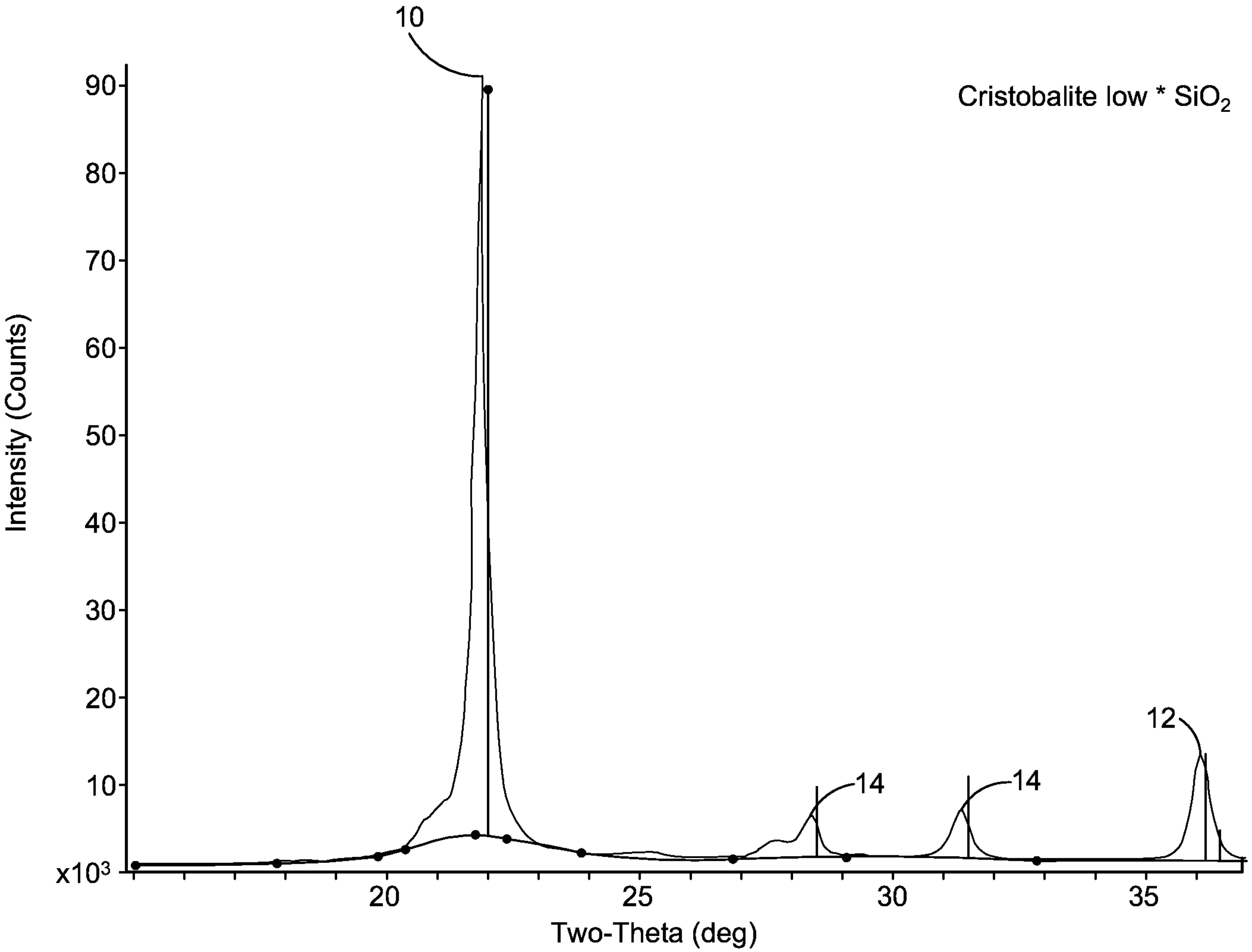
XRD Pattern of FP-4 (2H11B4) Showing Opal-C Phase plus Feldspars and possible Hematite

FIG. 2



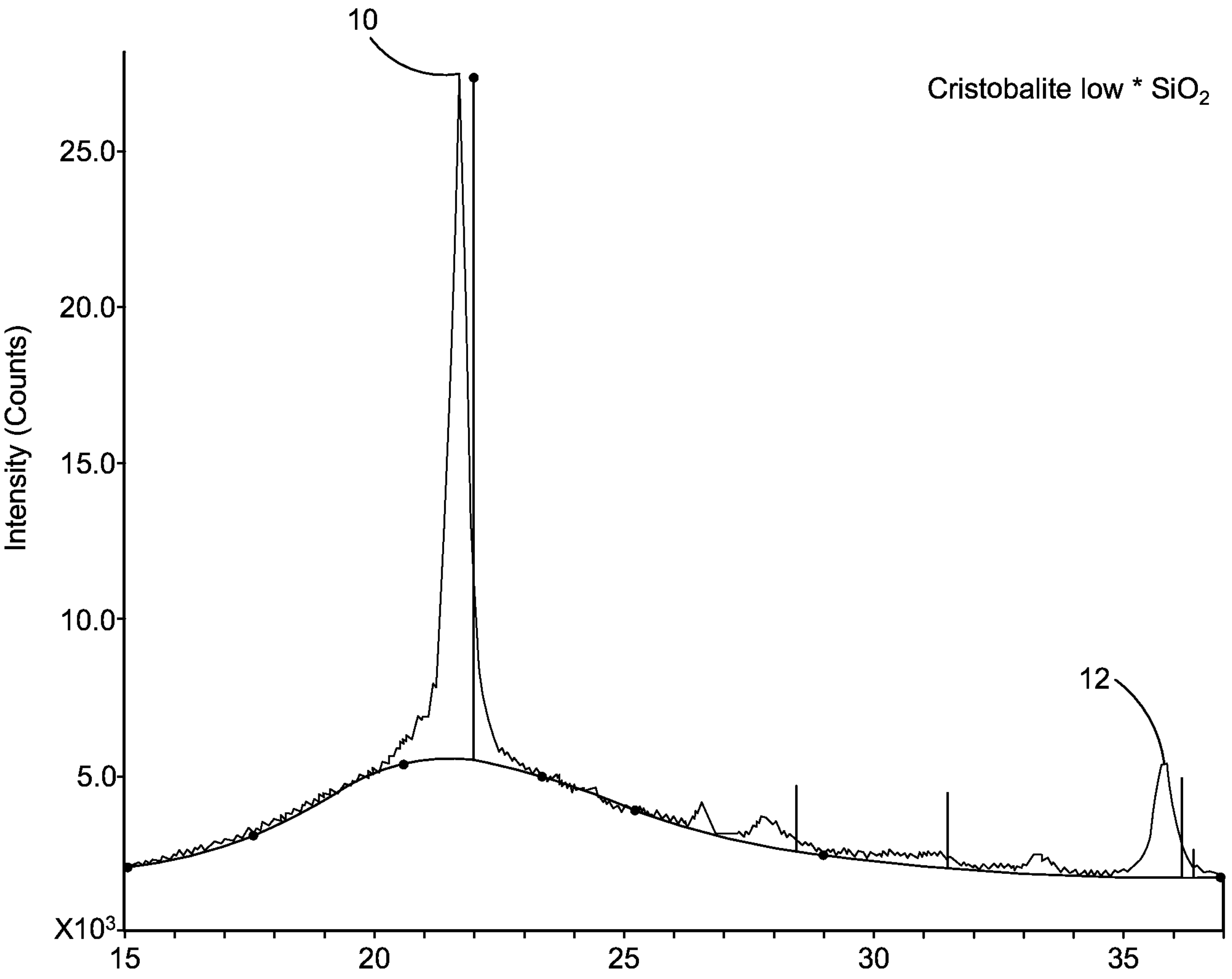
XRD Pattern of FP-6 (211F1) Showing Cristobalite Phase plus Feldspars

FIG. 3



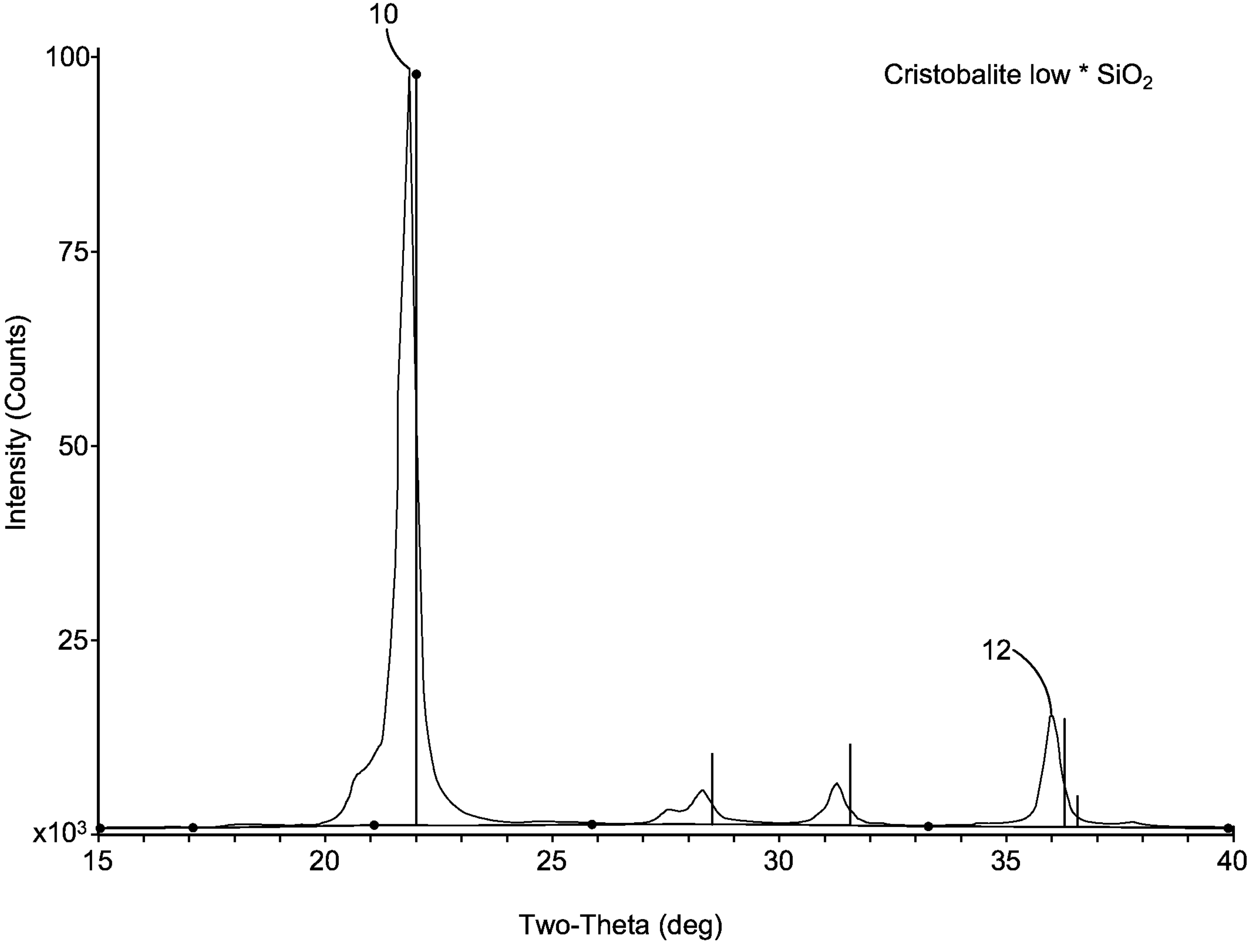
XRD Pattern of Dicalite 4500 Showing Cristobalite Phase plus minor Feldspars

FIG. 4



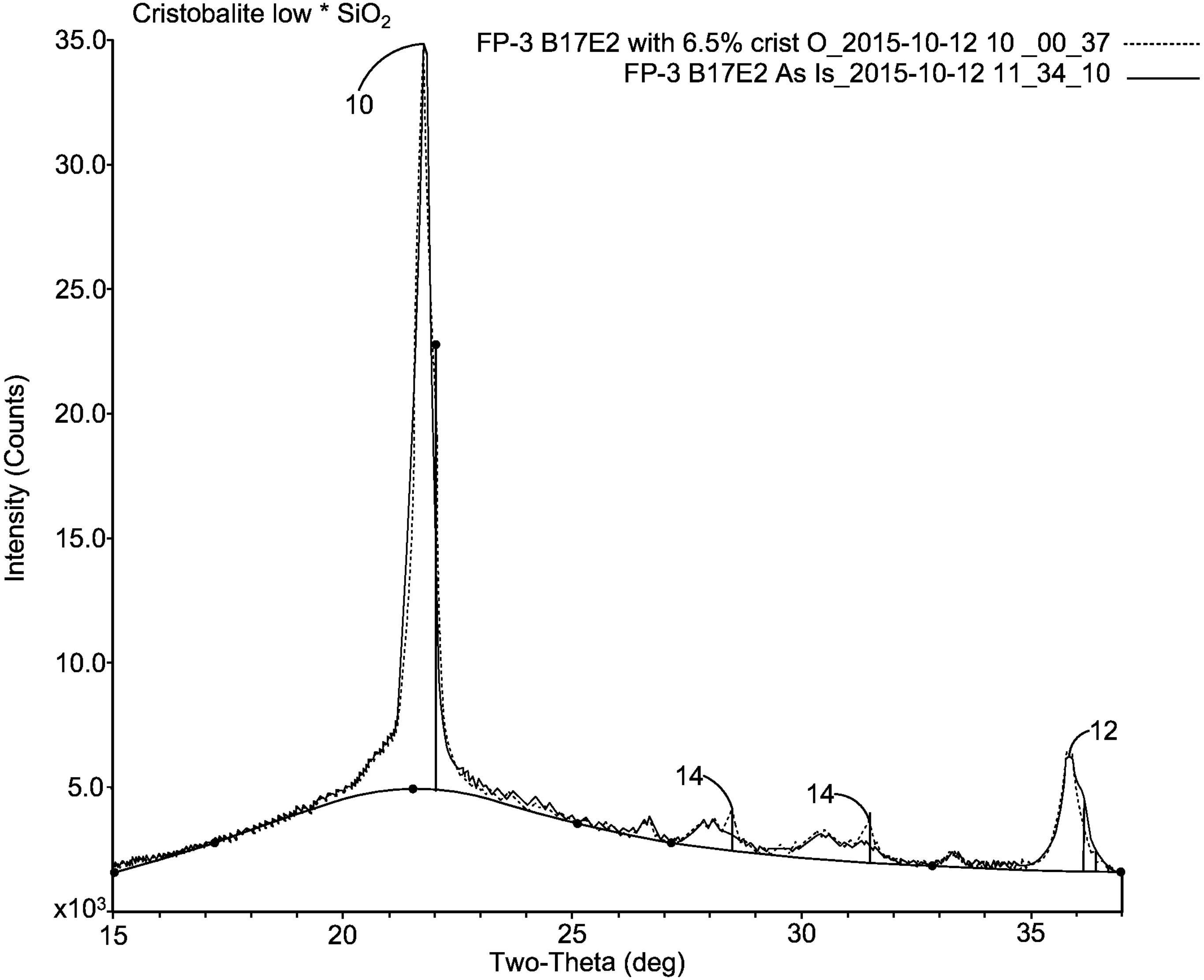
X-ray Diffraction Pattern of Sample "FP-2 B12C0"

FIG. 5



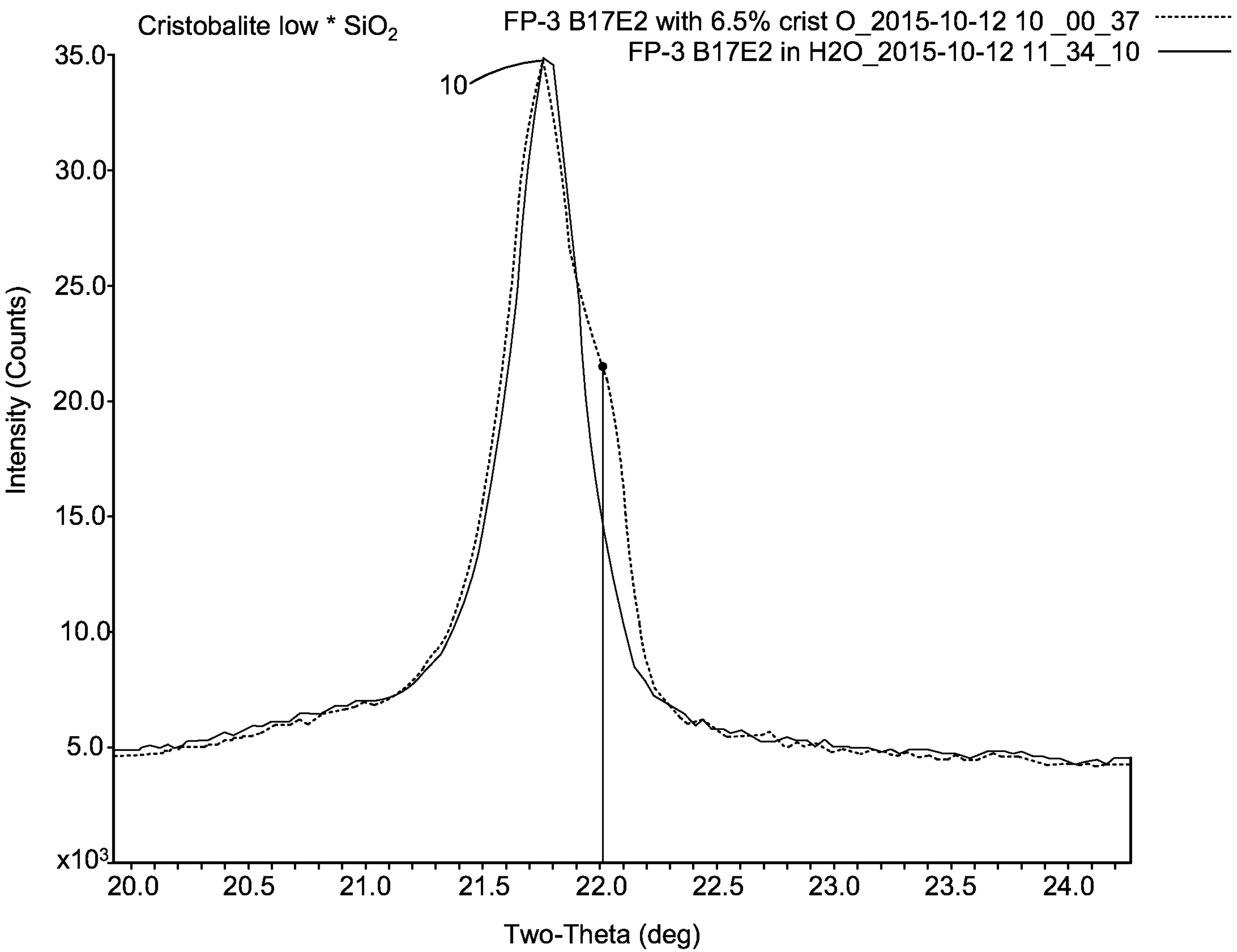
XRD Pattern of Sample "Celabrite 2A20A13F"

FIG. 6



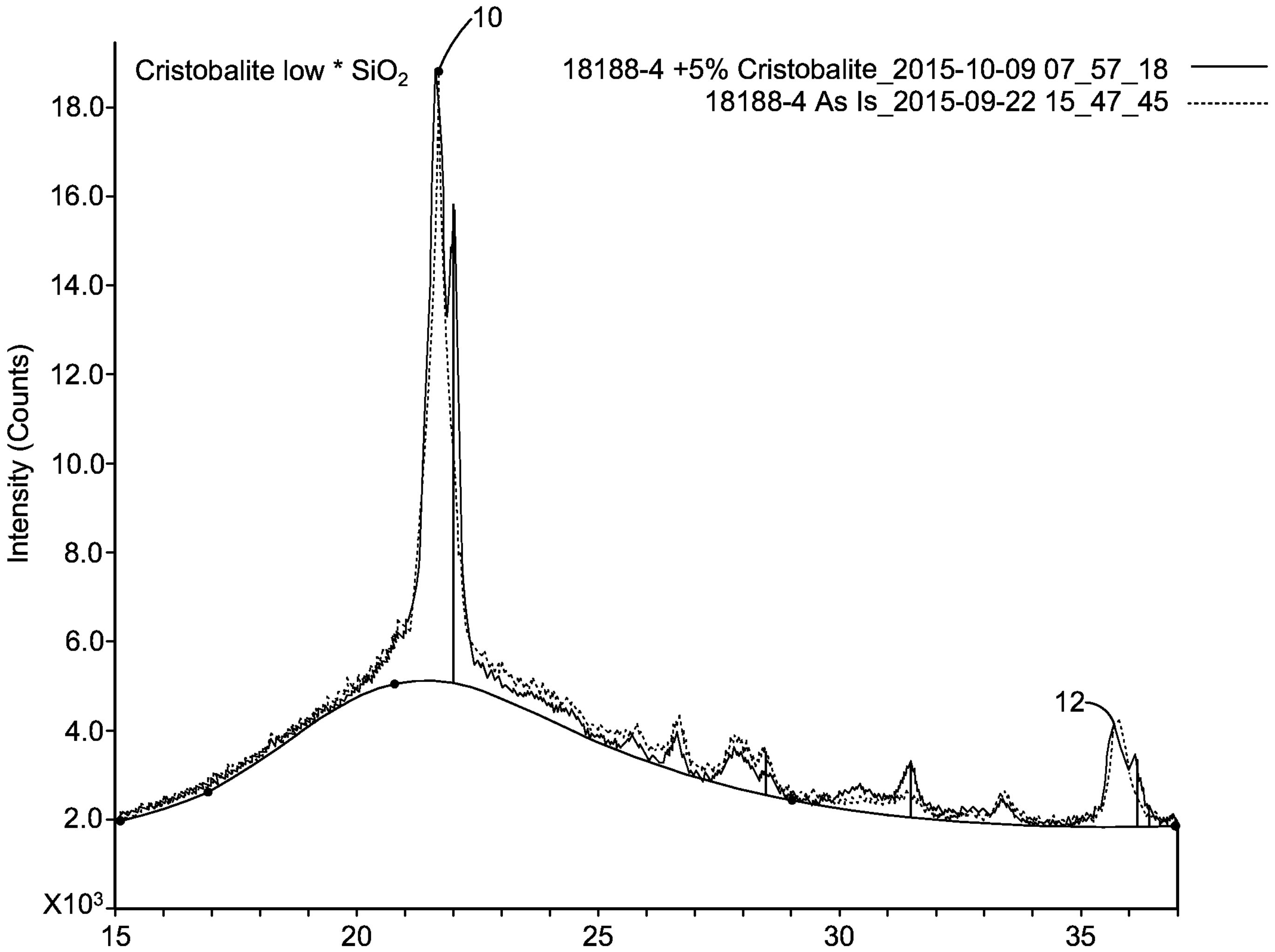
XRD Patterns of Sample "FP-3 B17E2" with and without Cristobalite Spike

FIG. 7



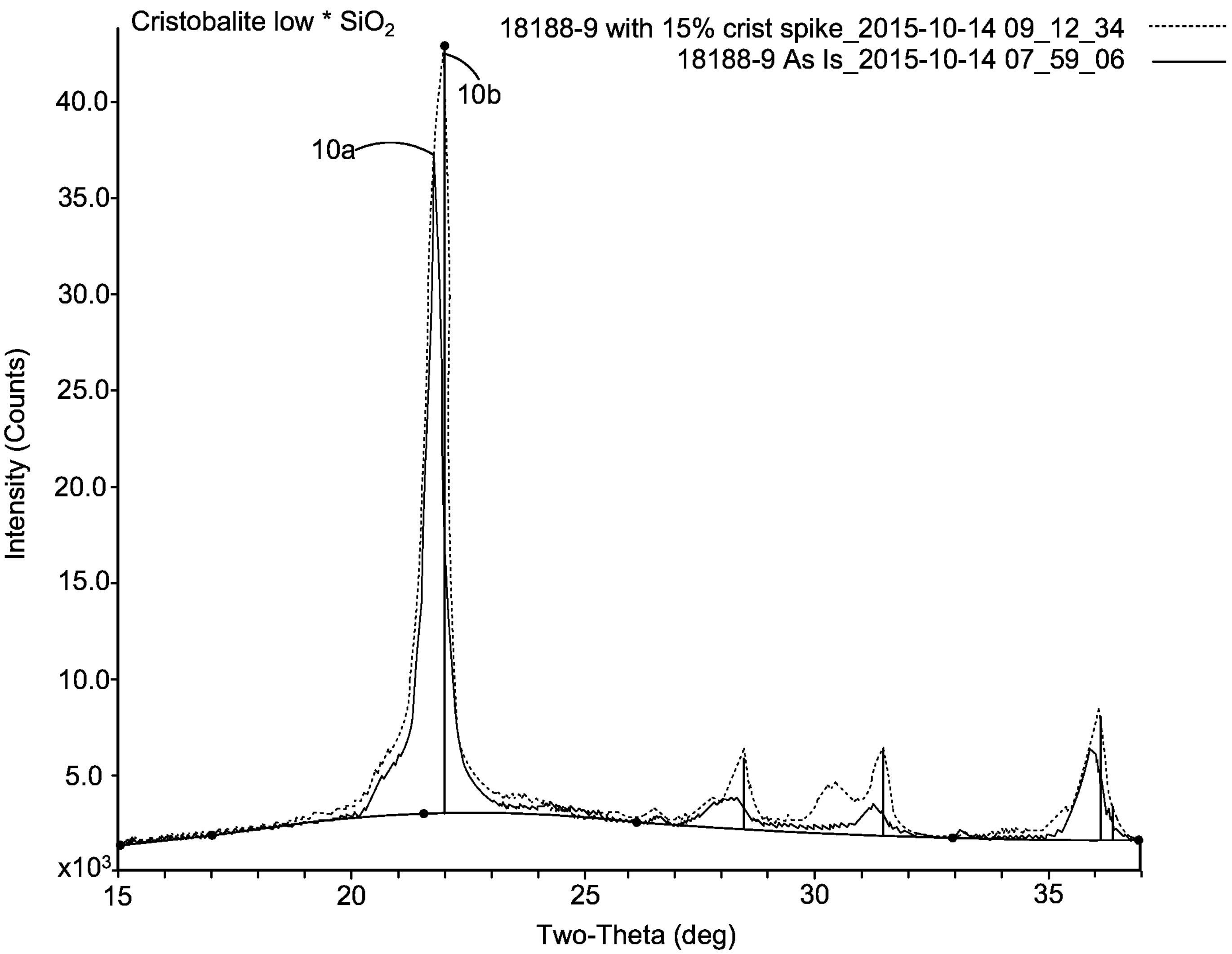
XRD Primary Peak of Sample "FP-3 B17E2" with and without Cristobalite Spike

FIG. 8



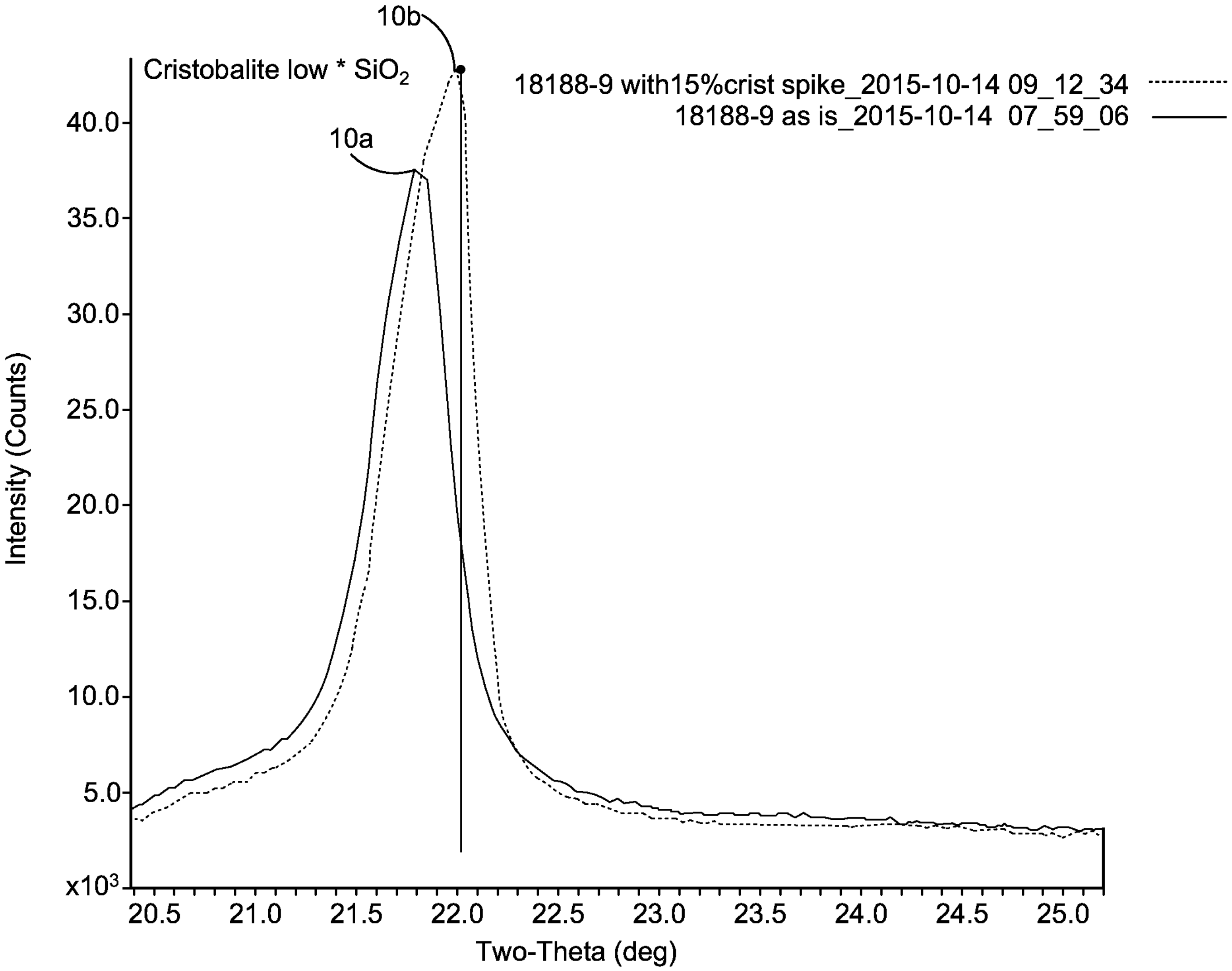
XRD Pattern of 18188-4 with 5% Cristobalite Spike

FIG. 9



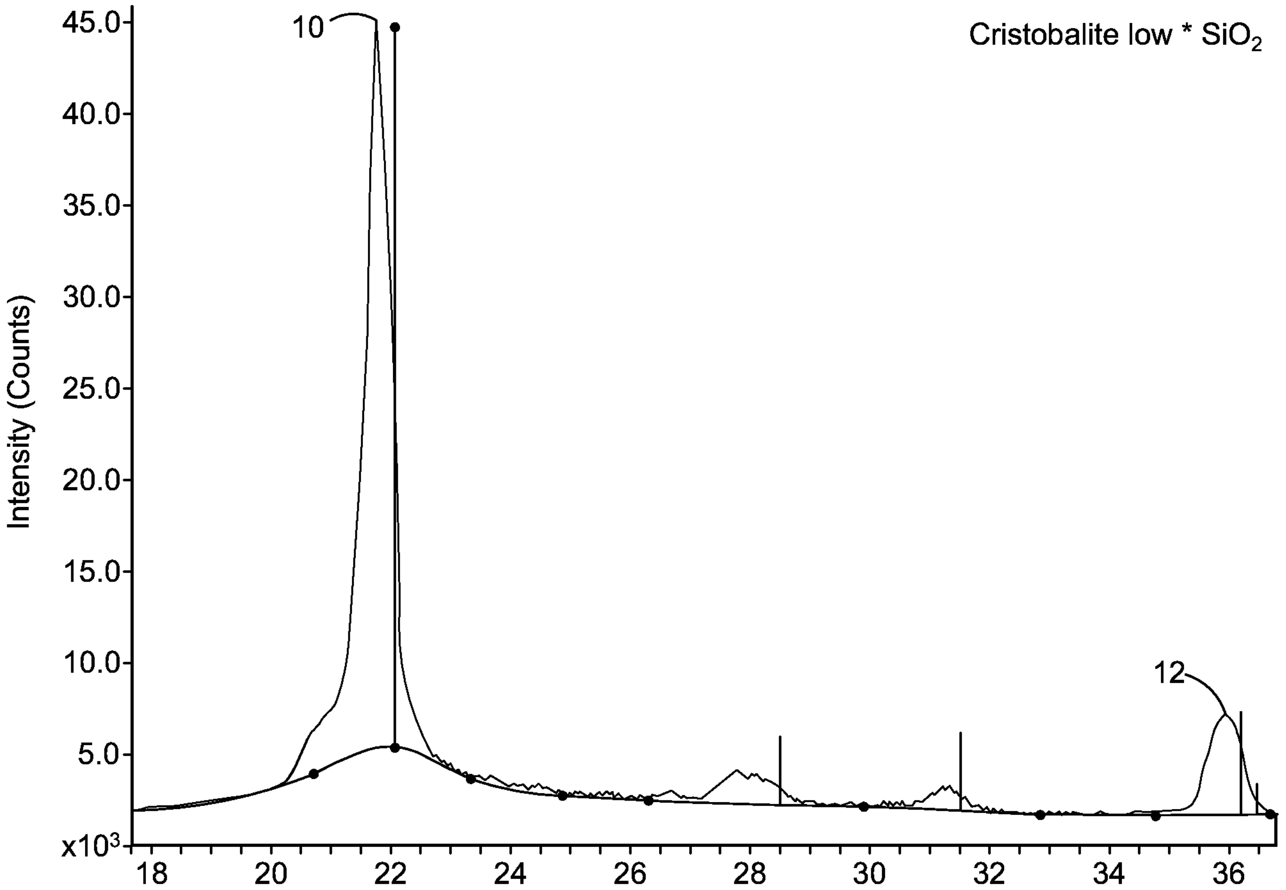
XRD Patterns of Sample 18188-9 with 15% Cristobalite Spike

FIG. 10



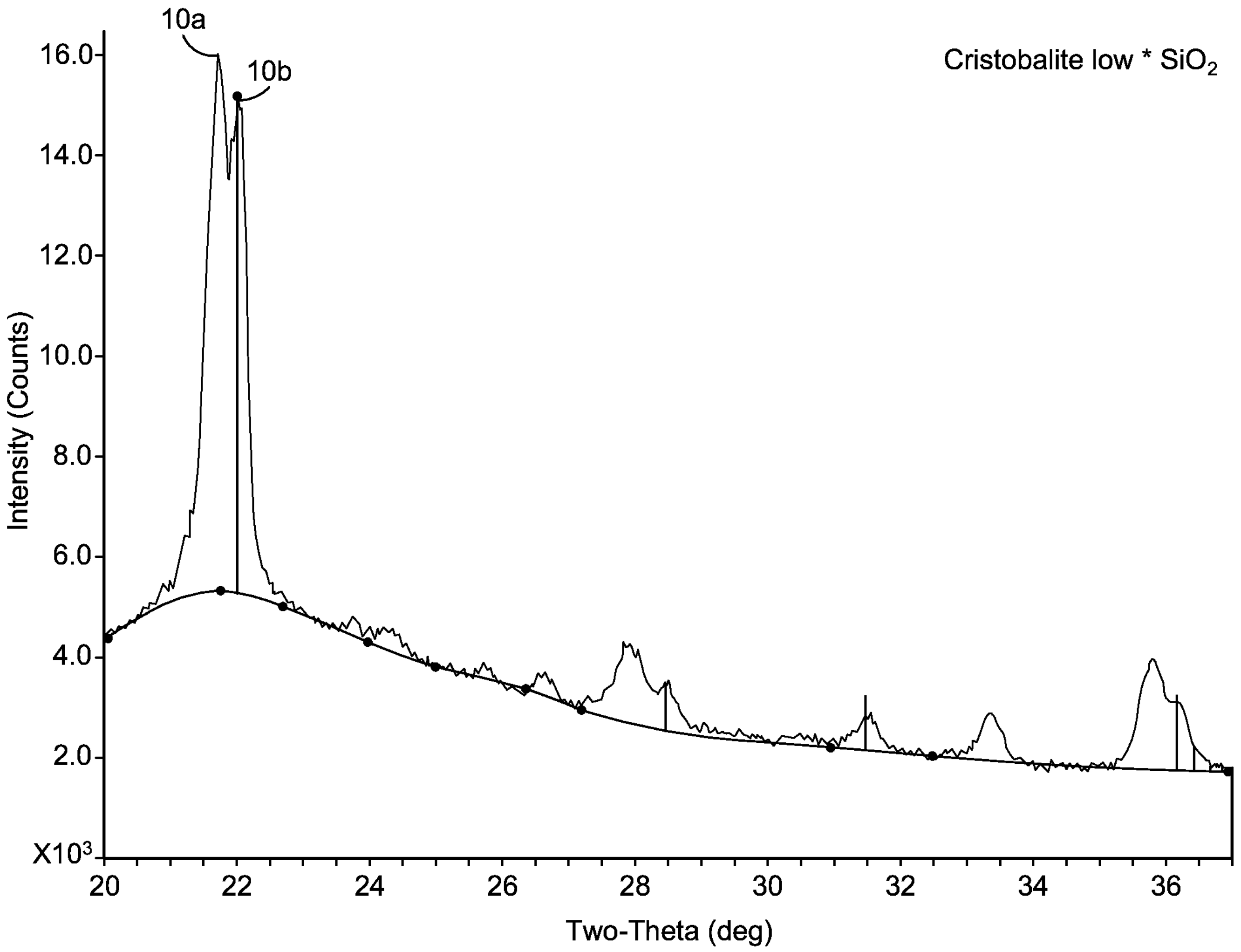
XRD Pattern of Sample 18188-9 Showing only the Primary Peak

FIG. 11



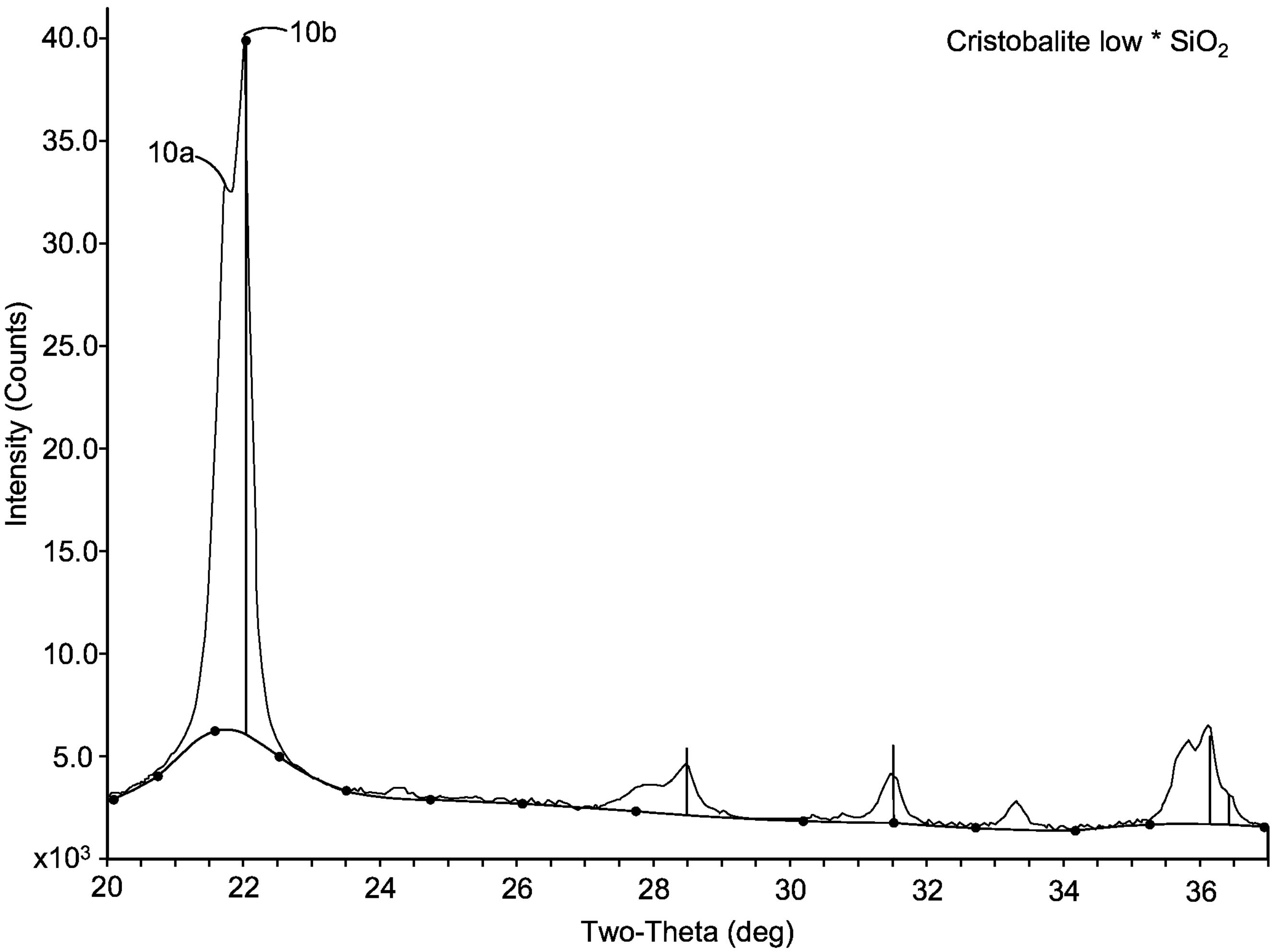
XRD Pattern of Sample "S31 15-4-7B"

FIG. 12



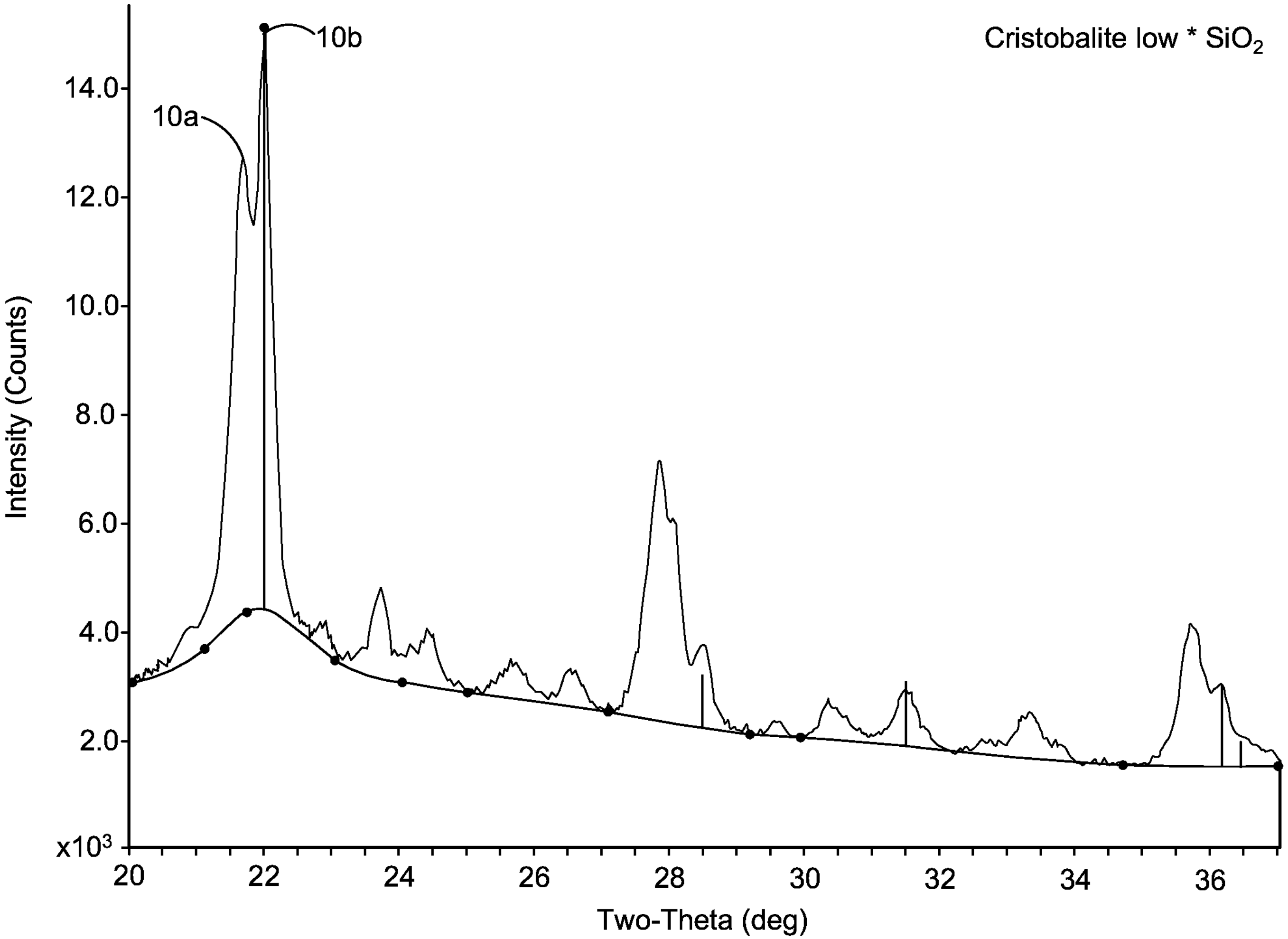
Diffraction Pattern of Sample HV2BH-E with 5% Cristobalite spike (NIST 1879A)

FIG. 13



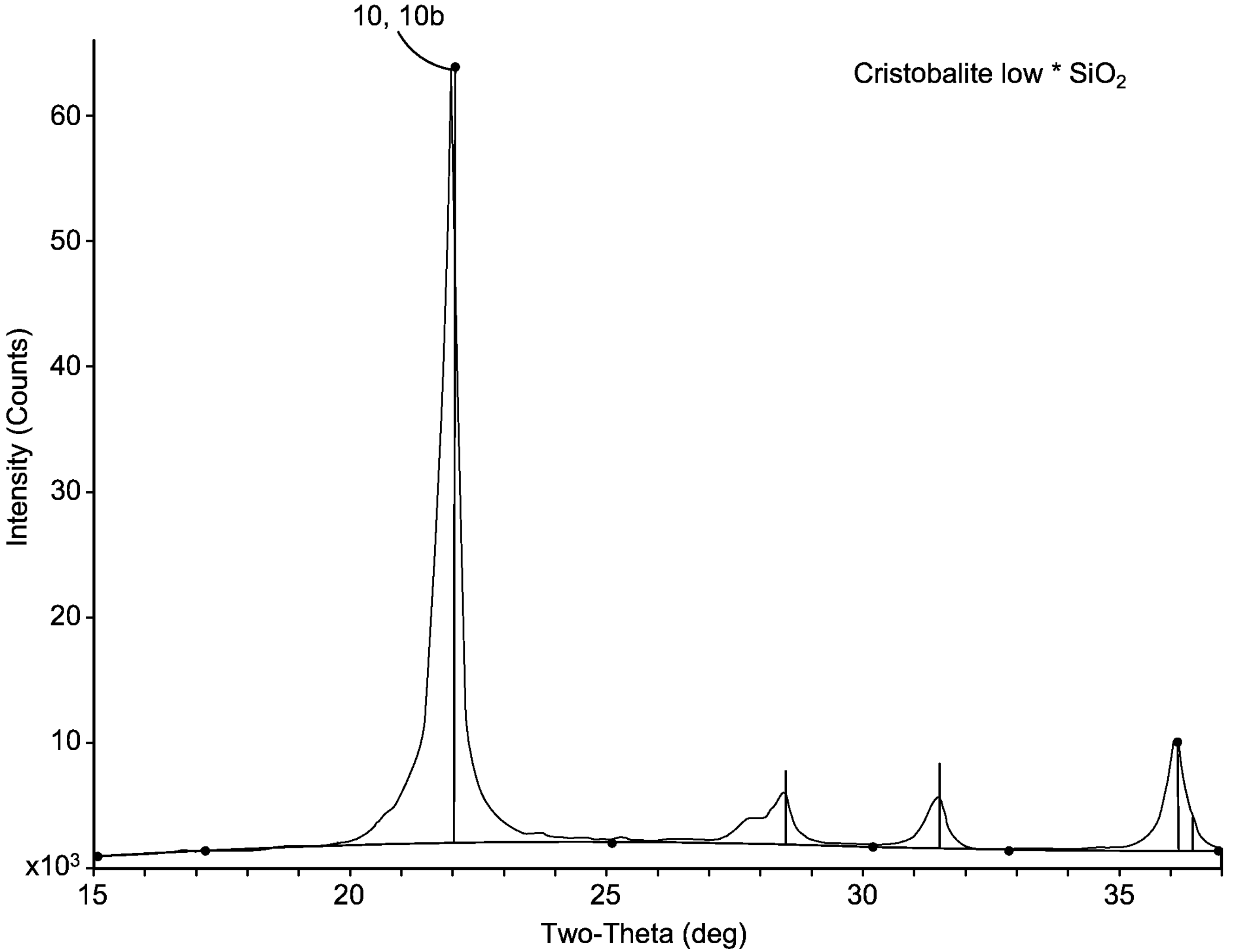
Diffraction Pattern of Sample HV2-F with 21% Cristobalite spike (NIST 1879A)

FIG. 14



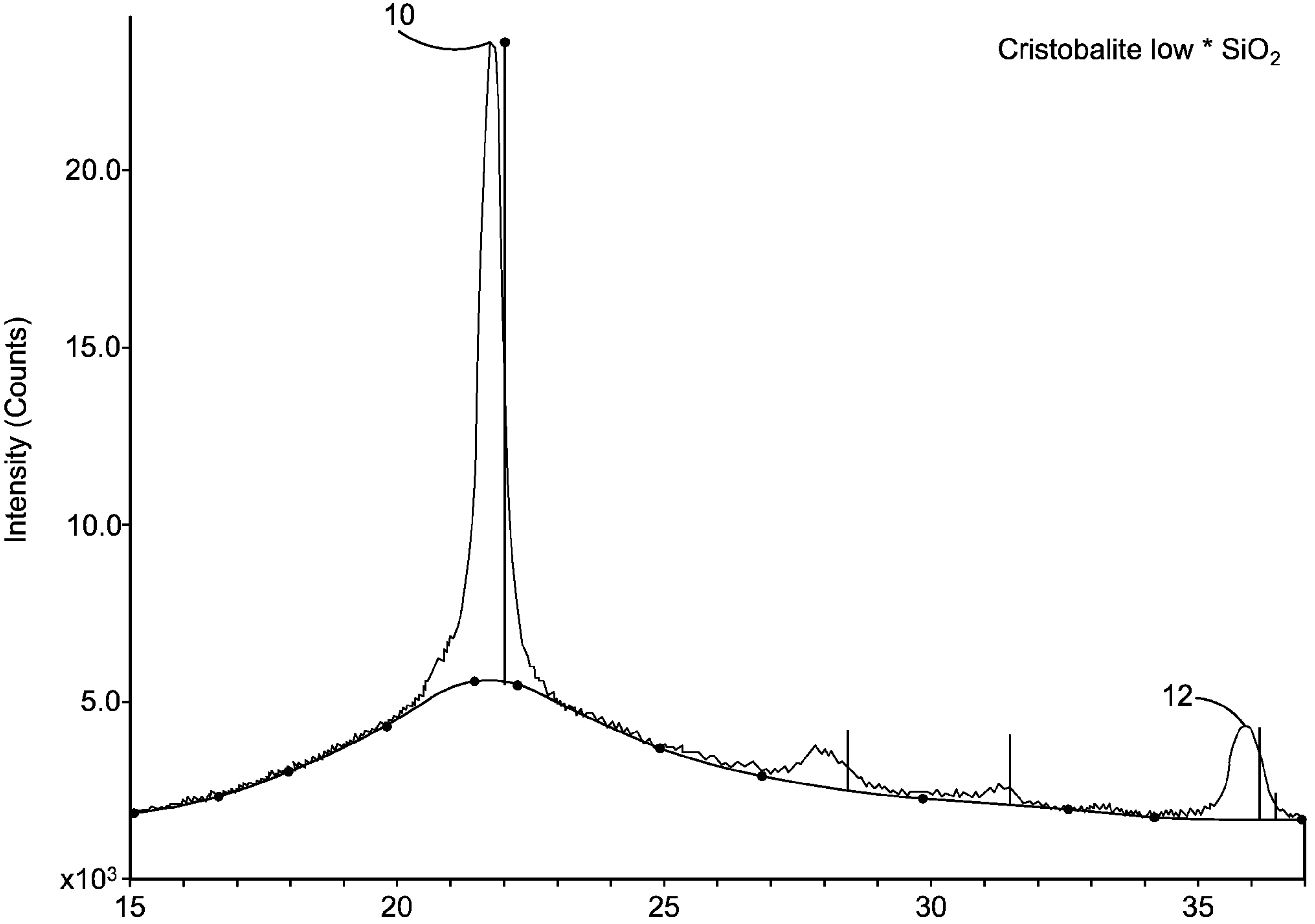
XRD Pattern of Sample S3115E with 5% Cristobalite spike (NIST 1879A)

FIG. 15



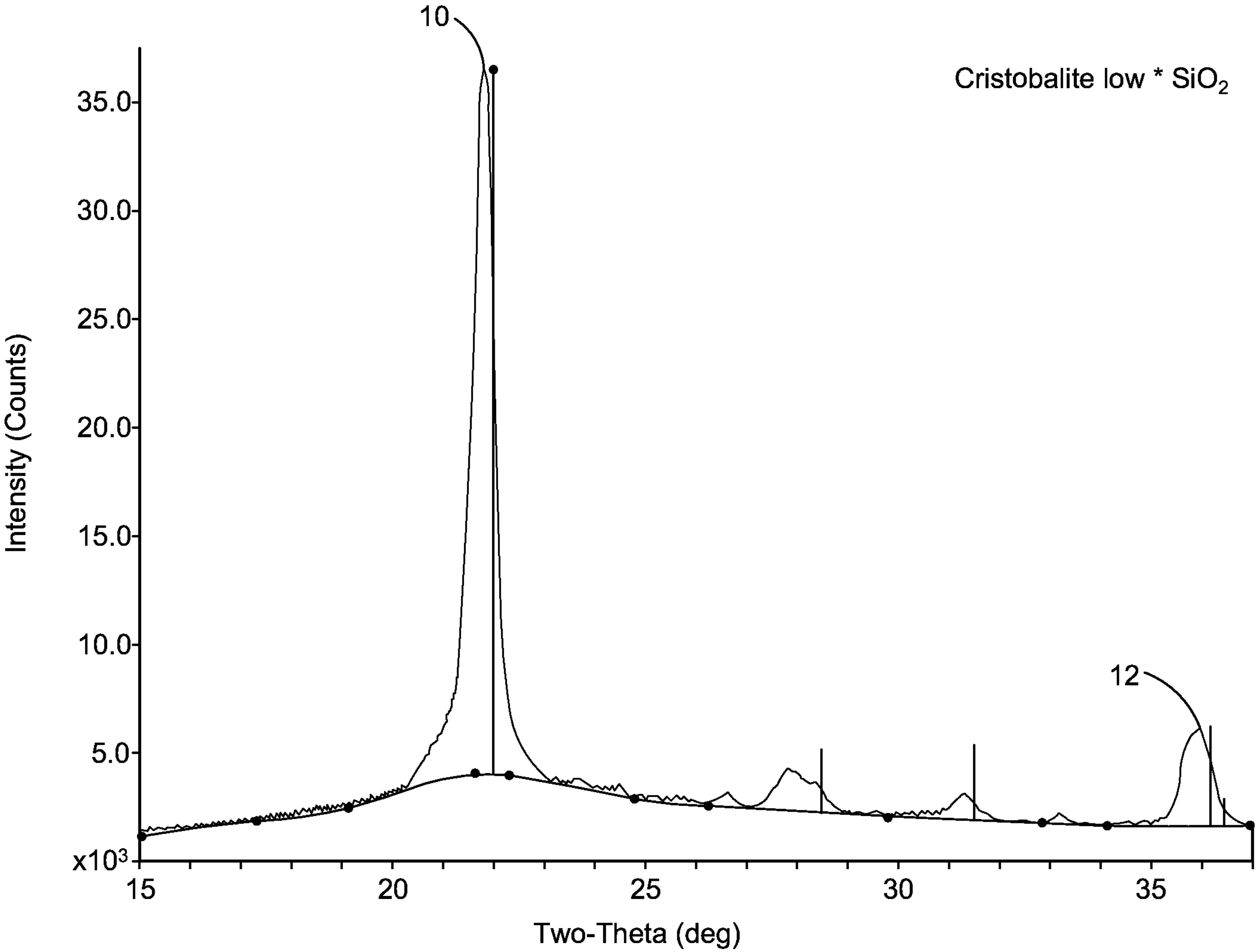
XRD Pattern of Sample LCS3-H with 28% Cristobalite spike (NIST 1879A)

FIG. 16



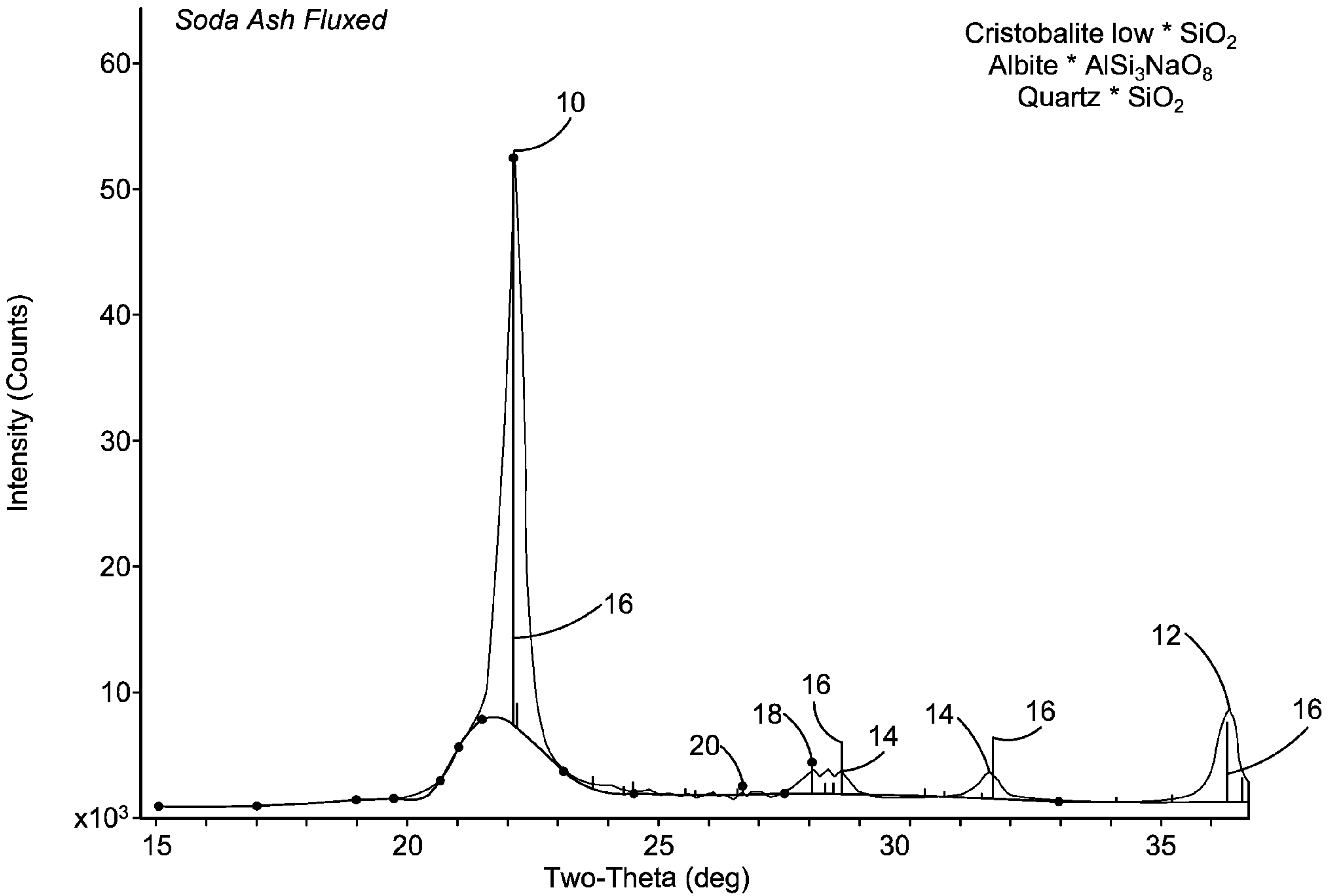
Diffraction Pattern of Sample FEBH Showing Opal-C plus minor Feldspar

FIG. 17



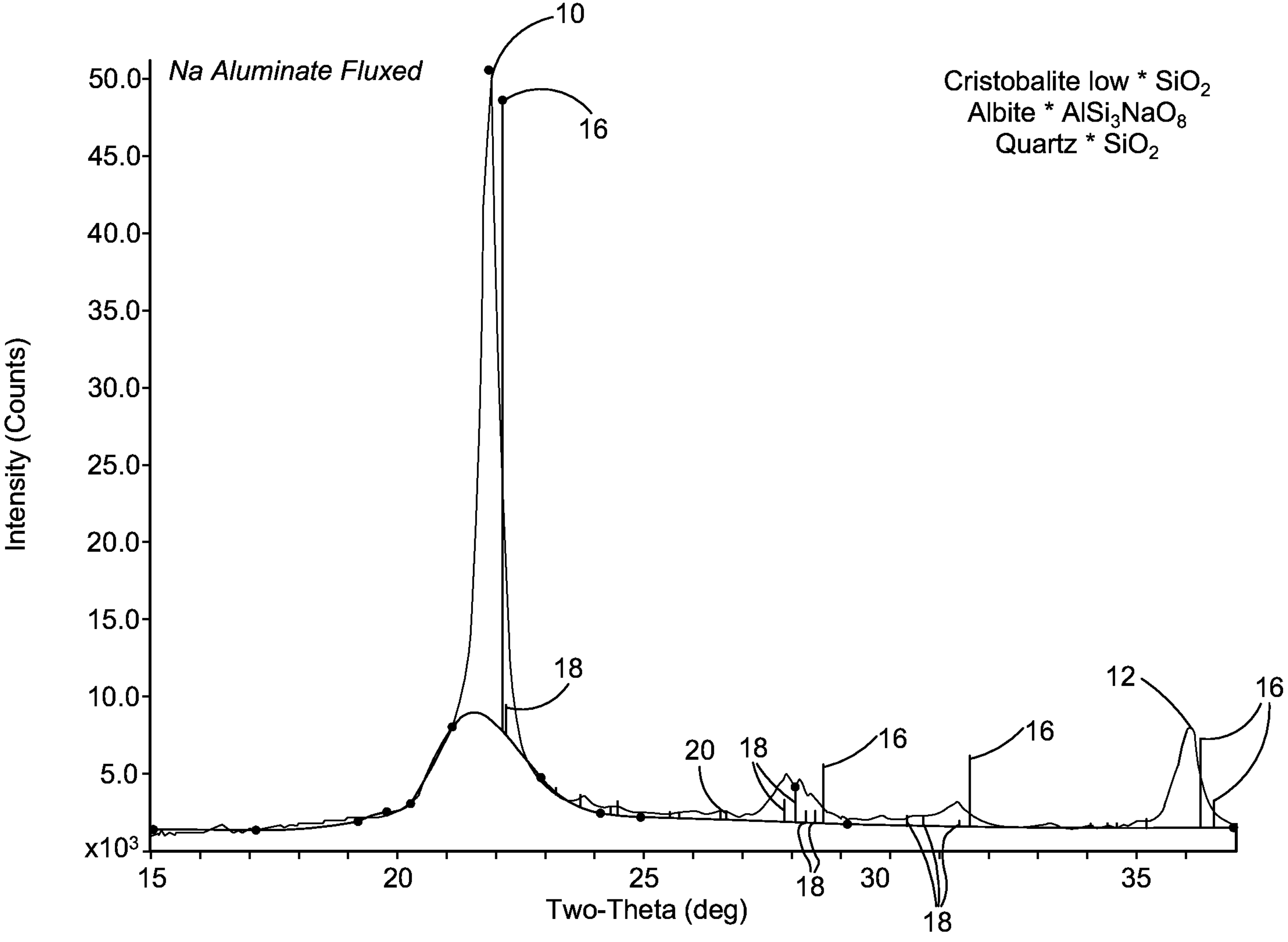
Diffraction Pattern of Example 16 (KD 15:30) Showing Opal-C plus Feldspar

FIG. 18



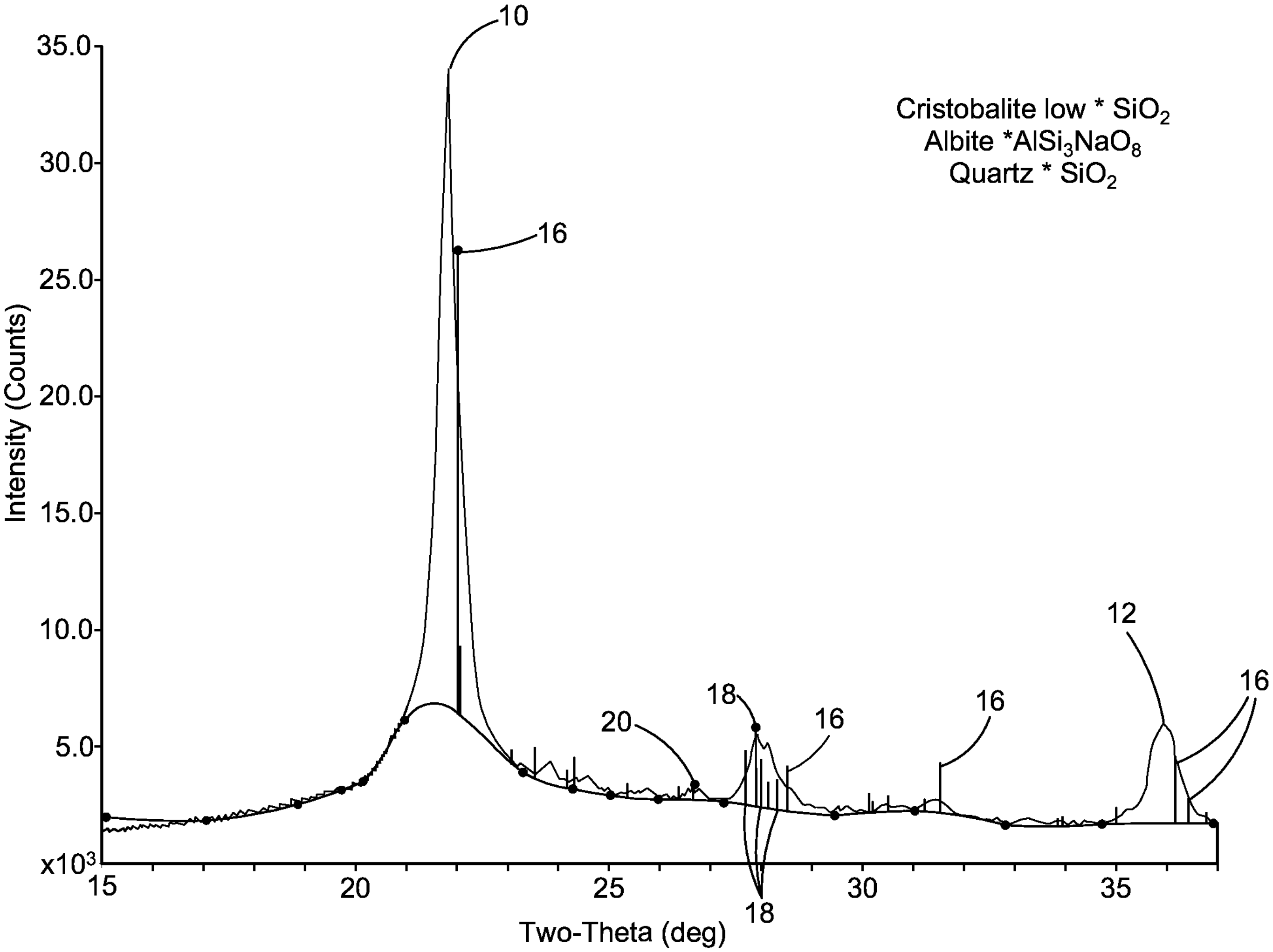
XRD Scan Pattern of Soda of Ash Flux-Calcined Diatomite
made from LCS-3, Showing the Presence of Cristobalite

FIG. 19



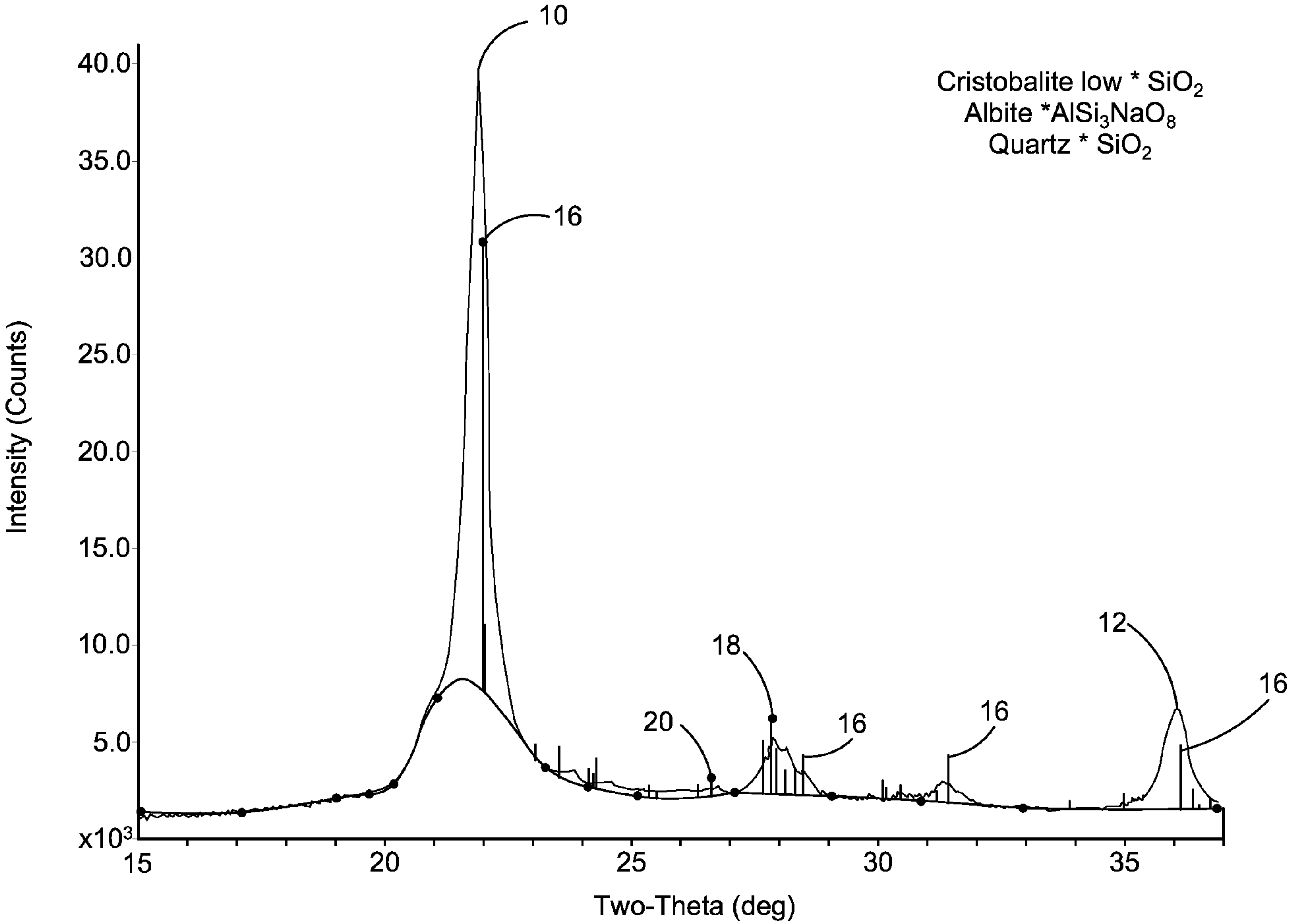
XRD Scan Pattern of Sodium Aluminate Flux-Calcined Diatomite made from LCS-3, Showing the Presence of Opal-C and 0.1 wt% Quartz

FIG. 20



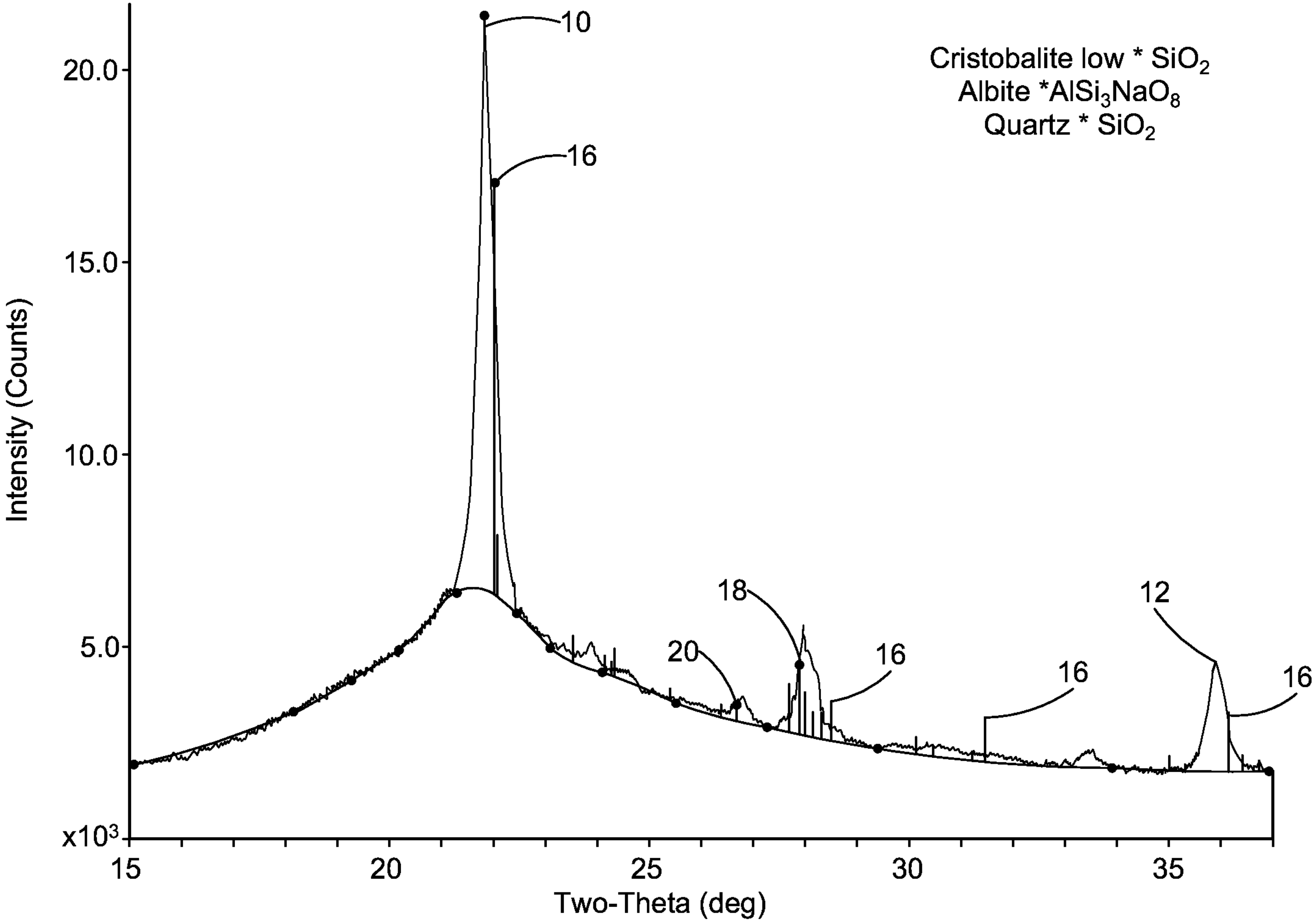
XRD scan pattern of soda ash and 0.3μ alumina flux-calcined diatomite made from LCS-3, showing the presence of opal-C and 0.3 wt% quartz

FIG. 21



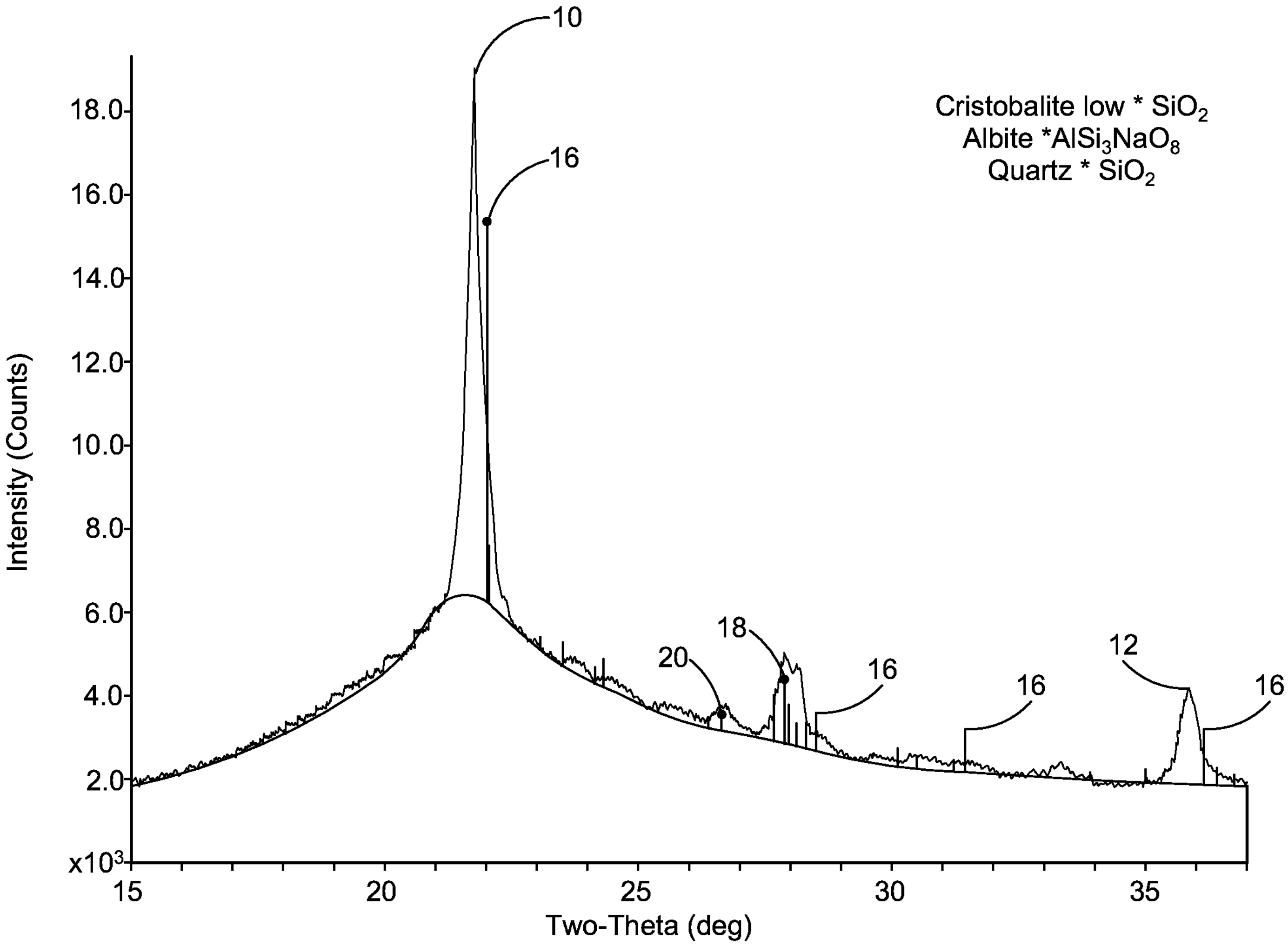
XRD scan pattern of soda ash and 1.7µ ATH flux-calcined diatomite made from LCS-3, showing the presence of cristobalite and <0.1 wt% quartz

FIG. 22



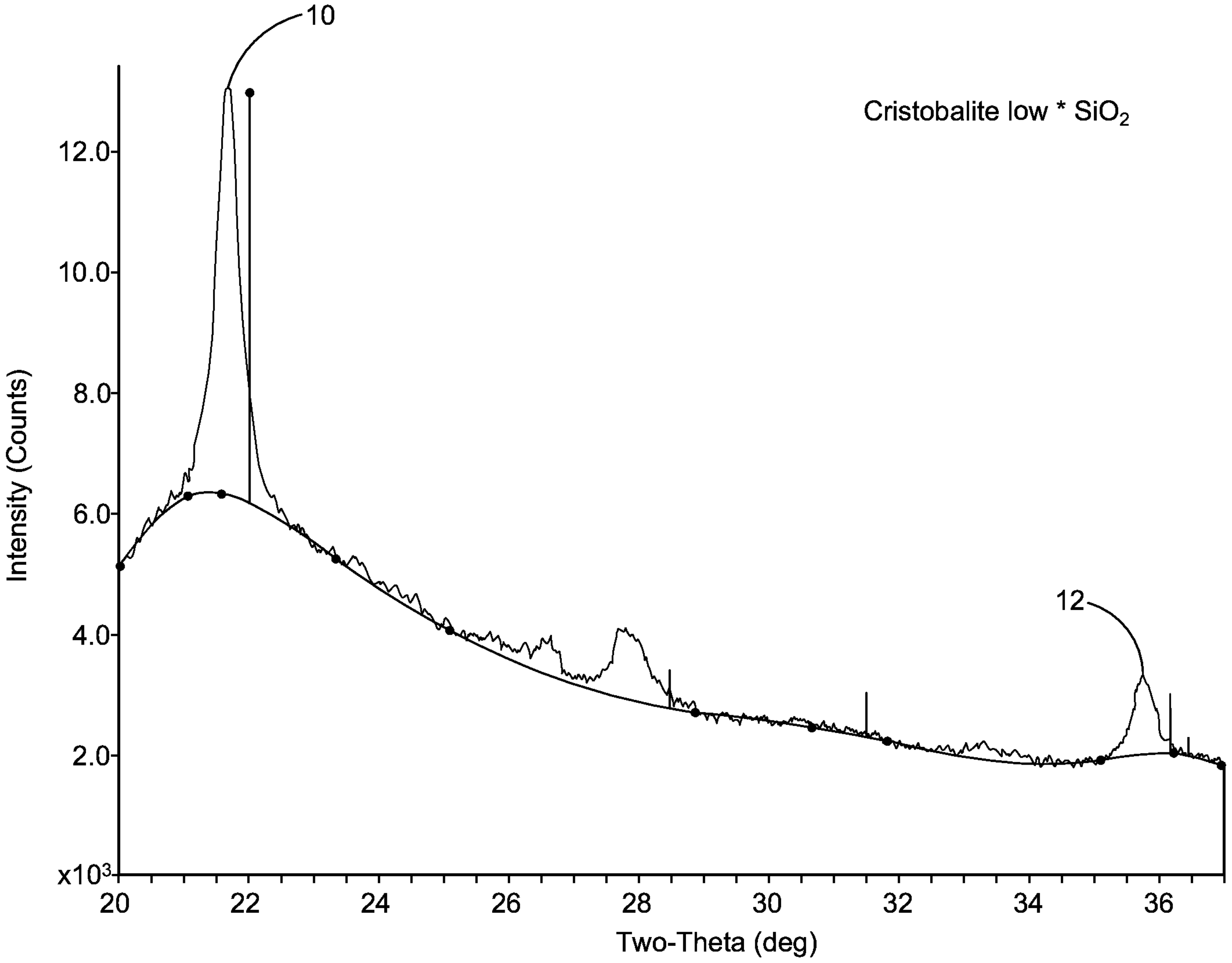
XRD scan pattern of calcined diatomite made from LCS-3, showing the presence of opal-C and 0.2 wt% quartz

FIG. 23



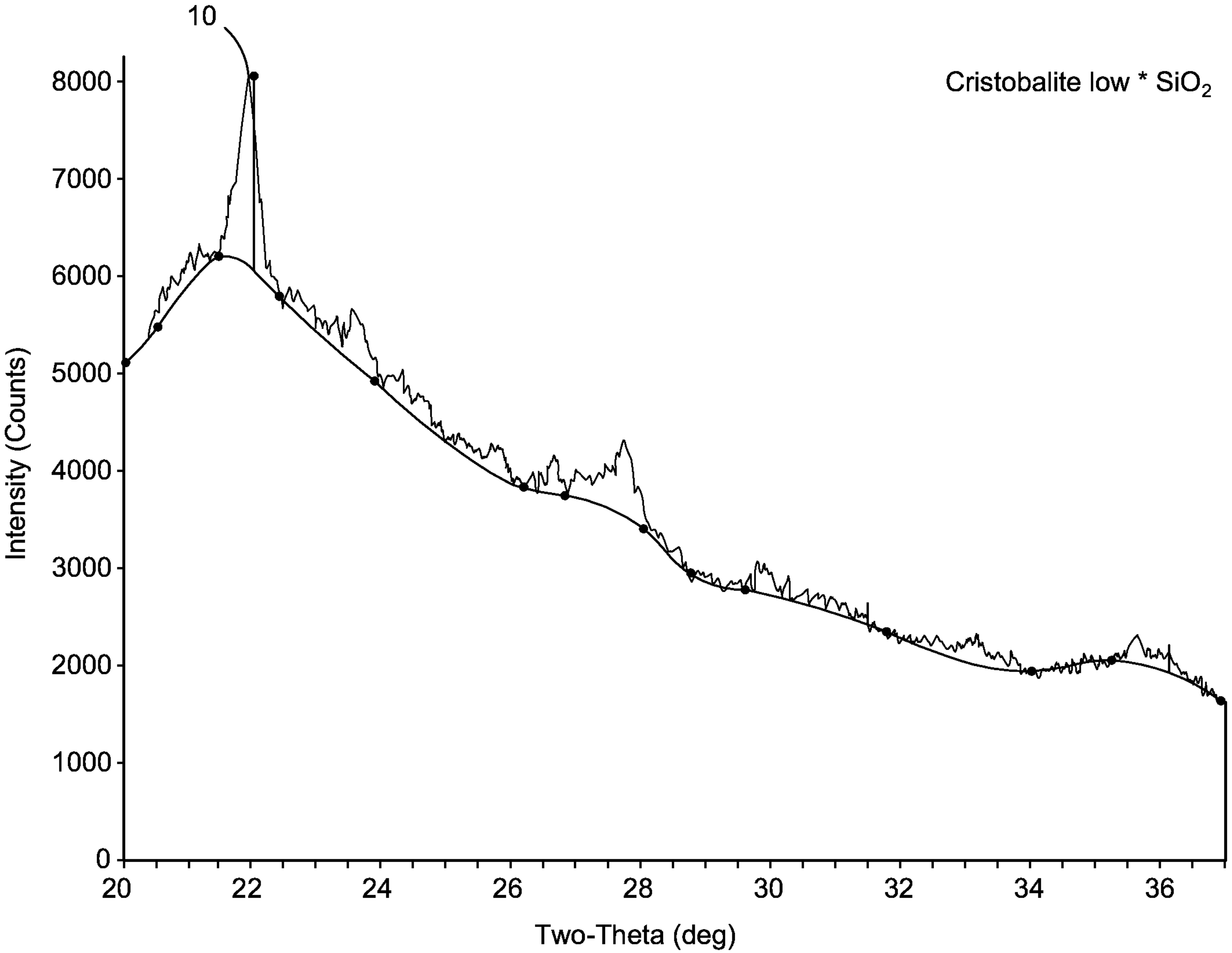
XRD scan pattern of calcined diatomite made from LCS-3, with ATH additive, showing the presence of opal-C and 0.25 wt% quartz

FIG. 24



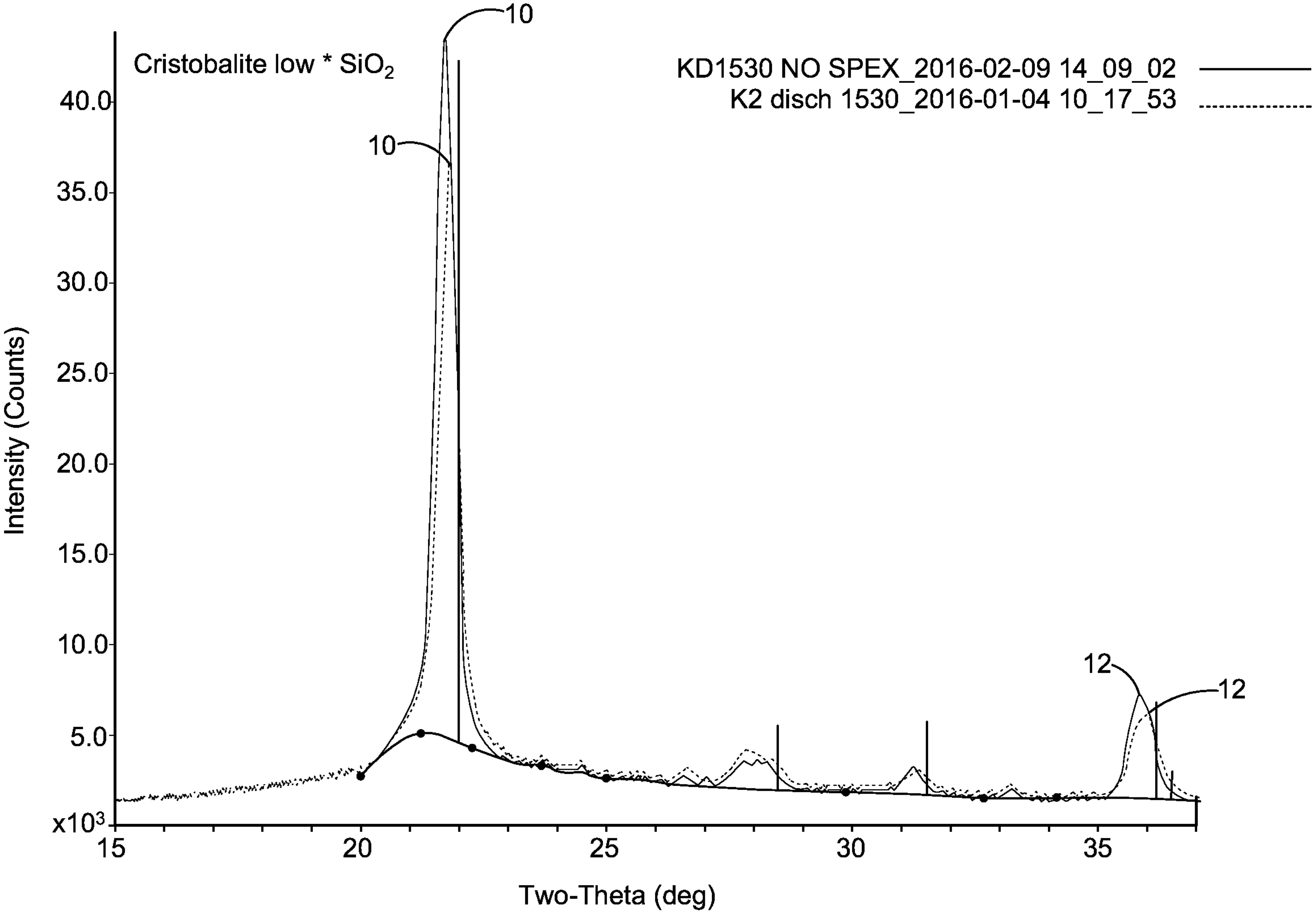
Diffraction pattern of control sample showing opal-C plus minor feldspar

FIG. 25



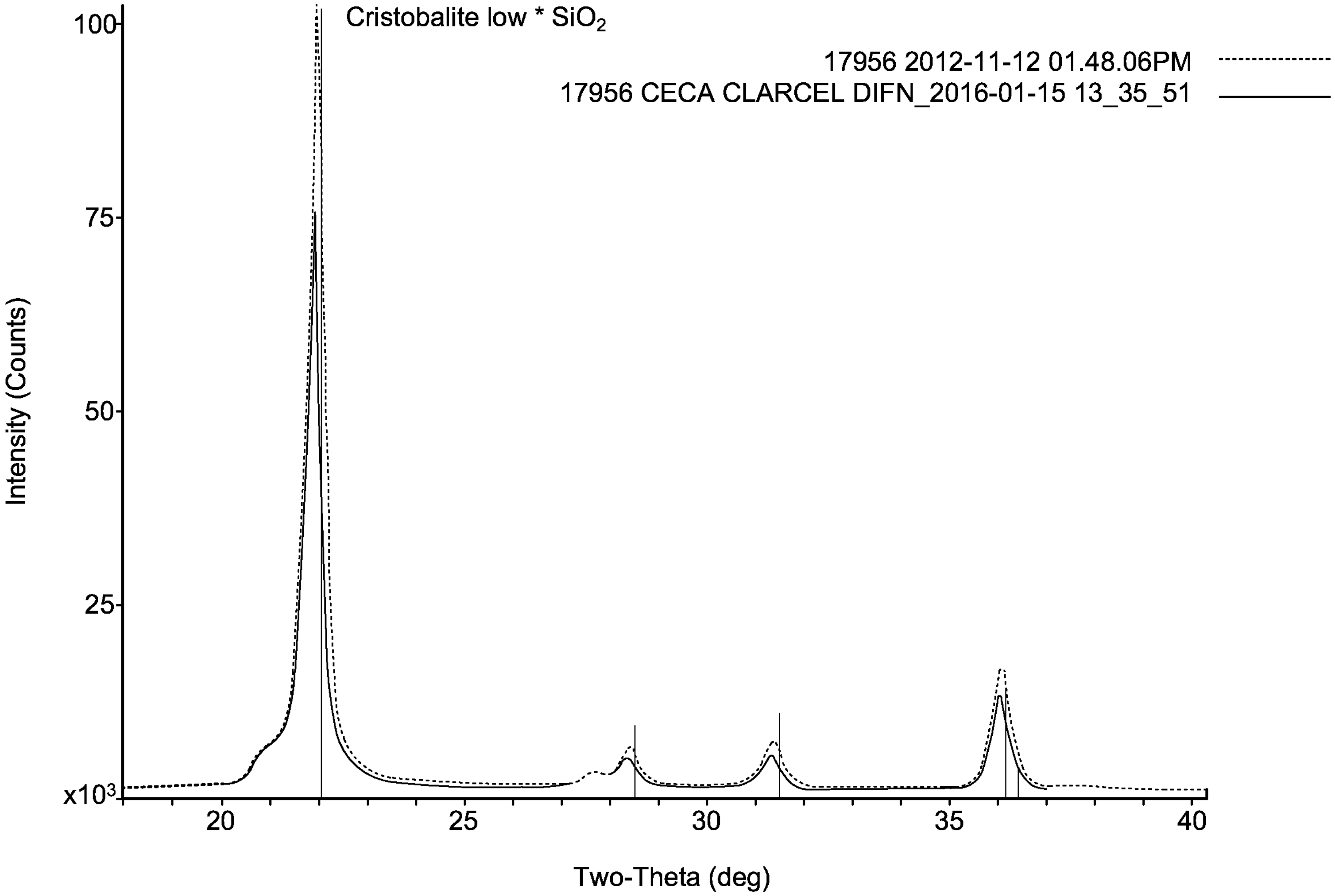
Diffraction pattern of test sample with 5% KASOLV showing possible cristobalite

FIG. 26



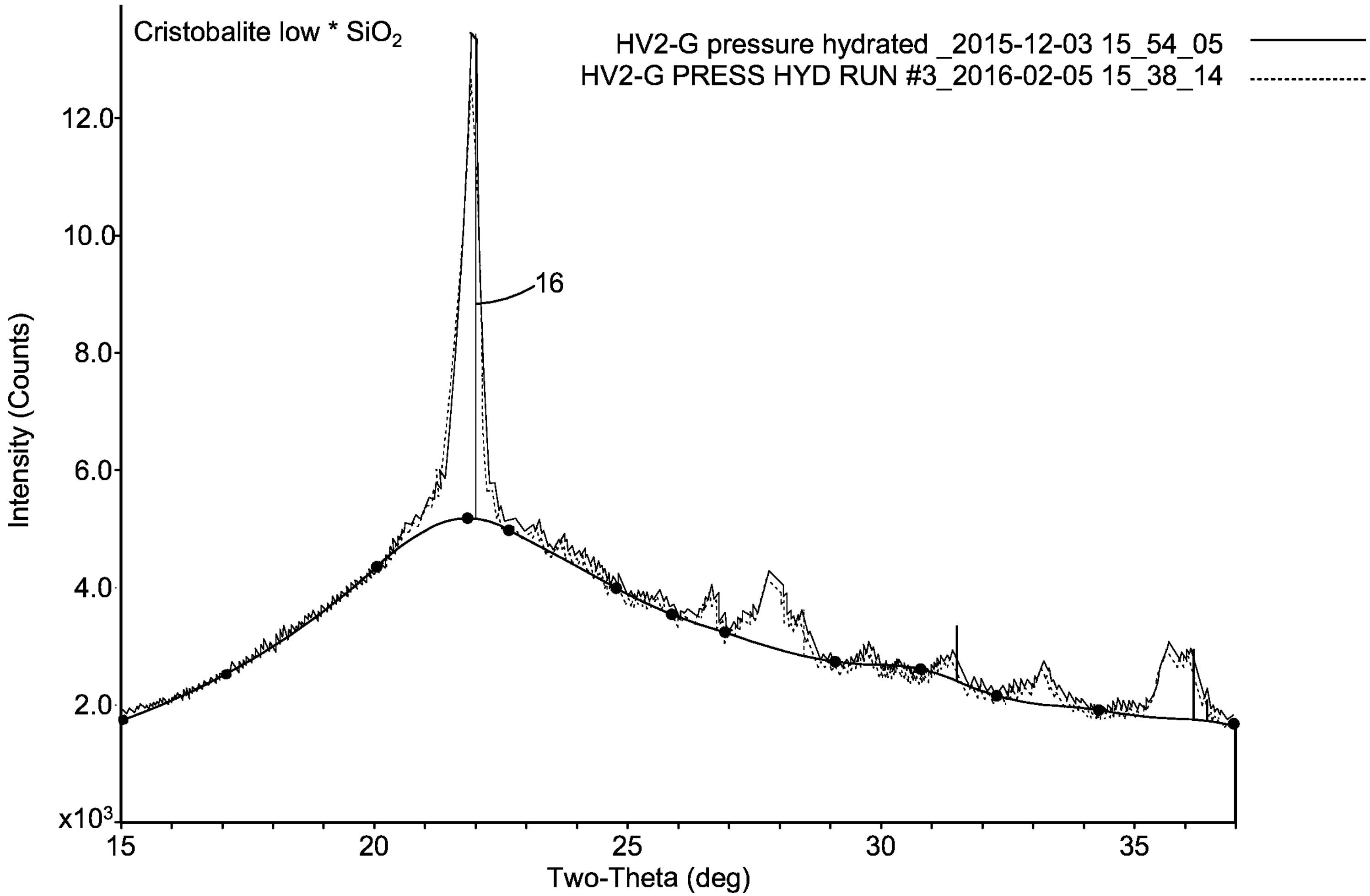
XRD Pattern of KD15:30 before and after fine grinding showing no phase change

FIG. 27



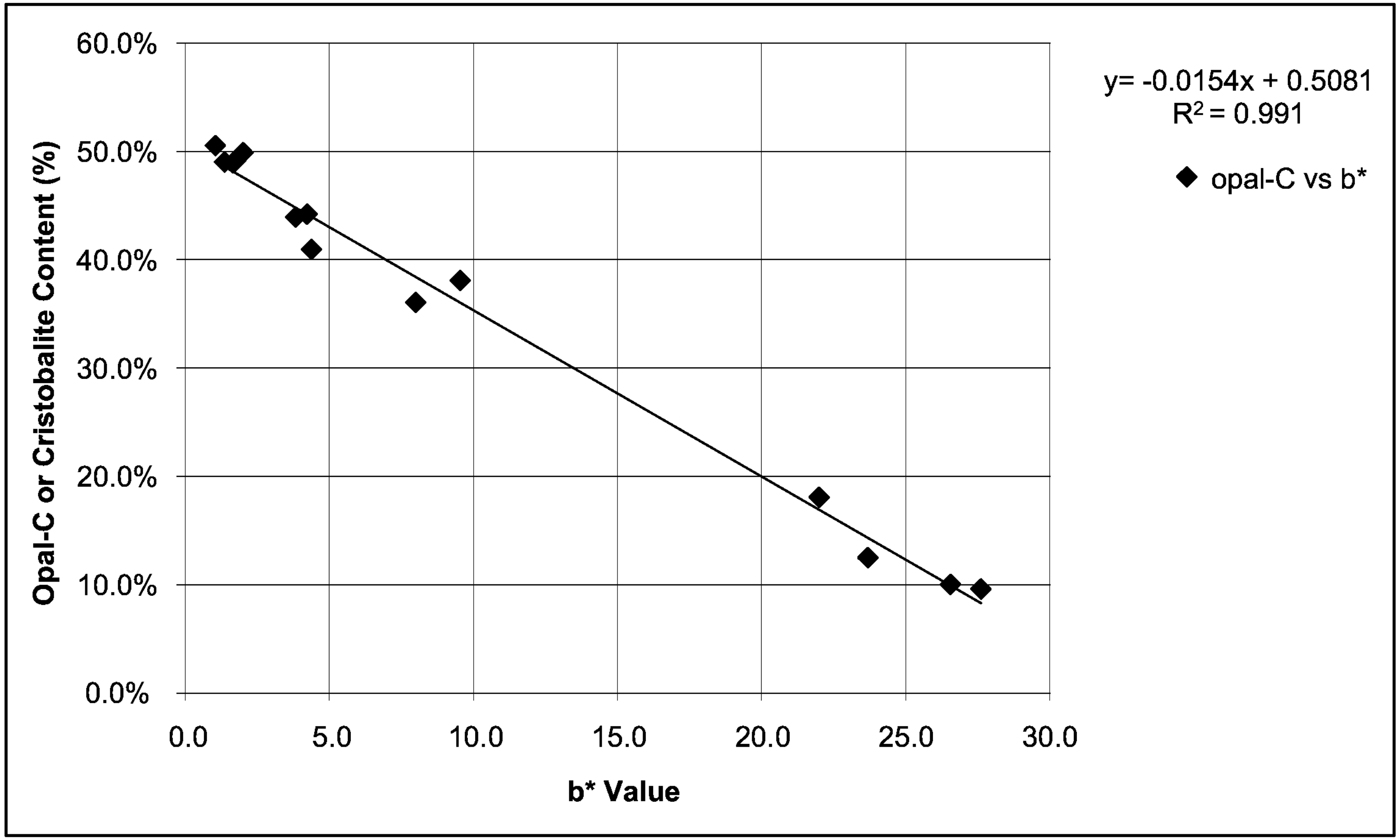
Overlaid XRD Pattern of Clarcel Dif-N Showing Partial Reversion to Amorphous Phase

FIG. 28



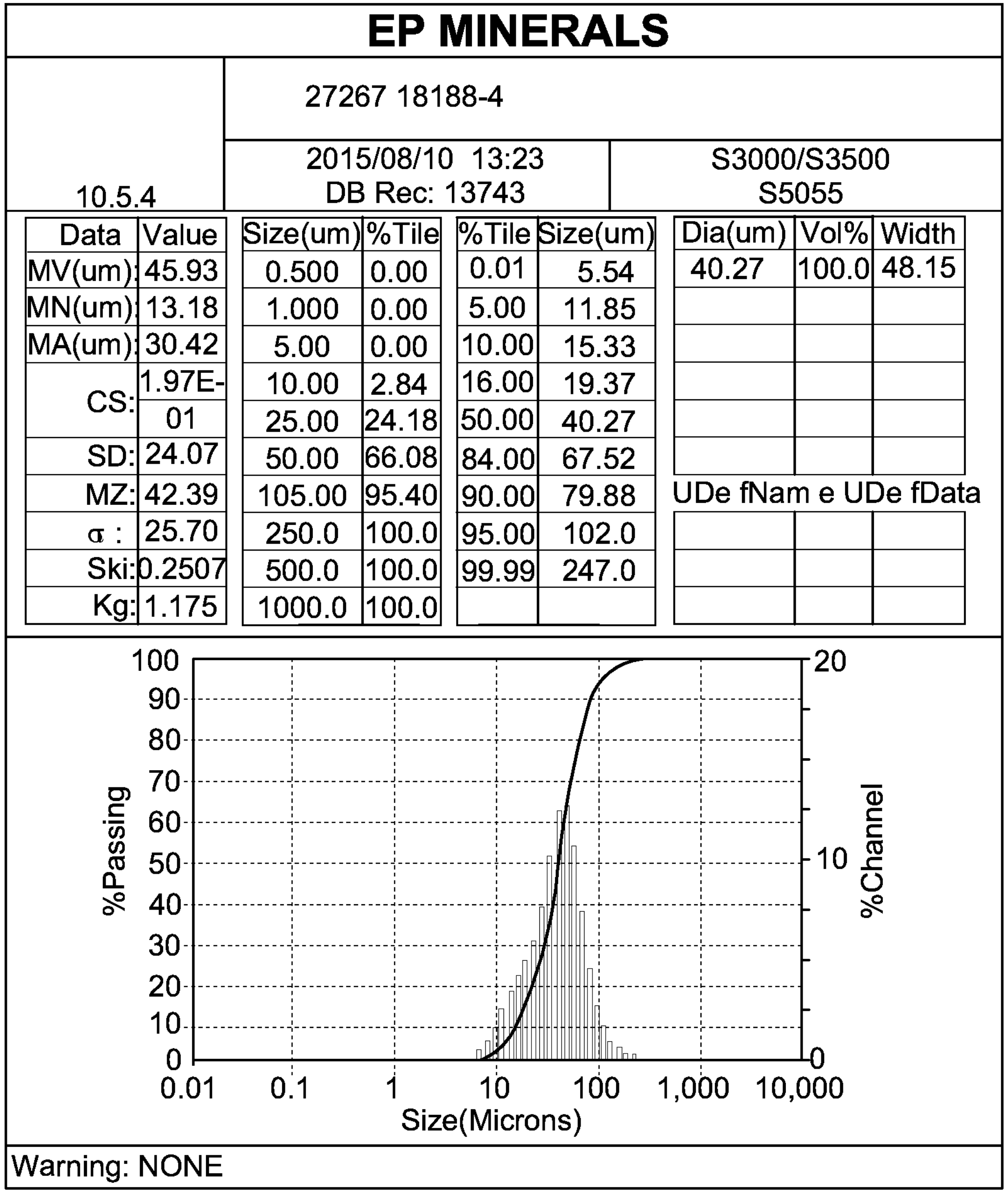
Overlaid XRD Pattern of HV2-G Showing Partial Reversion of Opal-C to Amorphous Phase

FIG. 29



Relationship of b* value to opal-C or cristobalite content in flux-calcined DE samples

FIG. 30



EP MINERALS

27267 18188-4

10.5.4

2015/08/10 13:23
DB Rec: 13743

S3000/S3500
S5055

Data	Value
MV(um):	45.93
MN(um):	13.18
MA(um):	30.42
CS:	1.97E-01
SD:	24.07
MZ:	42.39
σ :	25.70
Ski:	0.2507
Kg:	1.175

Size(um)	%Tile
0.500	0.00
1.000	0.00
5.00	0.00
10.00	2.84
25.00	24.18
50.00	66.08
105.00	95.40
250.0	100.0
500.0	100.0
1000.0	100.0

%Tile	Size(um)
0.01	5.54
5.00	11.85
10.00	15.33
16.00	19.37
50.00	40.27
84.00	67.52
90.00	79.88
95.00	102.0
99.99	247.0

Dia(um)	Vol%	Width
40.27	100.0	48.15

UDe fNam e UDe fData

Warning: NONE

FIG. 31a

SOP Name: NATURAL DE(*)

Distribution	Volume	Run time	30 Sec	Fluid	Natural DE		
Progression	Standard	Run #	Avg of 2	Fluid Ref Index	1.333	Loading Factor	0.1003
Up Edge(um)	1408	Particle	Natural DE	Above Residual	0	Transmission	0.959
Low Edge(um)	0.0215	Transparency	Transparent	Below Residual	0	RMS Residual	0.756%
Residuals	Enabled	Part. Ref. Index	1.45			Flow	60%
%Channels	64	Particle Shape	Irregular	Cell ID	1953	Usonic Power	20 Wat.
Analysis Mode	S3000/3500			Multi Run Delay	0 Min	Usonic Time	10 Sec
Filter	Enabled	DB Record	13743	Recalc Status	Original	Serial Number	S5055
Analysis Gain	Default (2)	Database	C/ProgramFiles\MicrotracFLEX10.5.4\Databases\EP Minerals.MD6				

Size(um)	%Chan	%Pass	Size(um)	%Chan	%Pass
1408	0.00	100.00	37.00	10.30	44.05
1184	0.00	100.00	31.11	7.84	33.75
995.6	0.00	100.00	26.16	6.10	25.91
837.2	0.00	100.00	22.00	5.08	19.81
704.0	0.00	100.00	18.50	4.39	14.73
592.0	0.00	100.00	15.56	3.66	10.34
497.8	0.00	100.00	13.08	2.74	6.68
418.6	0.00	100.00	11.00	1.81	3.94
352.0	0.00	100.00	9.25	1.10	2.13
296.0	0.00	100.00	7.78	0.65	1.03
248.9	0.34	100.00	6.54	0.38	0.38
209.3	0.51	99.66	5.50	0.00	0.00
176.0	0.77	99.15	4.62	0.00	0.00
148.0	1.17	98.38	3.89	0.00	0.00
124.5	1.85	97.21	3.27	0.00	0.00
104.7	2.95	95.36	2.750	0.00	0.00
88.00	4.79	92.41	2.312	0.00	0.00
74.00	7.55	87.62	1.945	0.00	0.00
62.23	10.76	80.07	1.635	0.00	0.00
52.33	12.75	69.32	1.375	0.00	0.00
44.00	12.52	56.57	1.156	0.00	0.00

Size(um)	%Chan	%Pass	Size(um)	%Chan	%Pass
0.972	0.00	0.00	0.02550	0.00	0.00
0.818	0.00	0.00	0.00	0.00	0.00
0.688	0.00	0.00	0.00	0.00	0.00
0.578	0.00	0.00	0.00	0.00	0.00
0.486	0.00	0.00	0.00	0.00	0.00
0.409	0.00	0.00	0.00	0.00	0.00
0.344	0.00	0.00	0.00	0.00	0.00
0.2890	0.00	0.00	0.00	0.00	0.00
0.2430	0.00	0.00	0.00	0.00	0.00
0.2040	0.00	0.00	0.00	0.00	0.00
0.1720	0.00	0.00	0.00	0.00	0.00
0.1460	0.00	0.00	0.00	0.00	0.00
0.1220	0.00	0.00	0.00	0.00	0.00
0.1020	0.00	0.00	0.00	0.00	0.00
0.0860	0.00	0.00	0.00	0.00	0.00
0.0720	0.00	0.00	0.00	0.00	0.00
0.0610	0.00	0.00	0.00	0.00	0.00
0.0510	0.00	0.00	0.00	0.00	0.00
0.0430	0.00	0.00	0.00	0.00	0.00
0.0360	0.00	0.00	0.00	0.00	0.00
0.0300	0.00	0.00	0.00	0.00	0.00

FIG. 31b

EP MINERALS

-FP-3 B17E2

10.5.4

2015/10/16 8:14
DB Rec: 14844

S3000/3500
S5055

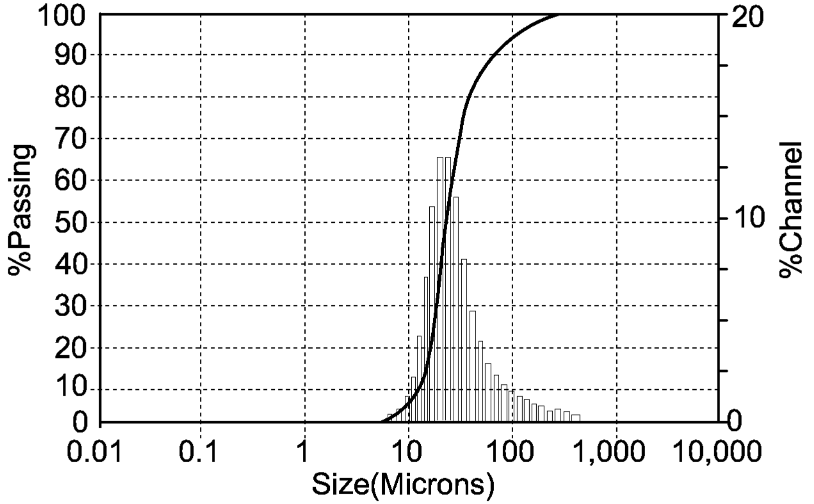
Data	Value
MV(um):	24.52
MN(um):	7.85
MA(um):	13.58
CS:	4.42E-01
SD:	11.16
MZ:	18.37
α :	17.01
Ski:	0.639
Kg:	2.561

Size(um)	%Tile
0.500	0.00
1.000	0.00
5.00	1.80
10.00	21.52
25.00	78.39
50.00	90.81
105.0	96.51
250.0	99.68
500.0	100.0
1000	100.0

%Tile	Size(um)
0.01	3.29
5.00	6.47
10.00	7.84
16.00	9.05
50.00	14.68
84.00	31.37
90.00	46.53
95.00	81.92
99.99	293.7

Dia(um)	Vol%	Width
14.68	100.0	22.32

UDe fName	UDe fData	



Warning: NONE

FIG. 32a

SOP Name: NATURAL DE(*)

Distribution	Volume	Run time	30 Sec	Fluid	Natural DE		
Progression	Standard	Run #	Avg of 2	Fluid Residual	1.333	Loading Factor	0.0957
Up Edge(um)	1408	Particle	Natural DE	Above Residual	0	Transmission	0.902
Low Edge(um)	0.0215	Transparency	Transparent	Below Residual	0	RMS Residual	0.494%
Residuals	Enable	Part. Ref. Index	1.45			Flow	60%
%Channnels	64	Particle Shape	Irregular	Cell ID	1953	Usonic Power	20 Wat.
Analysis Mode	S3000/3500			Multi Run Delay	0 Min	Usonic Time	10 Sec
Filter	Enabled	DB Record	14844	Recalc Status	Original	Serial Number	S5055
Analysis Gain	Default (2)	Database	C/ProgramFiles\MicrotracFLEX10.5.4\Databases\EP Minerals.MD6				

Size(um)	%Chan	%Pass	Size(um)	%Chan	%Pass
1408	0.00	100.00	37.00	3.08	86.92
1184	0.00	100.00	31.11	4.12	83.84
995.6	0.00	100.00	26.16	5.79	79.72
837.2	0.00	100.00	22.00	8.29	73.93
704.0	0.00	100.00	18.50	11.27	65.64
592.0	0.00	100.00	15.56	13.30	54.37
497.8	0.00	100.00	13.08	13.25	41.07
418.6	0.00	100.00	11.00	10.73	27.82
352.0	0.00	100.00	9.25	7.38	17.09
296.0	0.33	100.00	7.78	4.50	9.71
248.9	0.41	99.67	6.54	2.55	5.21
209.3	0.52	99.26	5.50	1.40	2.66
176.0	0.63	98.74	4.62	0.79	1.26
148.0	0.74	98.11	3.89	0.47	0.47
124.5	0.88	97.37	3.27	0.00	0.00
104.7	1.02	96.49	2.750	0.00	0.00
88.00	1.18	95.47	2.312	0.00	0.00
74.00	1.37	94.29	1.945	0.00	0.00
62.23	1.63	92.92	1.635	0.00	0.00
52.33	1.96	91.29	1.375	0.00	0.00
44.00	2.41	89.33	1.156	0.00	0.00

Size(um)	%Chan	%Pass	Size(um)	%Chan	%Pass
0.972	0.00	0.00	0.02550	0.00	0.00
0.818	0.00	0.00	0.00	0.00	0.00
0.688	0.00	0.00	0.00	0.00	0.00
0.578	0.00	0.00	0.00	0.00	0.00
0.486	0.00	0.00	0.00	0.00	0.00
0.409	0.00	0.00	0.00	0.00	0.00
0.344	0.00	0.00	0.00	0.00	0.00
0.2890	0.00	0.00	0.00	0.00	0.00
0.2430	0.00	0.00	0.00	0.00	0.00
0.2040	0.00	0.00	0.00	0.00	0.00
0.1720	0.00	0.00	0.00	0.00	0.00
0.1460	0.00	0.00	0.00	0.00	0.00
0.1220	0.00	0.00	0.00	0.00	0.00
0.1020	0.00	0.00	0.00	0.00	0.00
0.0860	0.00	0.00	0.00	0.00	0.00
0.0720	0.00	0.00	0.00	0.00	0.00
0.0610	0.00	0.00	0.00	0.00	0.00
0.0610	0.00	0.00	0.00	0.00	0.00
0.0430	0.00	0.00	0.00	0.00	0.00
0.0360	0.00	0.00	0.00	0.00	0.00
0.0300	0.00	0.00	0.00	0.00	0.00

FIG. 32b

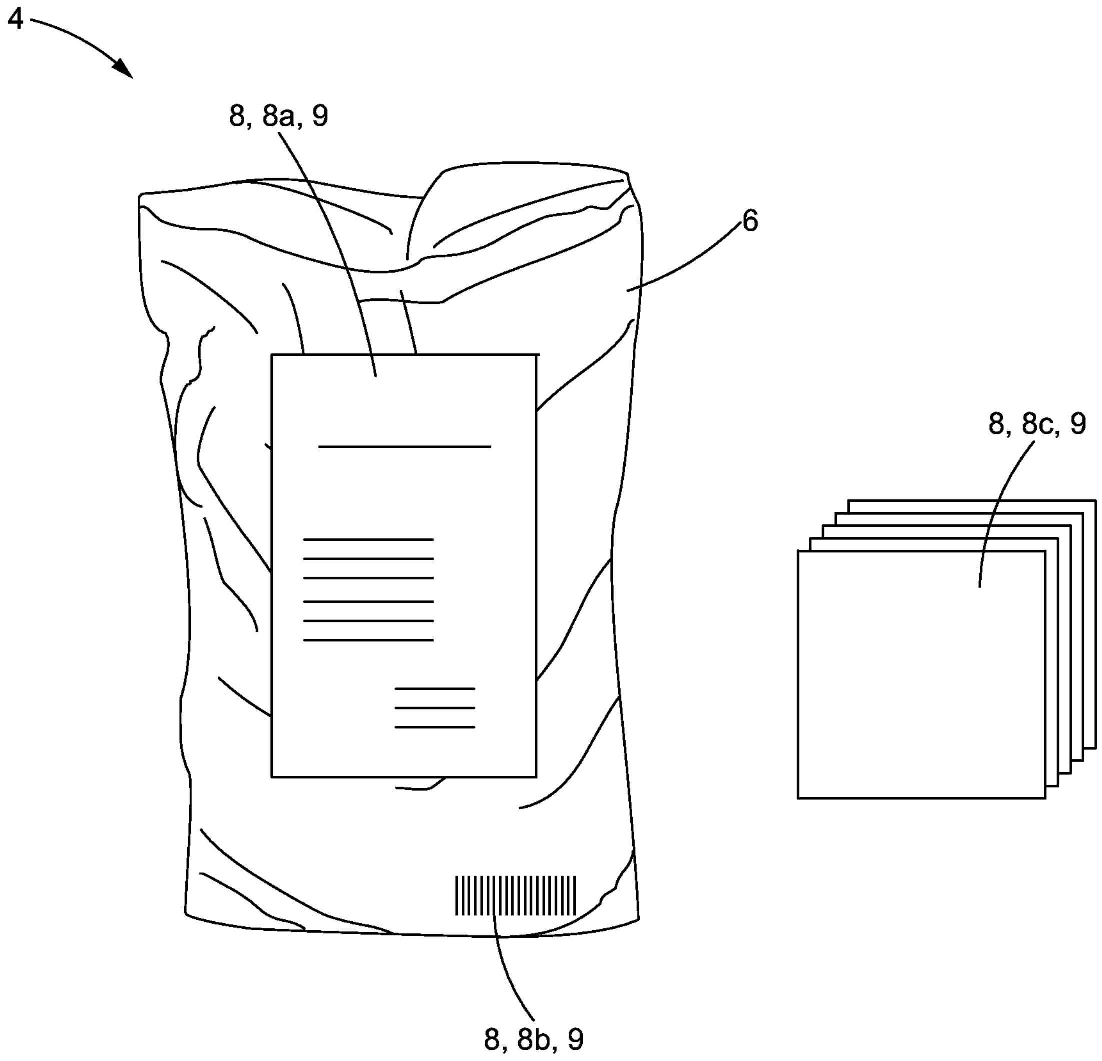


FIG. 33

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US2016/037816

A. CLASSIFICATION OF SUBJECT MATTER
IPC(8) - B01J 6/00; B01J 20/14; C04B 14/08; G01N 23/20 (2016.01)
CPC - B01D 37/025; B01J 20/041; B01J 20/14; B01J 20/3078; C04B 14/08; G01N 23/20 (2016.08)
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)
IPC(8) - B01J 6/00; B01J 20/14; C04B 14/08; G01N 23/20 (2016.01)
CPC - B01D 37/025; B01D 39/2075; B01J 20/041; B01J 20/14; B01J 20/3078; C04B 14/08; G01N 23/20 (2016.08)

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
USPC - 106/482; 501/154; 502/412; IPC(8) - B01J 6/00; B01J 20/14; C04B 14/08; G01N 23/20; CPC - B01D 37/025; B01D 39/2075; B01J 20/041; B01J 20/14; B01J 20/3078; C04B 14/08; G01N 23/20 (keyword delimited)

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
Orbit, Google Patents, Google Scholar, Google
Search terms used: silica, cristobalite, opal+, measure, ebc, asbc, calcium, iron, diatom+, kieselgur, kieselguhr, xrd, flux, calcined, differen+, distinguish+, lh

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X --- Y	US 2011/0195168 A1 (WANG) 11 August 2011 (11.08.2011) entire document	1-5, 8, 9, 11, 16 --- 10, 12-14
Y	US 2010/0176069 A1 (MEFFERT et al) 15 July 2010 (15.07.2010) entire document	10
Y	WO 2015/100050 A1 (IMERYS FILTRATION MINERALS INC) 02 July 2015 (02.07.2015) entire document	12, 13
Y	ELZEA et al., Distinguishing Well Ordered Opal-CT and Opal-C from High Temperature Cristobalite by X-Ray Diffraction, Analytica Chimica Acta, Vol. 286, 1994, Pgs. 107-116	14
A	ELZEA et al., TEM and X-Ray Diffraction Evidence for Cristobalite and Tridymite Stacking Sequences in Opal, Clays and Clay Minerals, Vol. 44, No. 4, 1996, Pgs. 492-500	1-16
A	US 2014/0171305 A1 (EP MINERALS LLC) 19 June 2014 (19.06.2014) entire document	1-16

☐ 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 08 August 2016	Date of mailing of the international search report 30 AUG 2016
Name and mailing address of the ISA/ Mail Stop PCT, Attn: ISA/US, Commissioner for Patents P.O. Box 1450, Alexandria, VA 22313-1450 Facsimile No. 571-273-8300	Authorized officer Blaine R. Copenheaver PCT Helpdesk: 571-272-4300 PCT OSP: 571-272-7774

(19)中华人民共和国国家知识产权局

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(85)PCT国际申请进入国家阶段日
2018.04.23

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WO2017/069808 EN 2017.04.27

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代理人 刘培培 黄爱娇

(51)Int.Cl.
B01J 6/00(2006.01)
B01J 20/14(2006.01)
C04B 14/08(2006.01)
G01N 23/2005(2018.01)

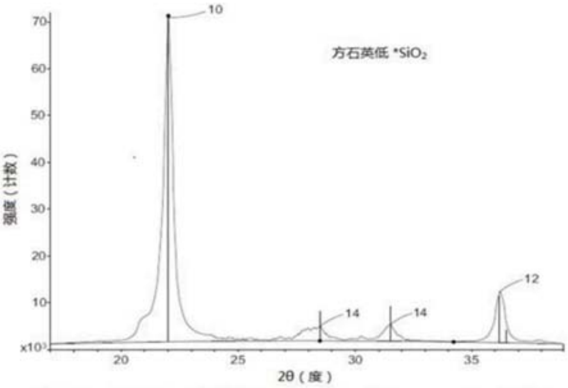
权利要求书1页 说明书67页 附图35页

(54)发明名称

蛋白石的助熔煅烧的硅藻土产品

(57)摘要

公开了一种硅藻土产品和使用该硅藻土产品的方法。该硅藻土产品可以包含钠助熔煅烧硅藻土，其中该硅藻土产品具有小于约1wt％的结晶二氧化硅含量，并且该硅藻土产品具有0.8达西至约30达西的渗透率。在一些实施例中，该硅藻土产品可以是颗粒或粉末形式。本发明还涉及含有低水平或不可检测水平的结晶二氧化硅的助熔煅烧二氧化硅产品。这些产品中的一些可以进一步表征为高渗透率、可测定含量的蛋白石-C以及水合形式的二氧化硅。



具有方石英相加少量（1至2%）长石的Celite® 501（样品#18362）的XRD图谱

权 利 要 求 书

1.一种硅藻土产品，其包含：

钠助熔煅烧硅藻土，

其中所述硅藻土产品具有小于约1wt％的结晶二氧化硅含量，

其中所述硅藻土产品具有在0.8达西至约30达西之间的渗透率。

2.根据权利要求1所述的硅藻土产品，其特征在于，所述硅藻土产品具有0.9达西至30达西之间的渗透率。

3.根据权利要求1所述的硅藻土产品，其特征在于，所述结晶二氧化硅含量为小于所述硅藻土产品的约0.1wt％。

4.根据权利要求1所述的硅藻土产品，其特征在于，所述硅藻土产品具有至少80wt％的生物二氧化硅含量。

5.根据权利要求1所述的硅藻土产品，其特征在于，所述硅藻土产品具有约1.5达西至约9达西之间的渗透率。

6.根据权利要求1所述的硅藻土产品，其特征在于，所述硅藻土产品具有大于所述硅藻土产品的约1wt％的蛋白石-C含量。

7.根据权利要求1所述的硅藻土产品，其特征在于，所述硅藻土产品具有大于所述硅藻土产品的约10wt％的蛋白石-C含量。

8.根据权利要求1所述的硅藻土产品，其特征在于，所述硅藻土产品为颗粒状产品。

9.根据权利要求1所述的硅藻土产品，其特征在于，所述硅藻土产品进一步包含总和大于约4wt％的矿物形式的铝和铁，或总和大于约7wt％的以氧化物表示的铝和铁。

10.根据权利要求1所述的硅藻土产品，其特征在于，所述硅藻土产品为再生过滤介质，所述再生过滤介质先前作为过滤介质已经使用过一次或多次并且已通过化学或热过程再生，所述再生过滤介质适用于在食品、饮料、化学制品、燃料、材料、水或生物制药中的至少一种的过滤工艺中再利用。

11.根据权利要求1所述的硅藻土产品，其特征在于，通过EBC方法测定的，所述硅藻土产品进一步包含约21ppm至900ppm的可溶性钙。

12.根据权利要求1所述的硅藻土产品，其特征在于，通过EBC方法测定的，所述硅藻土产品进一步包含约23ppm至45ppm的可溶性铁。

13.根据权利要求1所述的硅藻土产品，其特征在于，通过ASBC方法测定的，所述硅藻土产品进一步包含约4ppm至约14ppm的啤酒可溶性铁。

14.根据权利要求1所述的硅藻土产品，其特征在于，所述硅藻土产品可选地具有方石英含量，其中所述方石英含量进一步通过区别方石英和蛋白石-C的方法测定。

15.根据权利要求14所述的硅藻土产品，其特征在于，所述方石英含量是通过使用LH方法确定的。

16.一种制造硅藻土产品的方法，所述方法包括：

选择硅藻土矿石，其包含大于约2.6wt％的矿物形式的铝或大于约5wt％的作为氧化铝的铝；以及

用钠助熔剂煅烧所述硅藻土矿石，其中制造的硅藻土产品包含钠助熔煅烧硅藻土，该硅藻土产品具有的结晶二氧化硅含量小于约1wt％且渗透率为0.8达西至约30达西。

蛋白石的助熔煅烧的硅藻土产品

相关专利申请的交叉引用

[0001]　本专利申请要求于2015年10月23日提交的美国临时专利申请62/245,716的权益，并且要求于2016年3月28日提交的美国临时专利申请62/314,005的权益。

技术领域

[0002]　本发明涉及直接煅烧和助熔煅烧的生物二氧化硅产品，更具体地涉及包含低水平或不可检测水平的结晶二氧化硅和二氧化硅文档(如本文所定义)的直接煅烧和助熔煅烧的硅藻土产品，以及相关测试方法和制剂。该硅藻土产品可以包含已经在公共领域中的物理组分和新二氧化硅文档或新物理组分和新二氧化硅文档。

背景技术

[0003]　藻土，也称为硅藻土或砂藻土，是一种主要由硅藻的骨骼残骸(也称为壳)组成的天然沉积岩，而硅藻是通常存在于水中(例如湖泊和海洋)的一种单细胞植物。硅藻土已用于多种制造工艺和应用很多年，包括用作过滤介质、载体、吸收剂以及功能性填料。

[0004]　硅藻土是天然产生的，其由硅藻壳本身以及其他矿物(如粘土、火山灰、长石和石英)组成，它们通过沉积过程沉积到活硅藻的湖泊或海洋栖息地中。在形成时，硅藻壳由称为蛋白石-A的非晶的水合生物二氧化硅组成。在本专利的上下文中，我们将生物二氧化硅称为由生命形式产生的二氧化硅。产生生物二氧化硅的常见生命形式包括硅藻、放射虫、海绵、竹子、水稻和马尾。在形成时，硅藻壳不含任何结晶二氧化硅，但包含在硅藻土中的其它沉淀物可能包括石英(硅砂的主要组分)形式的结晶二氧化硅。石英几乎普遍存在于硅藻土的海洋(盐水)沉积物中，但一些硅藻土的湖泊(淡水)沉积物不含石英或含有可在加工过程中除去的足够大的石英颗粒。硅藻死亡后，随着时间的推移，蛋白石-A可能会部分脱水，并且可能在一系列阶段中从蛋白石-A转化为具有更短程的分子排列且含有更少水合水的蛋白石形式，如蛋白石-CT和蛋白石-C。经过很长一段时间并在适当的条件下，蛋白石-CT可以转化为石英。Eichhubl和Behl等人描述了在加州蛋白石-A在蒙特雷硅藻土(Monterrey diatomite)的形成过程中的自然风化过程。

[0005]　蛋白石-A、蛋白石-CT和蛋白石-C通常分别或共同地被称为蛋白石、玻璃状二氧化硅或非晶二氧化硅。

[0006]　在其最早的已知用途中，硅藻土在欧洲被用作洞穴壁画中的颜料，其可追溯至4万年前。硅藻土的现代工业用途开始于19世纪中后期，并在20世纪初得到扩展，当时发现可以通过热处理来改进材料的过滤性能。

[0007]　热改性硅藻土最早的用途发生在大约1913年，在这些过程中，将材料加热到其软化点以使硅藻壳团聚而形成更大的颗粒，从而提高产品的渗透率。该过程的主要功能是促进硅藻壳的团聚，因此可能称为烧结工艺最为合适，但它几乎完全被称为煅烧，可能是因为它使天然矿物部分或完全脱水。

[0008]　在引入煅烧硅藻土产品约十五年后，发现通过在煅烧过程中添加助熔剂可以进一

步改进硅藻土的性能。尽管自引入助熔煅烧硅藻土以来已经使用各种助熔剂，但钠基助熔剂如盐(氯化钠)或苏打灰已成为最常用的助熔剂。

[0009] 目前在硅藻土工业中常用的两种烧结工艺几乎普遍被称为直接煅烧和助熔煅烧，直接煅烧是不使用助熔剂的烧结工艺，而在助熔煅烧中，将助熔剂加入到硅藻土中以促进较低的软化温度和更大程度的颗粒团聚。这些工艺在硅藻土产品中产生不同的物理和光学变化。

[0010] 直接煅烧几乎总是会使天然硅藻土的颜色产生变化，从灰白色变为粉红色。这种颜色变化的程度可能与硅藻土的铁含量相关。直接煅烧通常对于生产具有约0.1至约0.6达西的低至中等渗透率的产品是有效的。在一些情况下，可以通过分离工艺如空气分级，通过除去煅烧产品中含有的细颗粒部分，而将直接煅烧产品的渗透率增加到超过这些水平，并达到约1达西。

[0011] 助熔煅烧通常会将天然硅藻土的颜色从灰白色变为亮白色，或者有时变为更亮的更浅的粉红色。助熔煅烧可以导致更大的颗粒团聚，并且可以用于生产具有约0.8达西至超过10达西的渗透率的产品。

[0012] 包含直接煅烧或助熔煅烧硅藻土的产品广泛用于微过滤应用中。它们主要用于由于被夹杂的固体的固有性质(如粘性和压缩性)而难以实现的固液分离。该产品通常以两种模式使用；作为预涂层，其中将该产品的层设置在随后作为固液分离界面的支撑面上，以及作为主体进料，其中将该产品引入到预过滤悬浮液中以改善和保持所分离和获取的固体的渗透率。这些产品可用于将较大或更多的颗粒从悬浮液中除去的初级(粗)过滤，以及除去并获取较细残留颗粒的二级(抛光)过滤。

[0013] 除了过滤应用之外，通过助熔煅烧显著改善硅藻土的白度和亮度，从而导致助熔煅烧硅藻土在涂料和塑料膜填料应用中的发展和广泛使用。

[0014] 在直接煅烧和助熔煅烧产品的开发过程中，知道了直接煅烧和助熔煅烧过程会导致硅藻土的蛋白石结构的组成的变化。虽然在开发该工艺时基本上理解了一些变化，但是该变化的某些方面直到最近才得以完全理解或表征。正如我们现在所理解的，硅藻土从蛋白石-A的改性过程伴随着连续脱水和短程分子排列的增加，蛋白石-A是在已经被用于生产硅藻土过滤和填料产品的硅藻土沉积物中最常见的蛋白石形式。包含约4至6wt％水合水的蛋白石-A转化为包含约0.2至1wt％水合水的蛋白石-C，如果暴露于更高的温度，可以转化为传统上表征为方石英的矿物相，或者在某些条件下，转化为不含水合水的二氧化硅的结晶形式的石英。

[0015] 方石英也可以在火山活动期间形成，或通过诸如石英的热处理的工业过程而形成。通过加热和冷却石英形成的方石英不是从蛋白石原料的脱水演变而来而是通过在高温下的重构结晶相变演变而来。

[0016] 在热处理过程中，硅藻土中所含的任何石英也可以转变成方石英。通常，当在不存在助熔剂的情况下煅烧硅藻土矿石时，石英不转化为方石英，但当在助熔剂存在下的情况下处理含有石英的硅藻土时，石英可转化为方石英。

[0017] 除了由处理的硅藻土矿石组成的产品外(可选地添加助熔剂)，还报道了许多包含硅藻土原料和其他粉末材料的许多产品，包括磨碎的天然玻璃、膨胀天然玻璃、磨碎的合成玻璃、热塑性聚合物、锌、锡、稻壳灰、沉淀二氧化硅、硅胶、纤维素、活性氧化铝、三水合氧化

铝、酸活化膨润土或活性炭。天然玻璃可以是珍珠岩、浮石、火山玻璃或黑曜石的形式。包含硅藻土和这些组分中的一种或多种的产品可以是混合物或复合物的形式，并且该复合物可以通过热烧结、与粘合剂的粘附或沉淀而形成。包含硅藻土和可选地这些其它组分中的一种或多种的产品，也可以含有传统上不正确地鉴定为方石英的蛋白石。例如，参见Palm et al的美国专利号5,776,353;6524489;6712974;Wang et al的PCT申请号PCT/US15/65572;以及Lu et al.的美国专利号8,242,050。

[0018] 尽管一些直接煅烧和助熔煅烧硅藻土产品以及包含它们的混合和共混产品可能是已知的，但对直接煅烧和助熔煅烧硅藻土产品的矿物学的理解以及用于表征它们的方法仍在发展。除了由发明人公开的新产品和新的分析技术之外，他们还确认了产品的矿物学各个方面，特别是以前未知的关于矿物学稳定性的方面。

[0019] 特别是，令人惊讶的和完全出乎意料的结果是，发明人已经确定，直接煅烧和助熔煅烧硅藻土的各种蛋白石相以及甚至似乎是方石英的至少一些部分将玻璃化(转化成类似玻璃的非晶固体)，并可以再水合。换言之，发明人已经观察到以下情况：(1)几周和几个月后，部分脱水形式的蛋白石、蛋白石-CT和蛋白石-C的很大一部分将玻璃化，并且可再水合以形成似乎是蛋白石-A的蛋白石；以及(2)几周和几个月后，被本发明人和文献归类为方石英的似乎完全脱水和去玻璃化的蛋白石的很大一部分将玻璃化，并且可再水合以形成似乎是蛋白石-C、蛋白石-CT和蛋白石-A的蛋白石。

[0020] 在地质时期认为是经过眨眼之间进行的这种玻璃化和再水合的行为是一个有趣的结果，这必定引起以下质疑：热改性硅藻土产品中包含的生物方石英是否实际上被正确认定为方石英，因为由石英的热处理形成的“方石英”尚未显示出玻璃化并水合以形成蛋白石。事实上，从地质学角度来看，方石英在环境条件下是亚稳相，且最终应该转化为石英，因为在环境条件下石英是稳定的结晶二氧化硅相。这通常需要数千甚至数百万年。

[0021] 多年来，某些科学机构和法规机构已经接受长期吸入结晶形式的二氧化硅、石英、方石英和鳞石英可能导致肺部疾病这一观点。虽然方石英可以通过石英或生物二氧化硅的热转化在工业过程中形成，但每个转化过程的阶段和转化的中间产物明显不同。在关于结晶二氧化硅的医学和健康文献中，并未总是考虑或理解这些显著差异，并且尚未完全研究。

[0022] 尚未证明吸入蛋白石的和大多数其他形式的非晶二氧化硅与吸入结晶形式的二氧化硅可能造成的健康风险相同。因此需要新的分析技术，使用户能够从硅藻土的产品中区分蛋白石和方石英。

[0023] 包含直接煅烧和助熔煅烧硅藻土产品的产品包含许多属性，包括物理和化学特性以及法规支持和危险通信特点。通常用于描述或表征这些产品的某些物理特性包括粒径分布、硅藻组合(硅藻壳所来源的硅藻种类)、材料的填充或离心湿密度、材料的亮度和色调以及许多本领域技术人员公知的其他特性。

[0024] 包括直接煅烧和助熔煅烧硅藻土产品的产品还可以通过许多化学或组成属性来表征，包括矿物学、结晶二氧化硅含量、许多物质(包括铁、钙、锑、铅、铬、砷等)的体相化学和可提取态化学(extractable chemistry)。

[0025] 除了我们称之为产品的物理组分的传统属性(如化学和物理属性)外，直接煅烧和助熔煅烧硅藻土产品还包含法规或技术支持特点，例如分析证书和安全数据表(SDS)。分析证书是生成的文件，其包括供应商和客户达成的某些特性的认证，这些特性可包括客户感

兴趣的几乎任何特性。世界各国政府和国际协议通常要求的安全数据表，包括关于产品的组成信息和健康危害警告，其主要设计为包括关于危害、暴露限值和材料的安全处理的信息。安全数据表及其前身文件(例如美国材料安全数据表(MSDS))多年来一直包含关于工作场所中使用的材料的有害组分(如结晶二氧化硅)的信息，由于长期吸入结晶二氧化硅会导致硅肺病的潜在风险已为人所知多年。自1987年国际癌症研究机构(International Agency for Research on Cancer)确定方石英、石英或鳞石英形式的结晶二氧化硅为可能的人类致癌物质以来，许多政府已经要求将关于结晶二氧化硅含量高于检测限或某些暴露限值的警告包括在安全数据表中。

[0026] 在现代商业中，直接煅烧和助熔煅烧硅藻土产品既包含物理组分，也包含数据组分(该数据组分包括如下定义的二氧化硅文档)，并且这两个组分，即物理和数据组分对于该产品在基本上所有国家的销售来说是必要的。因此，可以通过改进产品的物理组分或产品的相关数据组分(例如，二氧化硅文档)来开发新产品。在本申请中，发明人公开了新产品，其既包含含有低水平或不可检测水平的结晶二氧化硅的物理组分，又包含对应的二氧化硅文档(数据组分)。就本申请的目的而言，二氧化硅文档包括以下一项或多项内容：法规支持文件、危害披露、安全数据表、标签、产品标签、产品条形码、分析证书或其他电子或印刷形式的数据，这些其他电子或印刷形式的数据记录或公开包括硅藻土的产品中的结晶二氧化硅含量或不存在结晶二氧化硅含量。通过明确声明或由二氧化硅文档鉴定的产品含量中不存在结晶二氧化硅(例如方石英、石英、鳞石英)，从而在二氧化硅文档中公开不存在结晶二氧化硅。

[0027] 本公开教导了几种类型的新产品，包括但不限于：

[0028] 1.包含常规物理组分和新二氧化硅文档的产品。常规物理组分包括直接煅烧或助熔煅烧硅藻土。

[0029] 2.包含新物理组分和新二氧化硅文档的产品。新物理组分包括助熔煅烧硅藻土。

[0030] 3.用于表征包括直接煅烧和助熔煅烧硅藻土的产品以及用于制作新二氧化硅文档的新测试方法。

[0031] 在以上(1)和(2)中的每一个中，在一些实施例中，物理组分可以包含在一个包装中。如本文所用，“包装”是指袋子、桶或容器。然而，在一些实施例中，物理组分可以散装运输或提供(例如，在油轮等中)。二氧化硅文档可与一个独立包装、一批包装或散装物理组分有关。

[0032] 如本文所用，术语“约”意指所述值加或减20%。

发明内容

[0033] 根据本发明的一个方面，公开了一种硅藻土产品。该硅藻土产品可以包含钠助熔煅烧硅藻土，其中该硅藻土产品具有小于约1wt%的结晶二氧化硅含量，并且该硅藻土产品具有0.8达西至约30达西的渗透率。在一个改进例中，该硅藻土产品可以具有在0.9达西至30达西之间的渗透率。在进一步改进例中，该硅藻土产品可以具有在1.0达西至20达西之间的渗透率。在进一步改进例中，该硅藻土产品可以具有在1.5达西至约9达西之间的渗透率。在进一步改进例中，该硅藻土产品可以具有在1.5达西至4达西之间的渗透率。

[0034] 在一个实施例中，该硅藻土产品的结晶二氧化硅含量可以小于约0.1wt%。

[0035] 在一个实施例中，该硅藻土产品可具有至少75wt％的生物二氧化硅含量。在一个改进例中，该硅藻土产品可具有至少80wt％二氧化硅的二氧化硅含量。在进一步改进例中，该硅藻土产品可具有至少85wt％二氧化硅的二氧化硅含量。

[0036] 在一个实施例中，该硅藻土可以具有超过该硅藻土产品的约1wt％的蛋白石-C含量。在一种改进例中，该硅藻土产品可以具有超过该硅藻土产品的约10wt％的蛋白石-C含量。

[0037] 在一个实施例中，该硅藻土产品可以进一步包含总和大于约4wt％的矿物形式的铝和铁，或总和大于约7wt％的以氧化物表示的铝和铁。在另一个实施例中，该硅藻土产品可以进一步包含大于约2.6wt％的矿物形式的铝，或大于约5wt％的以氧化铝表示的铝。在另一个实施例中，该硅藻土产品可以进一步包含大于约1.75wt％的矿物形式的铁，或大于约2.5wt％的以氧化铁表示的铁。在一个实施例中，作为氧化物的测定可以通过波长色散X射线荧光(XRF)分析来确定。

[0038] 在一个实施例中，该硅藻土产品可以是先前作为过滤介质已经使用过一次或多次并且已经通过化学或热过程而再生的再生过滤介质。再生过滤介质可以适用于食品、饮料、化学制品、燃料、材料、水或生物制药中的至少一种的过滤工艺中的再利用。在一个改进例中，化学或热过程可以是热解、溶剂提取或气化。

[0039] 在一个实施例中，通过EBC方法测定的，该硅藻土产品可以进一步包含约21ppm至900ppm的可溶性钙。

[0040] 在一个实施例中，通过EBC方法测定的，该硅藻土产品可以进一步包含小于约160ppm的可溶性铁。在一个改进例中，通过EBC方法测定的，该硅藻土产品可以进一步包含小于约45ppm的可溶性铁。在另一个改进例中，通过EBC方法测定的，该硅藻土产品可以进一步包含约23ppm至45ppm的可溶性铁。

[0041] 在一个实施例中，通过ASBC方法测定，该硅藻土产品可以进一步包含小于约15ppm的可溶性铁。在一个改进例中，通过ASBC方法测定，该硅藻土产品可以进一步包含约4ppm至约14ppm的啤酒可溶性铁。

[0042] 在一个实施例中，通过ASBC方法测定，在任何后煅烧水合处理之前，该硅藻土产品可以进一步包含约13至14ppm的可溶性铁含量。

[0043] 在一个实施例中，根据EBC方法测定，该硅藻土产品可以进一步包含小于约160ppm的可溶性铝。在一个改进例中，通过EBC方法测定，该硅藻土产品可以进一步包含小于约120ppm的可溶性铝。在进一步改进例中，通过EBC方法测定，该硅藻土产品可以进一步包含小于约75ppm的可溶性铝。

[0044] 在一个实施例中，通过EBC方法测定，该硅藻土产品可以进一步包含小于约1ppm的可溶性砷。在一个实施例中，根据EBC方法测定，该硅藻土产品可以进一步包含小于约10ppm的可溶性砷。

[0045] 在一个实施例中，该硅藻土产品可以可选地具有通过区分方石英和蛋白石-C的方法测定的方石英含量。在一个改进例中，通过使用LH方法确定方石英含量。

[0046] 在上述任一个实施例中，该硅藻土产品可以是颗粒状产品。在上述任一个实施例中，钠助熔煅烧硅藻土可以为颗粒形式。

[0047] 在上述任一个实施例中，该硅藻土产品可以为粉末形式。在上述任一个实施例中，

钠助熔煅烧硅藻土可以为粉末形式。

[0048] 在上述任一个实施例中，结晶二氧化硅可以为可吸入结晶二氧化硅。

[0049] 在另一个实施例中，可以已经对该硅藻土产品进行了酸洗和冲洗以减少可溶性杂质。

[0050] 在另一个实施例中，通过ASBC方法测定，该硅藻土产品可以是经过水合过程以减少啤酒可溶性铁的处理产品。

[0051] 根据本发明的另一个方面，公开了一种制造硅藻土产品的方法。该方法可以包括，选择硅藻土矿石，其包含大于约2.6wt％的矿物形式的铝或大于约5wt％的作为氧化铝的铝，并且用钠助熔剂煅烧该硅藻土矿石，其中所制造的硅藻土产品包含钠助熔煅烧硅藻土，该硅藻土产品的结晶二氧化硅含量小于约1wt％且渗透率为0.8达西至约30达西。

[0052] 还公开了一种在初级或二级过滤中使用组合物作为预涂层或主体进料而过滤啤酒或酒的方法，所述组合物包含上述硅藻土产品中的任何一种。在该方法的一个改进例中，可以在二级过滤中使用，并且该组合物可以进一步包含二氧化硅干凝胶、二氧化硅水凝胶、丹宁酸或PVPP中的一种。

[0053] 根据本发明的另一个方面，公开了一种使用上述硅藻土产品的工艺。在一个实施例中，该工艺可以包括使用任一种上述硅藻土产品作为过滤介质。在一个改进例中，该工艺可以包括在过滤应用、细胞分离或血浆处理和分馏中使用任一种上述硅藻土产品作为过滤介质。

[0054] 根据本发明的另一个方面，公开了一种使组合物再生的方法。该方法可以包括用特征为pH值在约7至约12之间的液体来处理该组合物。在一个实施例中，该组合物可以包含上述硅藻土产品中的任一种以及二氧化硅干凝胶、二氧化硅水凝胶、丹宁酸或PVPP中的一种。

[0055] 根据本发明的另一个方面，公开了一种使组合物再生的方法。该方法可以包括向该组合物施加热能，该组合物可以包含上述硅藻土产品中的任一种以及二氧化硅干凝胶、二氧化硅水凝胶、丹宁酸或PVPP中的一种。

[0056] 根据本发明的另一个方面，公开了一种用于在滤板、滤芯或其他制造的过滤产品中使用任一种上述硅藻土产品作为组分或添加剂的工艺。

附图说明

[0057] 图1是具有方石英相加少量(1至2wt％)长石的Celite®501(样品#18362)的X射线衍射(XRD)图谱的图；

[0058] 图2是示出蛋白石-C相加长石和可能的赤铁矿的FP-4(2H11B4)的XRD图谱的图；

[0059] 图3是示出方石英相加长石的FP-6(2B11F1)的XRD图谱的图；

[0060] 图4是示出方石英相加少量长石的Dicalite®4500的XRD图谱的图；

[0061] 图5是样品“FP-2 B12C0”的XRD图谱的图；

[0062] 图6是样品“Celabrite®2A20A13F”的XRD图谱的图；

[0063] 图7是具有或不具有方石英尖峰的样品“FP-3 B17E2”的XRD图谱的图；

[0064] 图8是具有或不具有方石英尖峰的样品“FP-3 B17E2”的XRD主峰的图；

[0065] 图9是具有5wt％方石英尖峰的18188-4的XRD图谱的图；

[0066] 图10是具有15wt％方石英尖峰的样品18188-9的XRD图谱的图；

[0067] 图11是仅示出主峰的样品18188-9的XRD图谱的图；

[0068] 图12是样品“S31 15-4-7B”的XRD图谱的图；

[0069] 图13是具有5wt％方石英尖峰(NIST 1879A)的样品HV2BH-E的衍射图谱的图；

[0070] 图14是具有21wt％方石英尖峰(NIST 1879A)的样品HV2-F的衍射图谱的图；

[0071] 图15是具有5wt％方石英尖峰(NIST 1879A)的样品S3115E的XRD图谱的图；

[0072] 图16是具有28wt％方石英尖峰(NIST 1879A)的样品LCS3-H的XRD图谱的图；

[0073] 图17是示出蛋白石-C加少量长石的样品FEBH的衍射图谱的图；

[0074] 图18是示出蛋白石-C加长石的实施例15(KD 15:30)的衍射图谱的图；

[0075] 图19是由LCS-3制成的、苏打灰助熔煅烧的硅藻土的XRD扫描图谱的图，其示出存在方石英；

[0076] 图20是由LCS-3制成的、铝酸钠助熔煅烧的硅藻土的XRD扫描图谱的图，其示出存在蛋白石-C和0.1wt％的石英；

[0077] 图21是由LCS-3制成的、苏打灰和0.3μ氧化铝助熔煅烧的硅藻土的XRD扫描图谱的图，其示出存在蛋白石-C和0.3wt％的石英；

[0078] 图22是由LCS-3制成的、苏打灰和1.7μATH助熔煅烧的硅藻土的XRD扫描图谱的图，其示出存在方石英和<0.1wt％的石英；

[0079] 图23是由LCS-3制成的、煅烧的硅藻土的XRD扫描图谱的图，其示出存在蛋白石-C和0.2wt％的石英；

[0080] 图24是由LCS-3加入ATH添加剂制成的煅烧的硅藻土的XRD扫描图谱的图，其示出存在蛋白石-C和0.25wt％的石英；

[0081] 图25是示出蛋白石-C加少量长石的对照样品的衍射图谱的图；

[0082] 图26是示出可能有方石英的具有5wt％KASOLV®的测试样品的衍射图谱的图；

[0083] 图27是示出无相变的细磨前后的KD15:30的XRD图谱的图；

[0084] 图28是示出部分回复到非晶相的Clarcel DIF-N™的重叠XRD图谱的图；

[0085] 图29是示出蛋白石-C部分回复到非晶相的HV2-G的重叠XRD图谱的图；

[0086] 图30是示出助熔煅烧的DE样品中b^*值与蛋白石-C或方石英含量的关系的图；

[0087] 图31a-b示出了表示样品18188-4的粒径分布(PSD)的图和表格；

[0088] 图32a-b示出了表示样品FP-3B17E2的粒径分布的图和表格；以及

[0089] 图33是具有示例性二氧化硅文档的示例性产品的图示。

具体实施方式

[0090] 在历史上，直接煅烧和助熔煅烧硅藻土的生产者不可能区分某些形式的蛋白石(例如，也经常存在于包括直接煅烧和助熔煅烧硅藻土的产品中的蛋白石-CT和蛋白石-C)和方石英，并精确量化这些组分，因为尚不存在用于区分和精确量化硅藻土产品中二氧化硅矿物相的测试方法。因此，许多由传统分析技术表征的包含直接煅烧和助熔煅烧硅藻土的产品包含了夸大了结晶二氧化硅的实际含量的二氧化硅文档。因此，不可能提供以下产品：该产品包含直接煅烧和助熔煅烧硅藻土，具有法规和技术支持特点(即合适的二氧化硅文档)，这些特点记录这些产品可不含超过检测限的方石英，同时也不含超过检测限的石英

或鳞石英。这对于这些产品的实际应用很重要。如果产品不包含合适的二氧化硅文档，则其使用中不必要的限制和不必要的承诺成本会增加，从而限制其适用性，并可能导致被效率较低的产品或技术替代。

[0091] 传统上使用X射线衍射(XRD)来鉴定和量化硅藻土产品中的结晶二氧化硅相。这种方法是完善的，除了有干扰结晶相存在的一些情况以外，其通常能够以0.1wt％及以上的水平量化。XRD的问题不在于技术本身，而在于对结果的理解。硅藻土的方石英相和蛋白石相(蛋白石-CT和蛋白石-C)的衍射图谱有些类似。根据主衍射峰的位置，分析人员把蛋白石-C或蛋白石-CT误鉴定为方石英，并且将XRD图谱中的任何差异归因于晶体结构的缺陷和不规则性、小的晶粒尺寸或者仪器误差。与晶体结构和尺寸有关的一个复杂因素是，通过硅藻土的热处理形成的方石英的XRD图谱总是与通过石英砂的热处理形成的方石英(事实上的“标准”方石英晶体结构)的XRD图谱略有不同。这种差异是否归因于硅藻土中的非硅质杂质、非晶硅藻壳的形态或其他因素是未知的。然而，它引起的轻微模糊性增加了正确的相鉴定的不确定性。另一个混淆来源是方石英以两种形式存在，即α-方石英和β-方石英。β-方石英是高温相，它在200-300℃之间转化为α-方石英相，因此α-方石英相是通常在环境条件下存在的相。然而，通过机械约束和化学杂质，β-方石英相有时可以抵抗完全转化(参见Damby et al)。与α-方石英的XRD图谱相比，β-方石英的XRD图谱更近地与蛋白石-C的XRD图谱对齐。

[0092] 近年来，一些研究(包括Miles et al.和Hillier et al.的研究)已经表明，仅依赖于X射线衍射(XRD)的用于确定矿物(例如粘土和硅藻土)的混合物的方石英含量的标准分析技术，可能不能准确地将某些形式的蛋白石(如蛋白石-C)与方石英区分开来。Miles和Hillier都提出了区分方石英和蛋白石-C的新方法，并且当蛋白石-C是天然存在的时，这些方法特别有效，如在某些粘土产品中的情况一样。然而，这些依赖于粘土产品或矿石的蛋白石含量的溶解的方法(“溶解方法”)，在表征某些类型的、包含硅藻土的岩石的蛋白石-C含量方面不是有效的，因为其他矿物组成部分可能会保护蛋白石-C免于暴露在溶剂中。

[0093] 需要一种比传统方法(如本文所定义的)或溶解方法更好的方法，来确定宽范围组成的硅藻土的蛋白石-C(和/或蛋白石-CT)和方石英含量。如本文所用，“传统方法”是指使用XRD分析来测定和量化(使用该测定)硅藻土产品中的结晶二氧化硅相，其不考虑蛋白石相(蛋白石-C和蛋白石-CT)或方石英实际上是否存在，并且假定所述蛋白石相实际上为方石英。可以将方石英、石英或鳞石英中的每一个与其各自的标准(例如，石英为NIST SRM 1878b)进行比较以用于含量的量化，或者通过使用内标(例如刚玉)和可应用的相对强度比来进行量化。美国国家职业安全与卫生研究所(NIOSH)方法7500，是用于测定粉尘样品(包括含有硅藻土的粉尘)中可吸入的结晶二氧化硅的传统方法的一个例子。方法7500参考了许多可能的干扰相，包括云母、长石和粘土，但没有提到蛋白石-C或蛋白石-CT，并且在测试方法中没有提供这些相的量化。在传统方法中，硅藻土产品中结晶二氧化硅相的量化还包括蛋白石相(蛋白石-C和蛋白石-CT)含量。更具体地，这种传统方法将蛋白石相看作是方石英，如此，将方石英加上蛋白石相的组合定量为产品的“方石英含量”；这导致夸大产品的方石英含量(并且夸大产品的结晶二氧化硅含量)。

[0094] 本发明人开发了一种表征和量化产品的蛋白石-C和方石英含量的新技术。在本发明中不试图区分蛋白石-C和蛋白石-CT。尽管在本文讨论的产品中不可能同时存在蛋白石-C和蛋白石-CT，但如果两个相均存在，也不分别考虑蛋白石-C和蛋白石-CT相。相反，将两个

相的总和鉴定为蛋白石-C并且作为蛋白石-C来进行总定量(以wt％计)。换言之，如果两个相都存在，则将它们共同处理，就好像它们是一个相的一部分。因此，术语“蛋白石-C”在本文中用于表示蛋白石-C和/或蛋白石-CT，除非在其被使用的上下文中另有说明。

[0095] 他们已经使用他们的新技术来表征和量化一些直接煅烧或助熔煅烧的商业硅藻土产品的蛋白石-C(和/或蛋白石-CT)和结晶二氧化硅含量(例如方石英)，并且已经确定，物理组分已经处于公共领域的某些直接煅烧产品和某些助熔煅烧产品含有显著水平的蛋白石-C(和/或蛋白石-CT)但不含可检测水平的方石英。这一结果既令人惊讶又出乎意料，因为以前使用传统X射线衍射技术确定这些产品含有可检测水平的方石英，因此，错误地夸大了这些产品的二氧化硅文档组分。

[0096] 此外，在同样令人惊讶和出乎意料的结果中，发明人已经确定了某些组成的硅藻土矿石，其可以使用含钠的助熔剂进行助熔煅烧，以生产含有显著水平的蛋白石-C(和/或蛋白石-CT)但不含可检测水平的结晶二氧化硅的新产品。这些蛋白石的助熔煅烧的生物二氧化硅产品还可以满足颗粒过滤介质的其他严格要求，例如低湿体积密度和低可提取铁、钙、铝和砷。它们还可与其他材料(例如二氧化硅干凝胶和水凝胶、丹宁酸和聚乙烯聚吡咯烷酮(PVPP))结合使用，使其在特殊的固液分离(如葡萄酒和啤酒制造中常见的固液分离)中更有效。此外，这些蛋白石助熔煅烧的生物二氧化硅产品可通过酸洗进行进一步处理，以提高其用于高纯度过滤(例如，与专用饮料、专用化学品和生物制药制造相关的过滤)的适用性。酸洗提高了其适用性，因为它可以去除产品中存在的可能被溶解并转移到将被过滤的高纯度悬浮液中的微量杂质。由于与吸入结晶二氧化硅有关的问题，需要不含结晶二氧化硅的直接煅烧和助熔煅烧硅藻土产品。人们已经做出大量努力来致力于开发包含降低水平的结晶二氧化硅的直接煅烧和助熔煅烧硅藻土产品，但其技术有限且基本没有取得商业成功。对于传统上生产为白色的光亮粉末的助熔煅烧产品，将其分类以生产副产品填料和助滤剂产品，人们努力专注于开发含有低的或不含结晶二氧化硅的白色助熔煅烧产品，因为助熔煅烧硅藻土填料的规格要求产品具有高亮度和白度。

[0097] 对于本发明之一，本发明人决定不考虑产品的颜色而专注于开发含有降低的或不可检测水平的结晶二氧化硅的助熔煅烧助滤剂，并且已经取得成功。虽然这些既包含新物理组分又包含新二氧化硅文档的新产品在许多应用中作为功能添加剂的实用性有限，但其在用作过滤介质时具有突出的实用性。

[0098] 为了制备无结晶二氧化硅的助熔煅烧的生物二氧化硅产品，需要适当的选矿、确定的煅烧条件和后煅烧处理以及二氧化硅相的适当表征及其文档。选矿不仅涉及对存在的硅藻组合和硅藻壳状况的评估，而且还涉及对相关碎屑和沉淀矿物的表征。硅藻种类具有各种形状和大小，并且存在于任何特定硅藻土矿床中的种类确实会影响由其制成的成品的物理特性。例如，有些组合比其他组合更适合于特定过滤应用。此外，硅藻壳的总体状况或完整性会影响最终产品的特性。其中的一些硅藻土矿床或岩层含有大量小的硅藻壳碎片和很少的完整硅藻壳。使用这种原料制成的产品会影响起始形态，例如通过具有非常低的渗透率来影响。必须对矿石中存在的任何石英颗粒(相关的碎屑矿物)的相对数量和公称尺寸进行表征，以便可以预测加工过程中去除该相的可行性。有些矿石是不适合的，因为石英颗粒太细(亚微米)并且精细地分散在硅藻土基质内。除石英外，矿石中的非硅质材料也至关重要。足够数量的不含极细颗粒的铝和含铁矿物(相关的碎屑和/或沉淀矿物)的硅藻土矿

石，在助熔煅烧时倾向于去玻璃化并迅速形成方石英。虽然助熔剂的量和煅烧温度一般在助熔煅烧硅藻土产品的通常范围内，但是加工条件也很重要。应避免极高的温度(>1150℃)和极高的助熔剂量(>8wt％，以Na_2CO_3计)。最后，这些产品还包含适当的二氧化硅文档。没有这个基本要素，它们的实用性可能会受到很大的且不必要的限制。适当的二氧化硅文档是由使用本文所述的新测试方法/量化而来的。

测试方法的描述

蛋白石-C(和/或蛋白石-CT)与方石英

[0099] 蛋白石-C(和/或蛋白石-CT)和方石英之间具有可测定的区别特性，尽管并不总是精确。蛋白石常含有一些作为内部或附着的硅烷基团而存在的水，而方石英是无水的。因此，可以进行“烧失量测试”以查看样品中是否存在水合水。该测试应该在高温(例如980℃-1200℃，优选为982℃-1000℃)下进行足够时间(至少1小时)，以便化学键合的水有机会分离和挥发。对该处理前后的样品质量(精确到0.1mg)的精确测定使得能够对挥发物(包括水合水)进行量化，分辨率优于0.01％。美国测试和材料协会(ASTM)方法C571提供了一种用于确定包含硅藻土的样品的烧失量的合适方案。被确定为含有可测定(通常超过0.1wt％)的烧失量的样品可能是蛋白石-C(和/或蛋白石-CT)。

[0100] XRD(如块状粉末XRD)也可用于区分蛋白石-C和α-方石英。方石英的衍射图谱包含尖锐的布拉格峰，在22.02°，36.17°，31.50°和28.49°2θ处最为显著。与方石英相比，蛋白石-C(和/或蛋白石-CT)的衍射图谱轮廓较不清晰，其具有更宽和更少的峰，其可能指示径向散射而不是真正的布拉格峰。主峰和第二峰的位置与方石英的相似，但在31.50°和28.49°2^{θ}处的峰缺失或非常不明显。总之，蛋白石-C(和/或蛋白石-CT)衍射图谱与α-方石英的衍射图谱的不同之处在于：主峰(22°)和第二峰(36°)处于较高的晶面间距(低2θ角度)，使用“半高宽”(FWHM)统计量测定的蛋白石-C(和/或蛋白石-CT)存在更宽的主峰，蛋白石-C(和/或蛋白石-CT)在31.50°和28.49°2θ处具有轮廓不清的峰，以及更显著的非晶背景。为了更全面地描述XRD，例如块状粉末XRD、术语和实践，在此引用了Klug和Alexander在XRD实践中的体积。

[0101] 使用XRD区分蛋白石-C与β-方石英是比较困难的，然而Chao和Lu证明，通过将氧化铝含量小于10wt％的β-方石英样品研磨至细颗粒尺寸，大部分β-方石英转化为α-方石英相，并具有相应的XRD图谱峰位移。当将包含蛋白石-C(和/或蛋白石-CT)的硅藻土产品进行精细研磨，然后使用XRD分析时，没有发生这种情况，即没有峰位移。作为标准XRD实践，在进行块状粉末X射线衍射分析之前将本文所述的所有样品进行研磨。

[0102] 仅仅基于XRD图谱是很难区分的，Miles et al.提倡在非常高的温度(1050℃)下对样品进行24小时的热处理。理论上来说，蛋白石-C将会脱水并重结晶为方石英。衍射峰将变得更尖锐、更强烈，并且将会发生位移。较尖锐的衍射峰表明长程分子排列增加(较大的晶粒尺寸)。峰强度增加表明由该峰表示的结晶相的数量增加。峰位置的位移表明晶体结构的变化，伴随着相关晶面间距的增大或减小。如果原始样品中存在方石英，则衍射图谱不会显著改变。这种技术的潜在问题是，在样品是由单个颗粒组成的情况下，其中一些颗粒可能是蛋白石的，其他颗粒可能由方石英组成。加热该样品会将蛋白石相转化为方石英，但不影响方石英，并且随后没有太多论证可以证明原始样品中也不存在方石英。

[0103] Miles和Hillier等人的化学溶解技术存在另一个问题。Hillier et al.成功地证

明了氢氧化钠消化在确定各种粘土样品是否含有蛋白石相或方石英中的功效。NaOH能够溶解所有形式的二氧化硅，但与蛋白石相比，与结晶种类需要更多的接触时间。当用于硅藻土样品(天然的、直接煅烧和助熔煅烧的)时，Hillier的方法不能完全去除蛋白石相，包括蛋白石-A。这很可能是因为硅藻土颗粒在天然状态下涂覆有耐化学的沉淀物(如褐铁矿)，直接煅烧时涂覆有铁氧化物，助熔煅烧时涂覆有富含钠的玻璃状或类似玻璃的相。虽然延长NaOH接触时间确实增加了蛋白石相的溶解，但使用不同工艺和不同原料生产的硅藻土产品样品之间的结果可能不一致。

[0104] 确定样品中不存在方石英的一种相对简单的方法是，将方石英标准参考物质(即，美国国家标准与技术研究院(NIST)标准参考物质1879A)掺杂到样品中(添加已知量)，对掺杂样品进行XRD分析，然后比较原始未掺杂样品衍射图谱和掺杂样品图谱。如果掺杂样品衍射图谱仅增加了主峰和第二峰的强度，但不显示位置偏移或显示额外峰，则原始样品很可能包含方石英。如果主峰移动并变得更尖锐(或分解成两个分离的峰)，并且第二峰出现或轮廓变得更清晰，则在原始样品中存在蛋白石-C(和/或蛋白石-CT)而不是方石英。

[0105] 总之，为了确定包含硅藻土的产品的样品是否含有方石英或蛋白石-C(和/或蛋白石-CT)，并随后量化蛋白石-C(和/或蛋白石-CT)和/或结晶二氧化硅含量，涉及根据本文公开的改进方法(在下文中称为“LH方法”)的一些步骤。

[0106] 第一，通过高温烧失量试验确定样品是否含有水合水。例如，获得样品的(代表性的)第一部分，并且在此第一部分上进行烧失量试验。

[0107] 第二，进行块状粉末X射线衍射，并检查所得(第一)衍射图谱。例如，优选地，获得样品的(代表性的)第二部分，并且在该第二部分上进行粉末XRD。优选地，在XRD之前研磨第二部分。分析得到的(第一)衍射图谱是否存在蛋白石-C(和/或蛋白石-CT)和方石英。用得到的(第一)衍射图谱也可以分析样品的(代表性)第二部分中是否存在其他结晶二氧化硅相(例如，石英和鳞石英)。如果(第一)衍射图谱明显表明是蛋白石-C(或蛋白石-CT)，则不需要进一步的分析来确定样品是否包含方石英或蛋白石-C(和/或蛋白石-CT)。如本文前面所讨论的，蛋白石-C(和/或蛋白石-CT)衍射图谱与α-方石英的衍射图谱的不同之处在于：主峰(22°)和第二峰(36°)处于较高的晶面间距(低2θ角度)，使用“半高宽”(FWHM)统计量测定的蛋白石-C(和/或蛋白石-CT)存在更宽的主峰，蛋白石-C(和/或蛋白石-CT)在31.50°和28.49°2θ处具有轮廓不清的峰，以及更显著的非晶背景。

[0108] 如果(第一)衍射图谱对于是否存在蛋白石-C(和/或蛋白石-CT)和/或方石英而言存疑，则根据LH方法进行第二次XRD分析以确定是否存在蛋白石-C(和/或蛋白石-CT)和/或方石英。这次，所述分析，优选地，在掺杂方石英标准参考物质(NIST 1879a)的样品的另一个代表性部分上进行。例如，获得样品的(代表性的)第三部分，然后掺杂方石英标准参考物质(NIST 1879a)，并在第三部分上进行XRD。分析从第三部分的XRD的得到的(第二)衍射图谱。优选地，在XRD之前研磨第三部分。如果原始样品(例如，代表性的第二部分)包含蛋白石-C(和/或蛋白石-CT)，则方石英尖峰显著改变衍射图谱(来自其第二部分的衍射图谱)，其在22.02°和36.17°2θ具有可辨认的额外峰，以及在第三部分的(第二)衍射图谱中看到在31.50°和28.49°2θ具有更突出的峰。如果原始样品(更具体地说，其第二部分)包括方石英，则与第二部分的(第一)衍射图谱相比，方石英尖峰的添加(向第三部分)仅导致峰强度增加而没有其他显著变化(如在第三部分的(第二)衍射图谱中所见)。

[0109] 量化硅藻土样品的蛋白石C(和/或蛋白石-CT)含量可能是复杂的,因为其衍射图谱是宽峰和非晶背景的组合,并且硅藻土产品除了蛋白石之外通常还包含其它X-射线非晶相。根据LH方法,通过将第一衍射图谱的蛋白石-C(和/或蛋白石-CT)峰(如果存在两个相,则共同地)视为方石英,并相对于方石英标准(如NIST 1879a)对其定量,来获得估计定量。这种量化蛋白石-C(和/或蛋白石-CT)的方法,我们称为XRD方法,通常会低估蛋白石-C(和/或蛋白石CT)含量,但对于许多目的(例如制造质量控制)是有效的。为了清楚起见,这种XRD方法是umbrella LH方法的一部分。可选地(在LH方法下),通过在非常高的温度(例如,1050℃)下加热样品的代表性部分(例如,第四部分)较长时间(例如,24-48小时))直到该加热部分完全脱水来测定。这使蛋白石相完全脱水并形成方石英(减少非晶背景组分)。然后对第四部分进行XRD分析,并且可以相对于方石英标准物量化第四部分的所得(第三)衍射图谱中的方石英,以估计原始蛋白石-C(和/或蛋白石-CT)含量。优选地,在XRD之前研磨第四部分。只要在加热第四部分之前没有添加额外的助熔剂,并且温度保持在1400℃以下,则存在于第四部分中的任何石英都不会被转化为方石英。

[0110] 为了根据LH方法获得样品的总结晶二氧化硅含量wt%,将已鉴定的方石英(若有)的重量百分比、石英(若有)的重量百分比和鳞石英(若有)的重量百分比加在一起,以计算样品中结晶二氧化硅含量的总重量百分比。为了获得在样品的第二部分的(第一)衍射图谱分析期间发现存在的石英或鳞石英的重量百分比,石英或鳞石英可以分别与其各自的标准(例如,NIST SRM 1878b石英)对比来量化其含量,或通过使用内标(如刚玉)和合适的相对强度比来定量。如果通过LH方法确定存在方石英,则可以将在样品的第二部分的(第一)衍射图谱中看到的方石英与其各自的标准(例如NIST 1879a)进行比较以量化其含量,或者通过使用内标(如刚玉)和合适的相对强度比来量定量。在存在蛋白石-C(或蛋白石-CT)和方石英并且蛋白石-C(或蛋白石-CT)的主峰不能与方石英的主峰区分或分离的异常情况下,将蛋白石-C(或蛋白石-CT)和方石英作为一个相来定量并报告为方石英。由此报告的方石英的量将高于样品中的实际量。因为样品是产品的代表性样品,所以样品中的结晶二氧化硅含量的总重量百分比被认为准确地代表从中取出样品的产品中的结晶二氧化硅含量的总重量百分比。

[0111] 使用由MDI™ Datascan5软件控制的Siemens®D5000衍射仪(具有CuKα辐射、样品旋转、石墨单色器和闪烁探测器)来进行所有详细的块状粉末XRD。功率设置为50KV和36mA,步长为0.04°,每步4秒。JADE™(2010)软件用于XRD扫描分析。样品制备包括用氧化锆研磨介质在氧化锆瓶中进行SPEX®研磨。

渗透率和湿体积密度

[0112] 使用各种已制定的方法来确定硅藻土过滤介质的渗透率和堆积密度。这些参数可用于表征硅藻土产品在过滤应用中的表现。使用硅藻土渗透仪(美国专利号5,878,374)分析本文所述的样品的这些性能,该硅藻土渗透仪是一种自动化仪器,其从已知质量的硅藻土样品形成“滤饼”,然后测定计算渗透率和湿体积密度所需的所有必需参数。湿体积密度(WBD)和渗透率的计算公式如下:

[0113] 湿体积密度(g/ml)=m/(h*A)

[0114] 渗透率(达西)=(V*u*h)/(A*dP*t)

其中:

A＝滤饼的横截面积(cm^2)

dP＝滤饼上的压降(atm)

t＝流动时间(s)

m＝干样品质量(g)

u＝滤液粘度(cp)

V＝滤液体积(ml)

h＝滤饼高度(cm)

EBC可溶性金属(铁、钙、铝、砷)

[0115] 欧洲啤酒酿造协会(EBC)建立了一个公认的测试方法纲要，其中包括一个旨在确定过滤介质对滤液(即啤酒)的可溶性金属贡献的方法。EBC可溶性金属测试包括：将样品(2.5％浆液浓度)在环境温度下在1％邻苯二甲酸氢钾溶液(pH为4)中悬浮2小时，将该悬浮液过滤，然后使用AA或ICP分光光度计分析滤液中的金属含量。

ASBC铁

[0116] 美国酿造化学家协会(ASBC)也建立了一套与啤酒制造相关的测试方法，其中包括一种用于确定过滤介质对啤酒的可溶性铁贡献的方法。该方法在北美被广泛使用。该测试要求将助滤剂悬浮在脱气的室温啤酒(2.5％浆液浓度)中6分钟，过滤悬浮液，并使用比色法或原子吸收仪器分析法分析滤液的铁的收集。

光学性能

[0117] 可以使用国际照明委员会(CIE)定义的颜色空间将产品的光学性能表征为$L^*a^*b^*$颜色空间。“L^*”坐标是反射光强度的量度(0到100)。“a^*”坐标是红度(正值)或绿度(负值)的程度。“b^*”坐标是黄度(正值)或蓝度(负值)的程度。使用柯尼卡美能达(Konica Minolta®)色度计CR-400来测定本文所述样品的光学性能。

[0118] 已经观察到，在相同的煅烧条件(相同的助熔剂量和煅烧温度)下，来自不同化学组成的硅藻土矿石的助熔煅烧产品将具有用$L^*a^*b^*$颜色空间表示的不同的颜色和亮度。还观察到，助熔煅烧产品的颜色，尤其是b^*值与其中所含的蛋白石-C(和/或蛋白石-CT)的量(使用XRD方法测定)成反比。

可吸入的方石英和石英

[0119] 为了解决“块状材料中含有多少可吸入的结晶二氧化硅(RCS)”的问题，IMA计量工作组开发了一种标准化方法，称为SWeRF-尺寸加权可吸入分数(后来变为SWeFF或尺寸加权细粒分数)。这种方法量化了块状产品中可吸入颗粒的含量，如果在空气中吸入该颗粒，可能到达肺泡。其考虑了欧洲标准化委员会CEN EN481标准定义的粒径分布(PSD)分数(包括颗粒密度因子)和这些颗粒的结晶二氧化硅含量，称为尺寸加权细粒分数-结晶二氧化硅(SWeFFcs)。将该方法用于本文报告的样品结果。在每个样品的负500目(25um)部分上进行块状样品XRD测试，以确定细粒部分的结晶二氧化硅含量。使用Microtrac®S3500(超声波分散，颗粒折射率(RI)为1.48，流体RI为1.333，不规则颗粒形状，透明颗粒)确定每个原始样品的粒径分布。SWeFF计算中也使用1.15的平均颗粒密度。

包含已经在公共领域中的物理组分的天然、直接煅烧和助熔煅烧硅藻土产品的结晶二氧化硅含量

[0120] 根据EP Minerals、Imerys Filtration Minerals、Ceca、Dicalite公司和昭和化

学(Showa Chemical)的安全数据表(SDS)的结晶二氧化硅数据部分报道，表1、2和3示出了大量天然、煅烧和助熔煅烧硅藻土产品的结晶二氧化硅含量。EP Minerals、Imerys Filtration Minerals、Ceca、Dicalite公司和昭和化学是天然、煅烧和助熔煅烧硅藻土产品的制造商。“Celatom”是EP Minerals的商标，“Celite”、“Kenite”和“Celpure”是Imerys Filtration Minerals的商标，“Clarcel”是Ceca的商标，“Radiolite”是昭和化学的商标，“Dicalite”是Dicalite公司的商标。该表还示出了对应于二氧化硅文档的硅藻土产品的近似渗透率范围。

[0121] 如表所示，天然产品是一种硅藻土产品，其在足以干燥材料但又足够低以防止硅藻土的蛋白石-A组分的显著脱水和硅藻土的显著团聚的温度下进行热处理，其渗透率范围在小于0.01至略超过0.1达西之间。由于较低的处理温度，天然硅藻土产品通常被报道为含有低水平或不可测定水平的结晶二氧化硅(通常为石英形式)，尽管一些产品含有高达约4wt％的结晶二氧化硅。

[0122] 这些表还表明，根据提供其中所列产品的公司所采用的传统方法，所有商业的直接煅烧和助熔煅烧硅藻土产品都含有可检测水平的结晶二氧化硅。这些产品的渗透率和结晶二氧化硅含量的范围分别为0.01至超过20达西和小于5wt％至超过90wt％的结晶二氧化硅含量。

[0123] 表1.包含已在公共领域的物理组分的天然硅藻土产品的SDS文档和渗透率范围

生产商	产品			安全数据表信息					
	等级	渗透率达西	产地	石英wt%	方石英wt%	销售地	文档#	修订	年份
EP	Celatom MN-2, FN-1, FN-2, FN-6	0.01-0.12	美国			美国		9	2015
EP	Celatom MN-3, MN-4, MN-4HT, MN-23, LCS-3	n/a	美国			美国		9	2015
EP	Celatom MN-47, MN-51, MN-53, MN-74, MN-84, Drill-n-Dry™,天然原矿石	n/a	美国			美国		9	2015
EP	Celatom MP77, MP78, MP79	n/a	美国			美国		9	2015
EP	天然 DE AFA	n/a	美国			美国		9	2015
Imerys	混凝土用 Celite	n/a	美国，内华达州，芬利			美国	2213	5	2015
Imerys	渗滤-所有等级	n/a	美国，内华达州，芬利			美国	2800	7	2015
Imerys	Celpure S25, C25, C25i	0.025	美国，加			美国	3105	10	2015

			州，隆波克						
Imerys	Celpure S65, C65, P65, NP, 65i	0.065	美国，加州，隆波克			美国	3110	13	2015
Imerys	C206, C209, C209C, C230, C266, C266C, C292, C321, C392, C410, C441, C500, FC, Snow Floss, Snow Floss C, 混凝土用 Celite, Sil-O-Cel	n/a	美国，加州，隆波克	<4	<3	美国，亚洲	2200	12	2015
Imerys	Celite S, Kenite 100, Filter Cel, Filter Cel LV	n/a	墨西哥，萨科阿尔科（Zacoalco）			美国，拉丁美洲	3225	5	2015
Imerys	C209, C221, C221M, C221C, C280, C289, C400, C400A, C400D, C400TC, C490, C MNPP, Diactiv 21, Snow Floss	n/a	墨西哥，萨科阿尔科（Zacoalco）			美国，拉丁美洲	2209	10	2015
Imerys	CelTiX, CelTiX-P	n/a	墨西哥，萨科阿尔科（Zacoalco）			美国	2214	7	2015
Imerys	Diactiv 17, Diactiv 117, Diactiv 18C, Diactiv 18D,超滤	n/a	智利，阿里卡，	<1	<1	拉丁美洲	3520	6	2010
Dicalite	Dicalite 104, 143, 153, 183, BP3, BP5, BP8, CC1, CA3, SA3, D4A, D4C, D4R, IG3, IG33.	n/a	美国	<3	<5	欧洲	0011	3	2003
Dicalite	Dicalite 104, 183, BP-3, BP-5, CA-3, CA-5, D4A, D4C, D4R, D4AFA, 677, 677S, SA3	n/a	美国	<2			002	0	2014

[0124] 表2.包含已在公共领域的物理组分的煅烧硅藻土产品的SDS文档和渗透率范围

生产商	产品			安全数据表信息					
	等级	渗透率达西	产地	石英wt%	方石英wt%	销售地	文档#	修订	年份
EP	Celatom® FP-1, FP-2, FP-22	0.01-0.15	美国		<5	美国		14	2014
EP	Celatom® FP-3, FP-4, FP-6, FP-12	0.14-1.2	美国		10-40	美国		13	2014
Imerys	Celpure S100, C100, P100	0.1	美国，加州，隆波克	<1	<10	美国	3113	8	2015
Imerys	Celpure S300, C300, P300	0.3	美国，加州，隆波克	<1	<15	美国	3115	12	2015
Imerys	C350/C507	<0.02	美国，加州，隆波克	<3	<35	美国，亚洲	2303	2	2015
Imerys	C577, C577 NF, Filter Cell, Filter Cell NF, Celite BPP	0.1-0.2	美国，加州，隆波克	<3.5	<5.5	美国，亚洲	2320	8	2015
Imerys	Std Super Cel, SSC, Std Super Cel BP	0.2-0.3	美国，加州，隆波克	<3	<20	美国，亚洲	2310	6	2015
Imerys	C3Z, C201, C270, C271, C350, C505, C507, C512, C512 Z, C520, Hyflo PZ, CR, X-3	<0.9	美国，加州，隆波克	<3	<35	美国，亚洲	2300	11	2015
Imerys	C315, C350, C505, C512, C512Z, C520, C520-CB, C577, Celite CM-7, Kenite 101, Kenite 200, Filter Cel M, Diactiv 14, Standard Super Cel	<0.45	墨西哥，萨科阿尔科（Zacoalco）	<1	<53	美国，拉丁美洲	3230	12	2015
Dicalite	PS, Dicalite 215, Superaid, UF, SA-UF,	<0.5	美国	<5	<20		005	0	2014

	Speedflow, 231								
Ceca	Clarcel CBL	0.025-0.05	法国	<20	<20		89316901	2.01	2003
Ceca	Clarcel CBR	0.08-0.2	法国	<20	<60		89346901	2.02	2005

[0125] 表3.包含已在公共领域的物理组分的助熔煅烧产品的SDS文档和渗透率范围

生产商	产品			安全数据表信息					
	等级	达西	产地	石英wt%	方石英wt%	销售地	文档#	修订	年份
EP	Celatom® FW-6,FW-12, FW-14, FW-18, FW-20, FW-40, FW-50, FW-60, FW-70, FW-80, SP	0.4-7.5	美国		35-50	美国		12	2014
EP	Celatom® MW-25, MW-27, MW-31, Celabrite®, Celabloc®	n/a	美国		40-70	美国		13	2014
Imerys	Celpure S1000, C1000, P1000	1	美国，加州，隆波克	<1	<85	美国	3125	11	2015
Imerys	C110, C224, C226, C319, C501, C513, C522, 食用油用FA, C HSC, Hyflo, HSC, X-4, X-5	<1.3	美国，加州，隆波克	<4	<40	美国，亚洲	2400	12	2015
Imerys	Aqual-Cel, C269, C503, C535, C545, C560, C566, C578P, C580, X-6, X-7	<25	美国，加州，隆波克	<4	<50	美国，亚洲	2410	8	2015
Imerys	C219, C233, C263, C281, C388, C427A, C499, SFSF, SF, 白雾, CWPP8	n/a	美国，加州，隆波克	<2.5	<70	美国，亚洲	2420	8	2015
Imerys	C281, C535, C545, C555, C555R, C580, CPC, K300, K700, K1000, K2500, K3000, K5200, K5500, K5800, K7.5, Hyflo,游泳池, X-4, X-5, X-6, X-7	<25	美国，华盛顿州，昆西	<1	<60	美国，亚洲	3040	15	2015
Imerys	Micro-Ken 118, 140, 800, 801, 805, 811, 900	n/a	美国，华盛顿州，昆西	<1	<93	美国，亚洲	3045	3	2015

Imerys	C281, C281D, C281 USA, C499, Super Floss, Super Floss MX, Super Floss Q	n/a	墨西哥，萨科阿尔科（Zacoalco）	<1	<77	美国，拉丁美洲	3242	4	2015
Imerys	C281, C499, C501, C501-F, C503, C508, C535, C545, Diactiv 12, Diactive 34, Hyflo AN, Hyflo Z, Hyflo ZS, Hyflo SC, Kenite 700, Kenite 300	<1.1	墨西哥，萨科阿尔科（Zacoalco）	<1	<77	美国，拉丁美洲	3240	16	2015
Imerys	C110, C281, C281-A, C281-M, C388, C427, C501, C501-A, C503, C508, C513, C535, C535-QM, C545, C545-D, Celite BP-1, Celite FCFA, Celite SW, Diactiv 34, Hyflo AN, Hyflo Z, Hyflo ZS, Hyflo Super Cel, Kenite 700, Kenite 1000, Kenite 2500, Kenite 3000, Super Floss, Super Floss-P, Super Floss-MX, Super Floss-Q, QP-HSC,C564	<4	智利，阿里卡	<1	<77	拉丁美洲	3580	2	2010
Imerys	C503, C520A, C535, C545, Diactiv 7, Diactiv 8, Diactiv 9, Diactiv 10, Diactiv 11, Diactiv 12, Diactiv 13, Diactiv 14, Diactiv 14F,	<4	智利，阿里卡	<1	<67	拉丁美洲	3540	6	2009

	Diactiv 15F, Hyflo Super Cel, QS								
Imerys	Diactiv 16, 微细过滤		智利，阿里卡	<1	<51	拉丁美洲	3560	6	2010
Dicalite	Dicalite 341, Speedplus, 375, Speedex, 2500,游泳池, 4200, 4500, 4500C, 5000, 6000, 7000, WB-6, WB-6A	<12	美国	<5	<70		001	0	2014
Ceca	Clarcel DIC, DICB, DICH, DIFB, DIFBO, DIFD, DIFN, DIFR, FD		法国		65		891509-001	2.1	2011
昭和	Radiolite #600, 700, 900, 900S, 1100, Ace II, F, Deluxe W-50		日本，中国	非晶二氧化硅可能结晶			SW-1		2011

[0126] 如表1、2和3所示，公司在其安全数据表中报告结晶二氧化硅含量范围是业内的惯例。这些范围有时表达为“小于”某含量水平。当使用该报告格式时，其表示该产品含有高达所指示的数值(视情况而定)的可检测水平的石英或方石英。当不存在石英或方石英时，供应商不报告含量水平的范围。

[0127] 虽然该报告方法(如果能够理解的话)指出哪些商业产品含有(基于传统方法)可测定量的石英或方石英，但是该报告方法不能清楚地指出这些产品的平均或典型的结晶二氧化硅含量。因此，发明人将所选择的产品的实际测定结果(使用传统方法测定)包括在表4中。

[0128] 根据在EP Minerals的研究和开发实验室中所表征的，表4示出了许多包含已经在公共领域中的物理组分的商业硅藻土产品的渗透率和结晶二氧化硅含量(根据使用传统方法确定)。该表中的数据与表1、2和3的数据一致，并且显示使用传统的X射线衍射技术来表征晶体二氧化硅含量的具有在0.03至10达西之间的渗透率的硅藻土产品都包含高于检测限水平的结晶二氧化硅，其最低的结晶二氧化硅百分含量在0.1wt％水平，最高含量为80wt％以上。该表还显示，当使用传统方法测定时，所有直接煅烧和助熔煅烧产品都含有可测定水平的结晶二氧化硅，而一些天然硅藻土产品不含可测定水平的结晶二氧化硅。

[0129] 表4.通过传统方法测定的包含已经在公共领域中的物理组分的商业硅藻土产品的石英和方石英含量的估算

产品	样品 ID	渗透率（达西）	石英 (wt%)	方石英 (wt%)
Ceca Clarcel 78	23139	0.02	0.8	0.0
Imerys Celite S	20633	0.03	0.2	0.0
Ceca Clarcel Dif N	17956	n/a	0.0	80.4
EP Minerals FN-2	25037	0.06	0.1	0.0
EP Minerals MN-4	25061	0.01	0.0	0.0
Dicalite Superaid	19918	0.05	0.7	3.9
Ceca CBL	22602	0.06	11.0	15.0
Ceca CBL-3	22603	0.03	3.0	7.0
Ceca Clarcel CBR	3234	0.14	8.1	n/a
Imerys Celite 505	19154	0.04	0.7	4.2
Imerys Celite 512	24081	0.43	3.0	12.0
Imerys Celite 512	21881	0.79	11.4	25.2
Imerys Celite Std. Supercel	27115	0.20	4.4	4.7
Imerys Celite 577	27116	0.10	1.9	3.3
昭和 Radiolite 200	27117	0.10	2.1	7.9
昭和 Radiolite 300	27118	0.20	3.5	14.7
Imerys Cynergy 200	27121	0.20	2.1	3.4
EP Minerals FP-2	B12C0	0.20	0.0	16.0
EP Minerals FP-3	B17E2	0.24	0.0	18.6
EP Minerals FP-4	2H11B4	0.37	0.0	38.1
EP Minerals FP-6	2B11F1	0.70	0.0	71.1
Imerys Celite 501	18362	1.50	0.0	74.0
EP Minerals FW-6	1D17B14	0.72	0.0	17.7
EP Minerals FW-14	2E16I14	1.55	0.0	41.2
Imerys Celite 501	18362	1.50	0.0	45.9
Imerys Celite 508	22813	1.00	0.0	64.0
Imerys Celite Hyflo	22814	1.40	0.0	55.0
Imerys Celite 535	22800	2.80	0.0	58.0

Imerys Celite 545	27113	3.50	1.5	35.4
Chuo H-600	21196	2.60	3.0	23.0
Dicalite Speedex	21164	3.20	0.0	68.7
Dicalite Speedflow	19917	1.72	0.0	80.8
Dicalite 4500	24541	7.30	0.0	50.8
[1]昭和 Radiolite 500	21195	1.60	3.0	18.8
昭和 Radiolite 700	27119	2.20	1.2	50.5
[1]昭和 Radiolite 800	15291	1.11	1.3	10.1
昭和 Radiolite 900S	27120	4.10	1.9	35.6
昭和 Radiolite 1100	24340	4.50	1.2	58.0
EP Minerals FW-80	E19A1XR	9.89	0.0	47.9
Ceca Clarcel AK Starch	25084	9.40	0.0	38.7
Ceca Clarcel DIF BO	19894	0.90	0.1	41.0
Imerys Celite Superfloss	19638	n/a	0.0	85.2
Imerys Celite 281	19559	n/a	0.1	42.2
Imerys Kenite 2500	21838	5.27	0.0	45.2

[1] 昭和Radiolite 500和800为直接煅烧产品。

[0130] 用传统方法分析时，一些直接煅烧和助熔煅烧产品被报告含有非常低水平或不可检测水平的结晶二氧化硅。这些产品已在专利文献中进行了报道，但至今尚未商业化。参见例如美国专利号8,084,392(Lenz,et al)、美国专利号5,179,062(Dufour)和美国专利号9,095,842(Nannini et al)。

实施例

实施例1-包含公共领域中的物理组分和新二氧化硅文档的产品

[0131] 表5示出了在表4中列出的样品上使用用于区分蛋白石-C与方石英的LH方法的结果。几乎一半的样品已经从包含方石英的样品重新归类为包含蛋白石-C的样品。然而，其中只有少数样品完全不含结晶二氧化硅，因为大部分样品中仍然存在石英。尽管如此，通过使用LH法，将修订与这些样品相关的二氧化硅文档，以反映方石英的缺失以及降低水平或不可检测水平的结晶二氧化硅。

[0132] 表5.包含公共领域中的物理组分和新二氧化硅文档的产品

产品	**样品 ID**	**蛋白石-C（wt%）** [1]	**石英（wt%）**	**方石英（wt%）**
Ceca Clarcel 78	23139	0.0	0.8	0.0
Imerys Celite S	20633	0.0	0.2	0.0
Ceca Clarcel Dif N	17956	0.0	0.0	80.4
EP Minerals FN-2	25037	0.0	0.1	0.0
EP Minerals MN-4	25061	0.0	0.0	0.0
Dicalite Superaid	19918	3.9	0.7	0.0
Ceca CBL	22602	13.9	11.0	0.0
Ceca CBL-3	22603	6.6	3.0	0.0
Ceca Clarcel CBR	3234	0.0	8.1	22.9
Imerys Celite 505	19154	4.2	0.7	0.0
Imerys Celite 512	24081	12.0	3.0	0.0
Imerys Celite 512	21881	0.0	11.4	25.2
Imerys Celite Std. Supercel	27115	3.6	4.4	0.0
Imerys Celite 577	27116	1.3	1.9	0.0
昭和 Radiolite 200	27117	5.6	2.1	0.0
昭和 Radiolite 300	27118	11.3	3.5	0.0
Imerys Cynergy 200	27121	2.1	2.1	0.0
EP Minerals FP-2	B12C0	16.0	0.0	0.0
EP Minerals FP-3	B17E2	18.6	0.0	0.0
EP Minerals FP-4	2H11B4	38.1	0.0	0.0
EP Minerals FP-6	2B11F1	0.0	0.0	71.1
Imerys Celite 501	18362	0.0	0.0	58.0
EP Minerals FW-6	1D17B14	17.7	0.0	0.0
EP Minerals FW-14	2E16I14	0.0	0.0	41.2
Imerys Celite 501	18362	0.0	0.0	45.9
Imerys Celite 508	22813	0.0	0.0	64.0
Imerys Celite Hyflo	22814	0.0	0.0	55.0
Imerys Celite 535	22800	0.0	0.0	58.0
Imerys Celite 545	27113	0.0	1.5	35.4
Chuo H-600	21196	0.0	3.0	23.0
Dicalite Speedex	21164	0.0	0.0	68.7
Dicalite Speedflow	19917	0.0	0.0	80.8
Dicalite 4500	24541	0.0	0.0	50.8
[2]昭和 Radiolite 500	21195	18.8	3.0	0.0

昭和 Radiolite 700	27119	0.0	1.2	50.5
[2]昭和 Radiolite 800	15291	10.1	1.3	0.0
昭和 Radiolite 900S	27120	0.0	1.9	35.6
昭和 Radiolite 1100	24340	0.0	1.2	58.0
EP Minerals FW-80	E19A1XR	0.0	0.0	47.9
Ceca AK Starch	25084	0.0	0.0	38.7
Ceca Clarcel DIF BO	19894	0.0	0.1	41.0
Imerys Celite Superfloss	19638	0.0	0.0	85.2
Imerys Celite 281	19559	0.0	0.1	42.2
Imerys Kenite 2500	21838	0.0	0.0	45.2

[1]蛋白石-C量化是基于XRD方法的。

[2]昭和Radiolite 500和800为直接煅烧产品。

[0133] 图1至4是表5中列出的四种样品的X射线衍射图谱并叠加了低温方石英的标准棒状图谱。图1示出了Celite 501样品的图谱。该助熔煅烧的助滤剂包含方石英，但不含有石英或蛋白石-C。当前的SDS准确地反映了该信息。图2示出了FP-4样品和直接煅烧的助滤剂的XRD图谱。参考编号10标识图中的主峰，参考编号12标识第二峰。发现该样品包含蛋白石-C以及少量长石和可能的赤铁矿。应该修改该产品的二氧化硅文档以反映方石英的缺乏。图3是另一种直接煅烧的助滤剂FP-6的衍射图谱。在这种情况下，主要的结晶相是方石英，且不需要改变SDS。图4是助熔煅烧的助滤剂Dicalite 4500的衍射图谱。该样品也包含方石英，且当前的SDS反映了这一点。

[0134] 表6和表7展示了在表5中列出的许多样品上获得的物理和化学数据。

[0135] 表6:包含已在公共领域的物理组分的选择的硅藻土产品的物理和化学数据

样品	FP-2 B12C0	FP-3 B17E2	FW-6 1D17B 14	FW-14 2E16I1 4	Radio-lite 800	Cela-brite 2A20A 13F

类型	直接煅烧	直接煅烧	助熔煅烧	助熔煅烧	直接煅烧	助熔煅烧
总化学构成（XRF表示为氧化物）						
SiO_2 (wt%)	94.3	94.5	90.8	91.2	85.6	94.5
Al_2O_3 (wt%)	2.5	2.4	2.9	2.7	7.9	1.6
CaO (wt%)	0.6	0.6	0.4	0.7	1.0	0.4
MgO (wt%)	0.3	0.2	0.2	0.3	0.4	0.2
Na_2O (wt%)	0.4	0.4	3.8	3.1	1.6	2.1
K_2O (wt%)	0.2	0.3	0.3	0.3	0.7	0.1
Fe_2O_3 (wt%)	1.5	1.4	1.4	1.6	2.5	0.9
TiO_2 (wt%)	0.1	0.1	0.1	0.1	0.2	0.1
渗透率（达西）	0.20	0.24	0.72	1.55	1.11	
湿体积密度(g/ml)	0.37	0.36	0.32	0.33	0.33	
EBC 可溶性金属						
Fe (ppm)					75	
As (ppm)	3.3	3.2	5.8	1.3	1.2	
烧失量（wt%）	0.2	0.2	0.1	0.1	0.2	＜0.1
蛋白石-C /方石英分析						
主峰形心（Å）	4.09	4.08	4.08	4.07	4.08	4.06
FWHM (°2θ)	0.35	0.34	0.44	0.33	0.41	0.30
10°－37° 2θ之间的峰	2/4	2 /4	2 / 4	4 /4	3 /4	4 /4
蛋白石-C（wt%）[1]	16.0%	18.6%	17.7%	0.0%	10.1%	0.0%
方石英（wt%）	0.0%	0.0%	0.0%	41.2%	0.0%	56.8%
石英（wt%）	0.0%	0.0%	0.0%	0.0%	1.3%	0.0%

[1] 蛋白石-C的量化是基于XRD方法的。

注意:FP-2、FP-3、FW-6、FW-14和Celabrite是EP Minerals LLC的产品;Radiolite 800是昭和化学的产品。

[0136]　表7:包含已在公共领域的物理组分的额外选择的硅藻土产品的物理和化学数据

样品	Dicalite 4500	Kenite 2500	Celite 512	Celite Std. Supercel	FP-6 2B11F1
类型	助熔煅烧	助熔煅烧	直接煅烧	直接煅烧	直接煅烧
总化学构成（XRF表示为氧化物）					
SiO_2 (wt%)	91.7	90.1	90.0	89.0	91.9
Al_2O_3 (wt%)	2.3	2.0	5.0	5.4	4.7
CaO (wt%)	0.2	3.4	0.5	0.6	0.5
MgO (wt%)	0.1	0.3	0.7	0.9	0.3
Na_2O (wt%)	4.4	2.3	0.7	0.7	0.2
K_2O (wt%)	0.1	0.4	0.7	0.9	0.1
Fe_2O_3 (wt%)	0.9	0.9	1.6	1.9	2.0
TiO_2 (wt%)	0.1	0.1	0.2	0.3	0.3
渗透率（达西）	7.30	5.27	0.30	0.25	0.70
湿体积密度(g/ml)	0.31	0.36	0.40	0.33	0.42
EBC 可溶性金属					
Fe (ppm)	34	35	146	73	
As (ppm)	0.5	0.5	2.3	6.4	1.0
烧失量（wt%）	< 0.1	0.5	0.4	0.2	0.1
蛋白石-C /方石英分析					
主峰形心（Å）	4.06	4.06	4.07	4.08	4.06
FWHM (° 2θ)	0.32	0.31	0.37	0.44	0.31
10° – 37° 2θ之间的峰	4/4	4/4	3/4	2/4	4/4
蛋白石-C（wt%）[1]	0.0%	0.0%	13.4%	1.3%	0.0%
方石英（wt%）	52.1%	39.2%	0.0%	0.0%	71.1%
石英（wt%）	0.0%	0.0%	3.1%	3.5%	0.0%

[1] 蛋白石-C的量化是基于XRD方法的。

注意：Dicalite 4500是Dicalite Minerals的产品；Kenite 2500、Celite 512和Celite Standard Super-Cel是Imerys Filtration Minerals的产品；FP-6是EP Minerals LLC的产品。

[0137] 图5示出了样品FP-2(B12C0)(参见表4、5和6)的XRD图谱并叠加了α-方石英的标准棒状图谱。可以看出，FP-2主峰(图5中的参考编号10)和第二峰(图5中的参考编号12)发生偏移(较高的晶面间距)，并且在31.50°和28.49°2θ处的峰不明显。这些因素以及相对宽的FWHM表明所表示的二氧化硅相是蛋白石-C。由长石引起的小峰也很明显。

[0138] 图6示出了“Celabrite 2A20A13F”样品的XRD图谱并叠加了α-方石英的标准棒状图谱。该产品是一种助熔煅烧的细填料，该XRD图谱与“标准”方石英的XRD图谱相当匹配。

[0139] 图7和图8示出了样品“FP-3 B17E2”在添加方石英标准物的尖峰前后的XRD图谱。图8是样品“FP-3 B17E2”的XRD图谱中的主峰的放大图。在图7和图8中叠加了α-方石英的标

准棒状图谱。与未掺杂的样品的XRD图谱相比，方石英尖峰导致轮廓清晰的第二峰(见参考编号12)、在31.50°和28.49°2θ处的轮廓清晰的第三峰(见参考编号14)以及主峰肩部的可见“驼峰”(见参考编号10)。这是证明原始样品包含蛋白石-C而不包含方石英的相当明显的证据。

实施例2至6:包含新物理组分和新二氧化硅文档的助熔煅烧硅藻土产品

[0140] 在EP Minerals研究与开发实验室中，已经从选择的具有不寻常的化学组成的矿石制备了许多蛋白石的助熔煅烧的生物二氧化硅产品的样品。尽管有证据表明，当在较低温度下(即FW-6 1D17B14)进行助熔煅烧时，可从标准矿石形成蛋白石-C而不是方石英，但对于助熔煅烧产品通常不是这种情况。然而，对于这些选择的矿石，即使在高温(例如920℃至1150℃)下进行助熔煅烧时，也会形成蛋白石-C(和/或蛋白石-CT)。不受理论束缚，理论上这些矿石中异常高水平的微细分散的铝和铁的化合物在助熔煅烧过程中抑制方石英的形成，尽管其他因素也可能具有影响。表8提供了几种蛋白石的助熔煅烧的生物二氧化硅产品的关于加工条件、物理和化学特征以及二氧化硅相确定的信息。

表8:新的助熔煅烧硅藻土产品的五个实施例

样品	18184-3	18188-2	18188-4	18188-7	18188-9
类型	助熔煅烧	助熔煅烧	助熔煅烧	助熔煅烧	助熔煅烧
苏打灰添加水平（wt%）	2.0	2.0	2.0	5.0	8.0
煅烧温度（°C）	1038	954	1038	1104	1104
煅烧时间（min.）	40	40	40	40	40
总化学构成（XRF表示为氧化物）					
SiO_2 (wt%)	88.7	87.3	87.8	87.7	86.4
Al_2O_3 (wt%)	5.6	6.9	6.5	5.4	5.3
CaO (wt%)	0.6	0.6	0.6	0.6	0.6
MgO (wt%)	0.3	0.4	0.4	0.3	0.3
Na_2O (wt%)	1.4	1.5	1.5	2.6	4.0
K_2O (wt%)	0.2	0.2	0.2	0.2	0.2
Fe_2O_3 (wt%)	2.8	2.7	2.8	2.8	2.8
TiO_2 (wt%)	0.3	0.4	0.4	0.4	0.4
渗透率（达西）	1.27	1.16	1.66	4.43	8.91
湿体积密度(g/ml)	0.28	0.29	0.28	0.28	0.26
EBC可溶性金属					
Fe (ppm)	31	39	23	29	45
Ca (ppm)	54	90	43	39	41
Al (ppm)	69	116	54	29	21
As (ppm)	1.4	0.3	0.6	0.4	0.2
ASBC啤酒可溶性铁（ppm）	13		14		
烧失量（wt%）	0.2	0.5	0.3	0.1	0.1
蛋白石-C /方石英分析					
主峰形心（Å）	4.08	4.08	4.10	4.08	4.07
FWHM (°2θ)	0.39	0.43	0.39	0.46	0.50
10°－37° 2θ之间的峰	2/4	2/4	2/4	2/ 4	3/4
蛋白石-C（wt%）[1]	10.9%	2.6%	9.0%	16.1%	22.4%
方石英（wt%）	0.0%	0.0%	0.0%	0.0%	0.0%
石英（wt%）	0.0%	0.0%	0.0%	0.0%	0.0%

[1] 蛋白石-C的量化是基于XRD方法的。

[0141] 表8中列出的所有样品均由原矿石通过以下步骤制备：在120℃下干燥24小时；破碎(颚式破碎机)至负1.25厘米；(用锤磨机)研磨直至99％通过70目(210um)；使用联邦设备公司的旋风式分级机进行分级，并丢弃粗级分(平均10％)；加入苏打灰并使用油漆搅拌器混合；放入陶瓷坩埚中在马弗炉中煅烧；并以70目筛分将筛渣筛过筛网。

[0142] 图9示出了添加和未添加5wt％方石英尖峰的样品18188-4的XRD图谱。在图9中叠加了α-方石英的标准棒状图谱。从图9中可以看出，通过使用LH方法，很容易将方石英尖峰

与原始蛋白石-C相区分开来。这提供了坚实的证据证明，当使用LH方法时，对蛋白石-C相的鉴定是正确的。对于这五种助熔煅烧产品，二氧化硅文档中不需要包括关于结晶二氧化硅的警告，尽管使用传统方法的分析和XRD图谱的传统解释将表明，所有这些样品将认为包含与所列的蛋白石-C的百分比大致相同的方石英，因此需要结晶二氧化硅警告。因此，这些产品的组成和它们的二氧化硅文档都是新颖的。

[0143] 图10示出了样品18188-9的XRD衍射图谱，其叠加有添加了15wt％方石英尖峰的相同样品。在图10中叠加了α-方石英的标准棒状图谱。虽然在这种情况下，方石英主峰(10b)仍与蛋白石-C主峰(10a)重叠，但该尖峰的添加显示出图谱的显著变化，而不仅仅是强度的增加。图11是相同衍射图谱的放大图，但其仅集中在主峰区域。

[0144] 根据ASBC方案测定，样品18184-3和18188-4的分离经过后煅烧水合处理以减少啤酒可溶性铁。水合处理由以下步骤组成：向每个样品中加入6％去离子水，在密封容器中在90℃下加热5小时，然后在敞口容器中在105℃下干燥以除去任何剩余的游离水分。在样品18184-3中ASBC啤酒可溶性铁从13ppm降至7ppm，在18188-4样品中ASBC啤酒可溶性铁从14ppm降至4ppm。

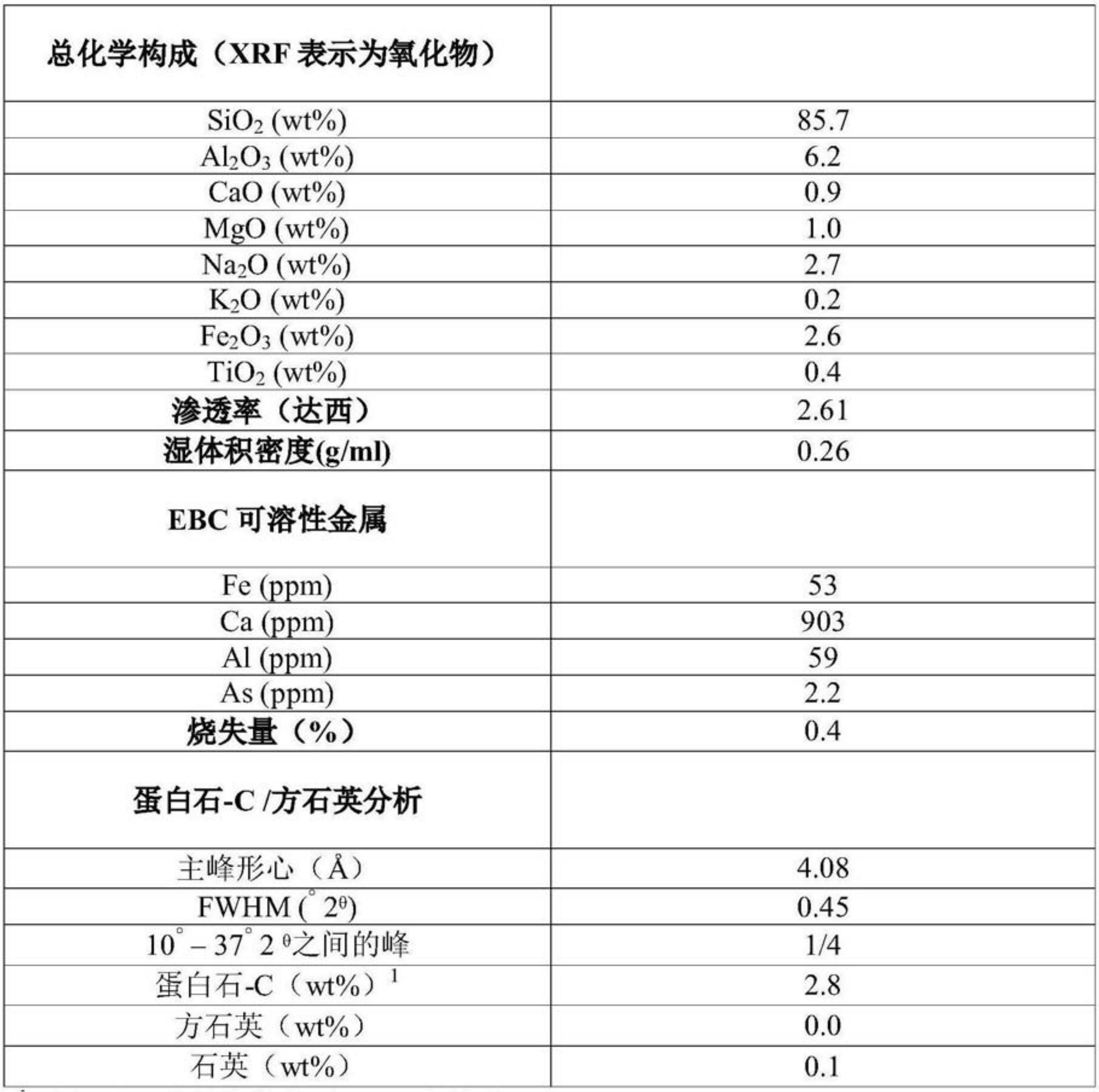
实施例7包含新物理组分和新二氧化硅文档的助熔煅烧硅藻土产品

[0145] 将硅藻土矿石(S31 15-4-7B 35-40)锤磨，干燥并使用联邦设备公司的旋风式分级机将其分级以获得两个尺寸级分。粗级分的质量收率为27％，粒径分布为d10＝30、d50＝73和d90＝141微米。通过与作为助熔剂的7wt％苏打灰混合，在马弗炉中在1038℃下煅烧40分钟，并通过70目筛网进行分散，从粗级分制备高渗透率产品。该产品具有30.5达西的渗透率和0.33g/ml的湿体积密度。图12示出了该样品的XRD衍射图谱。在图12中叠加了α-方石英的标准棒状图谱。主峰(10)偏移、FWHM以及缺乏明显的第三峰31.50°和28.49°2θ表明，存在的相是蛋白石-C。使用XRD方法计算的蛋白石-C的相对量为31.3wt％。再次，通过使用LH方法，正确的二氧化硅文档将显示产品的结晶二氧化硅含量是不可检测的，而包含通过传统方法开发的数据的传统二氧化硅文档将不正确地显示该样品含有约31wt％的结晶二氧化硅。

实施例8包含新物理组分和新二氧化硅文档的助熔煅烧硅藻土产品

[0146] 将来自另一矿床(SIS B-7)的矿石样品干燥、破碎、锤磨，然后在80目(177um)下过筛。将苏打灰(5wt％)与负80目部分混合，并将该混合物在电马弗炉中在927℃下煅烧40分钟。表9列出了所得产品的数据。在这种情况下，当用从LH方法开发的信息制作二氧化硅文档时，二氧化硅文档将显示0.1wt％为石英，但当使用传统方法制作二氧化硅文档时，其将显示约3wt％的组合的石英和方石英。

表9：实施例8-样品SIS B-7的产品数据



总化学构成（XRF 表示为氧化物）	
SiO_2 (wt%)	85.7
Al_2O_3 (wt%)	6.2
CaO (wt%)	0.9
MgO (wt%)	1.0
Na_2O (wt%)	2.7
K_2O (wt%)	0.2
Fe_2O_3 (wt%)	2.6
TiO_2 (wt%)	0.4
渗透率（达西）	2.61
湿体积密度(g/ml)	0.26
EBC 可溶性金属	
Fe (ppm)	53
Ca (ppm)	903
Al (ppm)	59
As (ppm)	2.2
烧失量（%）	0.4
蛋白石-C /方石英分析	
主峰形心（Å）	4.08
FWHM (° 2θ)	0.45
10° – 37° 2 θ之间的峰	1/4
蛋白石-C（wt%）[1]	2.8
方石英（wt%）	0.0
石英（wt%）	0.1

[1] 蛋白石-C的量化是基于XRD方法的。

实施例9至13：包含新物理组分和新二氧化硅文档的助熔煅烧硅藻土产品

[0147] 表10展示了在实验室生产(尚未在市场上买到)的几种助熔煅烧硅藻土产品和一种直接煅烧硅藻土产品的有关加工条件、物理和化学特性以及二氧化硅相确定的信息。其大多数但不是全部都包含蛋白石-C。加工条件包括助熔剂组成、助熔剂量、煅烧或烧结温度、煅烧时间、烧结时间等。表10中列出的所有样品均由不同原矿石通过以下步骤制备：

在120℃下干燥24小时；

破碎(颚式破碎机)至负1.25厘米；

(用锤磨机)研磨直至99%通过70目(210um)；

使用联邦设备公司的旋风式分级机进行分级，并丢弃粗级分(通常10%)；

加入苏打灰并使用油漆搅拌器混合；

放入陶瓷坩埚中在马弗炉中煅烧；

并以70目筛分将筛渣筛过筛网。

表10：新硅藻土产品的5个额外实施例

样品	**9** HV2BH-E	**10** HV2-F	**11** S3115-C	**12** S3115-E	**13** LCS3-H
类型	助熔煅烧	助熔煅烧	直接煅烧	助熔煅烧	助熔煅烧
苏打灰添加水平（wt%）	3.0	3.0	0.0	3.0	7.0
煅烧温度（°C）	1020	1140	1140	1020	1020
煅烧时间（min.）	40	40	40	40	40
总化学构成（XRF 表示为氧化物）					
SiO_2 (wt%)	84.7	85.6	82.6	80.7	88.3
Al_2O_3 (wt%)	6.5	6.6	8.3	8.2	3.3
CaO (wt%)	0.8	0.8	2.3	2.3	0.9
MgO (wt%)	0.4	0.4	0.7	0.8	0.3
Na_2O (wt%)	2.3	2.1	0.7	2.3	4.2
K_2O (wt%)	0.2	0.2	0.3	0.3	0.4
Fe_2O_3 (wt%)	2.9	3.2	4.2	4.2	1.8
TiO_2 (wt%)	0.4	0.4	0.6	0.6	0.1
渗透率（达西）	0.86	4.09	0.77	1.26	2.42
湿体积密度(g/ml)	0.30	0.28	0.47	0.44	0.32
EBC 可溶性金属					
Fe (ppm)	36	36	49	29	76
Ca (ppm)	152	95	460	541	253
Al (ppm)	70	72	152	64	25
As (ppm)	3.3	3.9	9.3	6.4	6.2
烧失量（wt%）	1.8	0.6	0.1	0.5	0.3
蛋白石-C /方石英分析					
主峰形心（Å）	4.09	4.09	4.09	4.09	4.06
FWHM (^{O} 2θ)	0.42	0.38	0.46	0.42	0.44
10^{O} – 37^{O} 2 θ之间的峰	2 /4	3/4	3/4	2/4	4/4
蛋白石-C（wt%）[1]	8.5%	27.1%	23.8%	7.6%	0.0%
方石英（wt%）	0.0%	0.0%	0.0%	0.0%	46.7%
石英（wt%）	0.1%	0.0%	0.0%	0.5%	0.0%

[1] 蛋白石-C的量化是基于XRD方法的。

[0148] 图13示出了添加5wt％方石英尖峰的样品HV2BH-E(表10)的衍射图谱。在图13中叠加了α-方石英的标准棒状图谱。再次，容易将蛋白石-C的主峰(10a)与方石英的主峰(10b)区分开来。图14示出了样品HV2-F的相似图谱。这两种样品都含有少量的长石和可能的赤铁矿。图15展示了具有5wt％方石英尖峰的样品S3115-E的衍射图谱并叠加了α-方石英的标准棒状图谱。该样品也包含大量长石、0.5wt％的石英和其他结晶相，但不含方石英。图16示出了掺杂有28wt％方石英尖峰的样品LCS3-H的XRD图谱，并叠加了α-方石英的标准棒状图谱。

在这种情况下，不能将添加的方石英主峰(10b)与原始主峰(10)区分开来。因此，原始样品很有可能包含方石英，虽然有些排列不佳。该样品含有相对较低的铝和铁百分比。当使用LH方法进行表征时，前四个样品的二氧化硅文档将显示不可检测水平的方石英，但四个中的两个将显示低水平的石英(分别为0.1wt％和0.5wt％)。当使用传统方法进行表征时，前四个样品的二氧化硅文档分别显示9wt％、27wt％、24wt％和8wt％的总结晶二氧化硅。当用LH方法或传统方法表征时，实施例13(LCS3-H)在添加尖峰之前将显示约47wt％的方石英。

实施例14至18：包含新物理组分和新二氧化硅文档的助熔煅烧硅藻土产品

[0149] 表11包含了从2015年12月在EP Minerals的韦尔(俄勒冈州)设备中进行的生产规模试验中收集的样品有关的数据。所有样品均用苏打灰助熔煅烧。实施例14是来自该生产规模试验的成品样品。实施例15和16是在实验室中分级的窑排放样品。实施例17和18是在控制条件下在实验室中进行助熔煅烧的窑进料的样品。

[0150] 表11：来自工厂试验的样品数据，2015年12月

样品	**14** FEBH 15:15	**15** KD 11:30	**16** KD 15:30	**17** 2-31 10:15	**18** 2-31 13:15
类型	助熔煅烧	助熔煅烧	助熔煅烧	助熔煅烧	助熔煅烧
煅烧温度（°C）	n/a	n/a	n/a	927	1020
煅烧时间（min.）	n/a	n/a	n/a	40	40
总化学构成（XRF表示为氧化物）					
SiO_2 (wt%)	89.7	85.6	85.6	86.0	83.4
Al_2O_3 (wt%)	3.9	5.8	5.4	5.5	6.0
CaO (wt%)	0.5	0.7	0.7	0.7	0.8
MgO (wt%)	0.3	0.4	0.4	0.4	0.4
Na_2O (wt%)	2.9	3.9	4.2	3.8	5.2
K_2O (wt%)	0.1	0.1	0.1	0.2	0.2
Fe_2O_3 (wt%)	1.6	2.8	3.0	2.7	3.2
TiO_2 (wt%)	0.2	0.3	0.4	0.3	0.4

渗透率（达西）	0.09	0.78	2.72	0.61	1.60
湿体积密度(g/ml)	0.42	0.30	0.35	0.32	0.31
EBC 可溶性金属					
Fe (ppm)	126	158	63	93	55
Ca (ppm)	106	184	107	197	226
Al (ppm)	43	53	33	46	37
As (ppm)	1.5	0.9	1.7	1.0	0.6
烧失量（wt%）	0.8	0.3	0.1	0.3	0.3
蛋白石-C /方石英分析					
主峰形心（Å）	4.08	4.08	4.08	4.07	4.09
FWHM (^{O} 2θ)	0.50	0.46	0.49	0.48	0.52
10^{O} – 37^{O} 2 θ之间的峰	2/4	3/4	3/4	3/4	2/4
蛋白石-C（wt%）[1]	18.5%	6.4%	31.9%	6.9%	6.7%
方石英（wt%）	0.0%	0.0%	0.0%	0.0%	0.0%
石英（wt%）	0.0%	0.0%	0.1%	0.0%	0.0%

[1] 蛋白石-C的量化是基于XRD方法的。

[0151] 图17示出了实施例14(FEBH)的XRD图谱。该样品包含蛋白石-C加少量长石。图18示出了与实施例16(KD 15:30)相关的XRD图谱。它又一次展示出了蛋白石-C的特征。这两种图谱是所有与该试验相关的典型图谱。在图17和图18中叠加了α-方石英的标准棒状图谱。

[0152] 对于这五个样品中的四个，当使用LH方法进行表征时，二氧化硅文档将显示不可检测水平的结晶二氧化硅，而实施例16(KD 15:30)将显示不含方石英，但含有0.1wt%的石英。使用传统方法进行表征时，五个样品将分别显示约18wt%、6wt%、32wt%、7wt%和7wt%的结晶二氧化硅。

实施例19:包含碱金属铝酸盐和新二氧化硅文档的硅藻土产品

[0153] Wang et al.的美国专利公布2014/0,035,243A1教导了一种通过使用碱金属铝酸盐作为助熔剂使硅藻土助滤剂中的可溶性铁含量降低的方法。在这个例子中，通过比较铝酸钠($NaAlO_2 \cdot xH_2O$)助熔样品和苏打灰助熔样品，研究在硅藻土的助熔煅烧过程中助熔剂对结晶二氧化硅形成的影响。将EP Minerals公司的一种天然硅藻土产品LCS-3用作起始材料，该产品由开采自内华达北部马蹄形盆地(Horseshoe Basin)矿床的矿石制成。表12列出了硅藻土的主要元素组成，其由波长色散X射线荧光(XRF)分析确定，并呈现在引燃基上。其具有相对较低的Al_2O_3含量。所使用的苏打灰为-325目(-44μm)，并且在使用之前以期望比例通过100目筛筛到硅藻土上。所使用的铝酸钠是潮湿的粉末并且含有24.6wt%的总游离水和结合水。将期望量的铝酸钠与0.5g相同的硅藻土预先混合并在研钵和研杵组中手工共研磨，然后通过100目筛筛到剩余的要进行煅烧的硅藻土上。将每种添加助熔剂的硅藻土样品在油漆搅拌器中的广口瓶中混合。通过在马弗炉中在649℃下加热40分钟，在陶瓷坩埚中进行助熔煅烧。冷却后，通过轻拍将助熔煅烧的样品分散通过70目筛。4wt%的苏打灰和8wt%的铝酸钠助熔的样品都具有相似的渗透率(约1.3-1.5达西)和相似的湿体积密度(约0.28g/cc)。助熔煅烧产品的分析结果(使用LH方法和XRD方法)示于表13和图19至20中。图

19示出了苏打灰助熔煅烧的硅藻土样品的结果，图20示出了铝酸钠助熔煅烧的硅藻土样品的结果。在图19和图20中叠加了α-方石英(16)、钠长石(18)和石英(20)的标准棒状图谱。两个样品在22°主峰(10)处具有大致相同的X射线衍射计数，然而，它们的二氧化硅结晶度显著不同：苏打灰助熔样品(图19)显示方石英的XRD扫描图谱，但是根据主峰(10)和第二峰(12)的移位以及在31.50°和28.49°2θ处不存在第三峰(14)证明铝酸钠助熔样品(图20)显然为蛋白石-C(也见表13)。在铝酸钠助熔产品中形成蛋白石-C而不是方石英，因此不需要在其安全数据表中将方石英列为健康危害。可以想象，含有小于0.1wt％或不可检测水平的石英的硅藻土原料将导致产品中少于0.1wt％或不可检测水平的石英，这使得安全数据表中也能够不列出石英。

[0154] 在实施例19中，对于这两种样品，当通过使用LH方法制作二氧化硅文档时，二氧化硅文档将分别显示约35wt％和0.1wt％的结晶二氧化硅，但是当通过使用传统方法制作时，其将分别显示约35wt％和约32wt％的结晶二氧化硅。

[0155] 表12.本研究中使用的天然硅藻土LCS-3的主要氧化物组成(引燃基)

	SiO_2	Al_2O_3	CaO	MgO	Na_2O	K_2O	Fe_2O_3	TiO_2	LOI
wt％	92.7	3.23	0.87	0.35	0.46	0.36	1.73	0.13	7.4

[0156] 表13.使用LH方法和XRD方法对具有或不具有Al添加剂的助熔煅烧的LCS-3基DE样品的XRD分析

助熔剂或添加剂* wt%	22°峰		第二和第三方石英峰			4Å相确定		石英 wt %	总结晶二氧化硅 wt%
	形心 Å	FWHM °	36.2°	31.5°	28.5°	相	wt %		
4.0% Na_2CO_3	4.02	0.378	有	有	有	方石英	34.5	ND	34.5
8.0% $NaAlO_2$	4.06	0.385	移动	差	差	蛋白石-C	32.4	0.1	0.1
5.1% Na_2CO_3 + 4.2% 0.3μ Al_2O_3	4.07	0.432	移动	差	差	蛋白石-C	24.0	0.3	0.3
5.0% Na_2CO_3 + 6.2% 1.7μ $Al(OH)_3$	4.06	0.436	是	差	差	方石英	28.5	<0.1	28.6
6.2% 18μ $Al(OH)_3$	4.07	0.311	移动	差	无	蛋白石-C	9.0	0.2	0.2
无	4.08	0.334	移动	差	无	蛋白石-C	8.5	0.25	0.25

*原样。

实施例20：包含氧化铝添加剂和新二氧化硅文档的硅藻土产品

[0157] Wanget al.的美国专利公布2015/0129490A1教导了一种通过使用氧化铝(Al_2O_3)

或氢氧化铝($Al(OH)_3$)的细粉末作为添加剂使硅藻土助滤剂中的可溶性铁含量降低的方法。氢氧化铝还被称为三水合铝或ATH。在本申请所述的一个实施例中，在硅藻土助熔-煅烧中将氧化铝或ATH添加剂与苏打灰结合使用。在该实施例中，研究了氧化铝或氢氧化铝对苏打灰助熔煅烧的硅藻土的结晶二氧化硅形成的影响。测试的铝添加剂包括来自美国宾夕法尼亚州哈特菲尔德的电子显微镜科学公司(Electron Microscopy Sciences,Hatfield,PA,USA)的0.3-μα-氧化铝粉末(目录号50361-05)和美国乔治亚州亚特兰大的胡贝尔工程材料公司(Huber Engineered Materials,Atlanta,GA,USA)的氢氧化铝粉末Hydral®。对样品的分析显示，前者具有<0.2wt％的游离水分和24.2m^2/g的比表面积，后者具有12.9wt％的游离水分、4.0m^2/g的比表面积和1.7μm的中值粒径。在当前实施例中使用实施例19中使用的相同的天然硅藻土LCS-3和苏打灰以及相同的实验步骤和条件。用5.1wt％苏打灰和4.2wt％0.3μ-氧化铝制成的样品具有0.88达西的渗透率和0.33g/cc的湿体积密度，而用5.0wt％苏打灰和6.2wt％1.7μ氢氧化铝(Hydral 710)制成的样品具有1.2达西的渗透率和0.29g/cc的湿体积密度。

[0158] 图21示出了苏打灰和0.3μ-氧化铝助熔煅烧的硅藻土样品的结果，图22示出了苏打灰和1.7μATH助熔煅烧的硅藻土样品的结果。在图21至22中叠加了α-方石英(16)、钠长石(18)和石英(22)的标准棒状图谱。对产品的分析表明，虽然图19的苏打灰助熔样品具有方石英的XRD扫描图谱，但是根据主峰和第二峰(10、12)的位移以及不存在第三峰证明(也参见表13)，3μ氧化铝的添加将该相改变为蛋白石-C相(见图21)。然而，将1.7μATH添加到硅藻土的助熔煅烧中并不抑制方石英形成(表13，图22)。如果使用不含石英的硅藻土作为原料，则可以避免添加了0.3μ氧化铝的产品中剩余0.1wt％以上的石英。

[0159] 在实施例20中，当通过使用LH方法表征时，二氧化硅文档将显示该产品分别含有约0.3wt％和29wt％的结晶二氧化硅，但是当通过使用传统方法表征时，其将显示分别含有约24wt％和约29wt％的结晶二氧化硅。

实施例21：包含氧化铝添加剂和新二氧化硅文档的硅藻土产品

[0160] Wang et al.的专利公布WO 2015/0,069,432A1教导了一种通过使用氢氧化铝或三水合铝(ATH)作为添加剂使硅藻土助滤剂中的可溶性砷含量降低的方法。在本申请所述的一个实施例中，ATH粉末在硅藻土直接煅烧中用作添加剂。在该实施例中，研究了ATH对直接煅硅藻土中结晶二氧化硅形成的影响。测试的ATH添加剂是来自美国密歇根州南菲尔德的R.J.Marshall公司(R.J.Marshall Co.,Southfield,MI,USA)的粉末，其具有18μm的中值粒径、1.0m^2/g的比表面积和<1wt％的游离水分。使用与实施例19中使用的相同实验步骤并在相同条件下，进行含有或不含ATH添加剂的相同天然硅藻土LCS-3的直接煅烧。含有和不含6.2wt％ATH的直接煅烧样品分别具有0.16和0.15达西的渗透率和0.25和0.34g/cc的湿体积密度。

[0161] 图23示出了直接煅烧硅藻土样品的结果，图24示出了具有ATH添加剂的直接煅烧硅藻土样品的结果。在图23至24中叠加了α-方石英(16)、钠长石(18)和石英(22)的标准棒状图谱。通过它们的XRD扫描图谱，即主峰和第二峰(10、12)分别位于比方石英的对应峰低的角度，且不存在第三峰(图23-24以及表13)，证明方石英不在任何产品中形成。如果使用非石英硅藻土作为原料，则可以避免两种产品中剩余0.1wt％以上的石英。

[0162] 在实施例21中，当通过使用LH方法表征时，二氧化硅文档将显示该产品分别含有

约0.2wt％和约0.3wt％的结晶二氧化硅，但是当通过使用传统方法表征时，其将显示均含有约9wt％的结晶二氧化硅。

实施例22：包含硅酸钾粘合剂和新二氧化硅文档的硅藻土产品

[0163] Nannini et al.的美国专利9,095,842教导了一种通过向天然硅藻土中加入硅酸钾并煅烧而生产具有高渗透率范围的、低结晶二氧化硅含量的硅藻土产品的方法。使用该技术制备了一种样品，并与不含硅酸钾添加剂的相同材料的直接煅烧样品(即对照样品)进行比较。使用称为Celawhite^{TM}的天然硅藻土产品作为起始材料。将5wt％的硅酸钾(KASOLV®16硅酸钾)加入到Celawhite的一个代表性部分中，然后将该部分和不含添加剂的Celawhite的另一代表性部分放置在陶瓷坩埚中并且在实验室马弗炉中在1038℃下直接煅烧45分钟。冷却后，通过70目筛将两个样品分散并进行分析。与对照样品(不含硅酸钾添加剂的样品)的0.13达西的渗透率为相比，添加剂的使用将产品的渗透率提高至0.29达西。主衍射峰也比对照样品降低约80％(从6.2％降至1.3％，使用XRD方法量化)。对照样品的主峰(10)(图25)表示蛋白石-C。有趣的是，与对照样品相比，含有5wt％KASOLV®的测试样品的主峰(10)向表示方石英的峰移动(参见图26)。图25和26分别示出了对照样品和测试样品的衍射图谱。在图25-26中叠加了α-方石英的标准棒状图谱。

[0164] 在实施例22中，当通过使用LH方法表征时，二氧化硅文档将显示该直接煅烧对照产品不含结晶二氧化硅，但是当通过使用传统方法表征时，其将显示含有6.2wt％的结晶二氧化硅。通过任一种方法，含有硅酸钾添加剂的直接煅烧样品将具有显示1.3wt％方石英的二氧化硅文档。

实施例23：包含新二氧化硅文档的复合过滤介质

[0165] Wang et al.的PCT专利申请PCT/US15/65572教导了一种在助熔剂存在或不存在的情况下生产硅藻土和膨胀珍珠岩的复合过滤介质的方法。在该发明的某些实施例中，该复合过滤介质可以包含不超过0.1wt％的结晶二氧化硅或蛋白石-C或蛋白石-CT的任何相。在该发明的其他实施例中，该复合过滤介质可以含有根据LH方法量化的蛋白石-C或蛋白石-CT，这些相通过传统方法可能表征为方石英。在进一步其他实施例中，根据通过任一方法确定，该复合过滤介质可以含有少量方石英。表14中列出了这些复合过滤介质产品的一些例子。所有这些产品含有小于0.1wt％或不可检测量的石英。

[0166] 表14.实施例23-对选择的硅藻土-珍珠岩复合产品的XRD分析

实施例23	进料和工艺参数				复合产品结晶度					
	DE/珍珠岩质量比	助熔剂		温度°C	22° 2θ 峰		28.5° 2θ 峰	LOI wt%	4-Å 相	
		类型	wt%		d Å	FWHM °2θ			相	wt%
1	75/25	没有	0	982	4.08	0.33	无	0.43	蛋白石-C/CT	<0.1
2	50/50	Na_2CO_3	1.0	982	4.06	0.30	无	0.80	蛋白石-C/CT	0.5
3	50/50	Na_2CO_3	2.0	927	4.03	0.34	差	1.1	方石英	1.2
4	25/75	Na_2CO_3	2.0	927	4.05	0.29	差	1.2	蛋白石-C/CT	0.5
5	75/25	Na_2CO_3	5.0	871	4.06	0.42	差	0.17	蛋白石-C/CT	17.5
6	50/50	Na_2CO_3	5.0	871	4.06	0.40	差	0.19	蛋白石-C/CT	13.3
7	25/75	Na_2CO_3	5.0	871	4.08	0.40	差	0.29	蛋白石-C/CT	5.8
8	50/50	Na_2CO_3	7.0	704	4.06	0.31	差	1.2	蛋白石-C/CT	2.3
9	50/50	Na_2CO_3	7.0	760	4.02	0.35	差	0.63	方石英	2.9
10	25/75	Na_2CO_3	7.0	760	4.06	0.34	无	0.64	蛋白石-C/CT	1.3
11	50/50	H_3BO_3	3.0	816	4.06	0.29	无	0.99	蛋白石-C/CT	0.1
12	50/50	K_2CO_3	5.0	816	4.05	0.33	无	1.4	蛋白石-C/CT	1.2
13	50/50	K_2SiO_3	5.0	816	4.06	0.29	差	1.5	蛋白石-C/CT	1.3
14	25/75	K_2SiO_3	6.8	816	4.06	0.27	差	1.2	蛋白石-C/CT	1.4

实施例24:研磨以区分蛋白石-C和β-方石英

[0167] 为了确认在包含硅藻土的产品中鉴定为蛋白石-C的二氧化硅相不是排列不佳的β-方石英,根据Chao和Lu提供的证据,在研磨前后分析实施例16中所述的样品。他们发现,研磨包含少于10wt%氧化铝的含有β-方石英的样品将导致从β-方石英到α-方石英的相变。因此,如果事实上原始样品包含β-方石英,则研磨后在XRD图谱中应该会有明显的显著峰位移和额外峰。图27示出了样品KD 15:30在研磨前(图27中的KD 1530 NO SPEX)和研磨后(图27中的K2 disch 1530)的XRD图谱。图27中叠加了α-方石英的标准棒状图谱。使用具有陶瓷介质的Spex®研磨机研磨一部分样品。研磨前材料的d90为122um,研磨后d90为43um。从图27中可以看出,样品的研磨没有导致显著的峰位移,也没有在图谱中出现额外峰。研磨后的样品确实具有稍低的峰强度,但这很可能是由于粗大的原始样品中蛋白石-C相的不均匀分布。

实施例25:相转化

[0168] 图28示出了Ceca Clarcel DIF-N®样品(样品#17956)的两种XRD图谱。图28中叠加了α-方石英的标准棒状图谱。首先在2012年11月对样品进行了分析(图28中的17956 2012-11-12),然后将其储存在密封的塑料容器中。仅在三年之后,在2016年1月重新分析了该样品(图28中的17956 CECA CLARCEL DIFN_2016-01-15)。通过定期监测控制标准来解释X射线管强度的差异后,图谱差异仍然表明约25%的方石英含量的净损失,即从80%方石英降至60%方石英。该样品也含有少量长石,且长石的量在三年内没有变化。

[0169] 图29示出了2015年11月在实验室中制备的样品的相似结果。图29中叠加了α-方石英的标准棒状图谱。使用XRD分析了该助熔煅烧样品(HV2-G),然后在压力下使其重新水合(图29中的HV2-G压力水合_2015-12-03)。仅在两个月后再次进行分析(图29中的HV2-G PRESS HYD RUN#3_2016-02-05)。二氧化硅相(这次是蛋白石-C)再次降低约25%,从6.2%

降至约4.7%。包含在该样品中的少量石英和更显著的长石不受两个月老化期和压力再水合的影响。

实施例26:利用光学方法估计二氧化硅相量

[0170] 表15示出了在完全相同的加工条件下(7wt%苏打灰,在927℃下助熔煅烧40分钟)从具有不同体相化学的硅藻土矿石助熔煅烧的助熔煅烧样品的数据。数据显示$L^*a^*b^*$颜色空间的b^*值与样品中包含的蛋白石-C(和/或蛋白石-CT)或方石英的量之间具有明确的反比相关。图30直观地示出了这种关系。由于这些样品没有进行用于表征蛋白石-C(和/或蛋白石-CT)和方石英的LH方法的第三步(与方石英标准分开),因此不可能明确地确定一些样品上的二氧化硅相。然而,似乎助熔煅烧样品的色调与存在的特定二氧化硅相的量之间的关系通过蛋白石-C延伸到了方石英。虽然不是绝对的,但在这些煅烧条件下b^*值小于3表明存在于样品中的二氧化硅相可能是方石英。相反,b^*等于或大于3表明存在的相很可能是蛋白石-C(和/或蛋白石-CT)。

[0171] 公开了一种用于包含直接或助熔煅烧硅藻土的产品,并且更具体地用于包含直接或助熔煅烧硅藻土的颗粒产品的加工控制方法。该产品的蛋白石-C(和/或蛋白石-CT)或方石英含量可能会根据起始硅藻土矿石的矿物组成而变化,该矿石是直接或助熔煅烧制造工艺的来源。为了确保成品的含量保持一致(并确保准确的含量公开),可能在发货给客户/经销商之前对产品的样品进行测试。XRD测试可能很耗时。以下描述了一种有效的方法来控制产品质量并确认含量公开的持续准确性。

[0172] 该方法使用产品的光学性能来估计产品(包含硅藻土)的方石英或总体的蛋白石-C和蛋白石-CT wt%含量。该方法包括选择用于测试的产品的代表性第一测试样品。该方法进一步包括确定用于生产产品的第一测试样品的工艺参数,并且将估计该产品的方石英wt%含量或(总体)蛋白石-C和蛋白石-CT wt%含量。工艺参数可以包括但不限于以下一种或多种:助熔剂组成和量、煅烧温度、烧结温度、煅烧时间、烧结时间、窑内停留时间或窑内气氛组成。

[0173] 该方法进一步包括确定该产品的第一测试样品的光学性能。光学性能包括但不限于以下一种或多种:颜色空间值:b^*值、a^*值或L^*值。例如,可使用柯尼卡美能达(Konica Minolta®)色度仪CR-400等来确定颜色空间值b^*值、a^*值或L^*值,以感测该第一测试样品的值。

[0174] 该方法进一步包括根据工艺参数和产品的(第一测试样品的)光学性能,应用模型来估计该产品的第一测试样品的方石英wt%含量或(总体)蛋白石-C和蛋白石-CT wt%含量。

[0175] 在一个实施例中,可以使用该模型来估计该第一测试样品的方石英wt%含量是否高于待测试产品的可接受的方石英阈值。例如,如果具有给定的一组工艺参数的第一测试样品被确定为具有小于3的感测光学b^*值,则该模型可以配置为,估计方石英以高于期望可接受的方石英阈值(例如第一测试样品的0wt%)的水平,存在于该第一测试样品中(并且通过扩展该产品)。在其他实施例中,期望可接受的方石英阈值(对于相同或不同的产品)可以不同。在一些实施例中,该模型可用于估计第一测试样品的总体蛋白石-C和蛋白石CT wt%,并将其与另一阈值或可接受的阈值范围进行比较。

[0176] 在又一个实施例中,根据工艺参数和所测定的第一测试样品的光学性能,可以使

用该模型估计第一测试样品的具体方石英wt％含量和/或总体蛋白石-C和蛋白石-CT wt％含量。在该实施例中，通过该模型来确定/估计方石英wt％含量和/或总体蛋白石-C和蛋白石-CT wt％含量的具体值，而不是估计含量是否大于期望阈值wt％。与上面类似，可以将估计的wt％含量与期望阈值或范围进行比较。在任一情况下，该方法可以使用包括处理器和存储元件的控制器，来估计第一测试样品的方石英或总体蛋白石-C和蛋白石-CT wt％含量。

[0177] 该处理器可以是本领域已知的微处理器或其他处理器。该处理器可以配置为执行指令并生成控制信号，该控制信号用于估计/确定产品(由一组工艺参数产生)的第一测试样品的方石英wt％含量或总体蛋白石-C和蛋白石-CT wt％含量，作为该产品的第一测试样品的所测定的光学性能的函数。可以将该指令读入或并入计算机可读介质中(例如存储元件)，或向外部提供给处理器。在可选地实施例中，可以使用硬连线电路来代替软件指令或与软件指令组合来实现控制方法。本文使用的术语“计算机可读介质”是指参与向处理器提供指令以供执行的任何非暂态介质或介质的组合。这种介质可以包括除暂态、传播信号之外的所有计算机可读介质。计算机可读介质的常见形式包括，例如存储棒或任何磁性介质、光学介质或计算机处理器可从中读取的任何其他介质。控制器不限于一个处理器和存储元件。控制器可能是几个处理器和几个存储元件。

[0178] 该模型配置为，基于通过方石英wt％含量(根据LH方法确定)或总体蛋白石-C和蛋白石-CT wt％含量(根据LH方法确定)作为在与该产品的第一测试样品相同或相似的工艺参数下制造的多种测试产品的光学性能的函数的线性回归(和/或另一种数学关系)而确定的一个或多个关系，来估计该产品的方石英或总体蛋白石-C和蛋白石-CT wt％含量。如果工艺参数相同则更好。

[0179] 如果由该模型估计的方石英wt％含量未达到阈值比较(例如，高于可接受的阈值)，则该方法可以进一步包括对该产品的第一测试样品或来自相同产品的代表性的第二测试样品进行XRD分析。在一些实施例中，如果该模型估计的总体蛋白石-C和蛋白石-CT wt％未达到蛋白石-C和蛋白石-CT的阈值比较(例如，大于阈值，超出阈值的预期或可接受范围，或者在一些实施例中，小于阈值)，则该方法可包括对该产品的第一测试样品或来自相同产品的代表性的第二测试样品进行XRD分析。

[0180] 如果XRD分析的结果也表明方石英wt％含量高于可接受的阈值，则该方法进一步包括从销售库存等中除去该产品或从其获得第一(和第二)测试样品的很多/一批产品。销售库存是指可供发货给经销商或客户的库存。

[0181] 该方法可以进一步包括，调整在制造产品中使用的一个或多个工艺参数(例如，煅烧时间或温度、添加的助熔剂的wt％等)和/或硅藻土矿石来源，并且重复上述一些或全部方法步骤，直到由该模型估计或由XRD分析确定的任何存在的方石英处于或低于可接受的阈值(wt％含量)水平(通过阈值比较)。在一些实施例中，该方法可以进一步包括，调整在制造产品中使用的一个或多个工艺参数(例如，煅烧时间或温度、添加的助熔剂的wt％等)和/或硅藻土矿石来源，并且重复上述一些或全部方法步骤，直到由该模型估计或由XRD分析确定的总体蛋白石-C和蛋白石-CTwt％通过总体蛋白石-C和蛋白石-CT的期望阈值比较。

[0182] 为了构建该模型，针对一组工艺参数(例如，助熔剂组成和量、煅烧温度和煅烧时间)选择多种测试产品。测定每种测试产品的光学性能(例如，颜色空间值：b^*值、a^*值或L^*

值)。根据LH方法，测定每种测试产品的的方石英wt％含量。根据LH方法(优选地根据XRD方法量化)，测定每种测试产品的总体蛋白石-C和蛋白石-CT wt％含量。然后进行线性回归分析(例如，参见图30)，以确定测试产品(由该组工艺参数产生的)的wt％方石英含量或(总体)wt％蛋白石-C和蛋白石-CT含量作为该测试产品的光学性能的函数的函数。可选地，或者除此之外，可以使用其他适当的数学分析，来确定测试产品(由该组工艺参数产生的)的wt％方石英含量或总体wt％蛋白石-C和蛋白石-CT含量作为该测试产品的光学性能的函数的合适的数学关系。优选地，针对多组不同的工艺参数(及其各自的测试产品)重复该分析以提供一个稳健模型，来估计各种具有不同工艺参数的产品的wt％方石英含量或蛋白石-C和蛋白石-CT含量的总体wt％。与上面类似，可以使用包括处理器和存储元件的控制器来完成构建该模型。该处理器可以是本领域已知的微处理器或其他处理器。该处理器可以配置为执行指令并生成控制信号，该控制信号用于确定测试产品(由该组工艺参数产生的)的wt％方石英含量或wt％蛋白石-C(和蛋白石-CT)含量作为该测试产品的光学性能的函数的关系。可以将该指令读入或并入计算机可读介质中(例如存储元件)，或向外部提供给处理器。在可选地实施例中，可以使用硬连线电路来代替软件指令或与软件指令组合来实现控制方法。控制器不限于一个处理器和存储元件。控制器可以是几个处理器和几个存储元件。

[0183]　表15：不同硅藻土矿石的助熔煅烧样品的颜色空间和二氧化硅相数据

样品	L*	a*	b*	主峰形心（Å）	FWHM (Å)	相	量（%）
W18184	67.8	14.1	22.1	4.067	0.43	蛋白石-C	18.1%
W18203	70.5	13.7	26.7	4.088	0.42	蛋白石-C	9.6%
W18206	66.1	16.2	27.7	4.088	0.39	蛋白石-C	9.5%
W18208	64.0	15.3	26.6	4.095	0.41	蛋白石-C	10.0%
W18213	72.1	12.2	23.8	4.081	0.41	蛋白石-C	12.4%
W18222	94.0	-0.2	1.1	4.059	0.37	方石英	50.4%
W18225	93.4	0.1	1.5	4.060	0.40	方石英	48.9%
W18228	91.3	1.2	4.3	4.067	0.40	蛋白石-C	44.2%
W18241	93.4	-0.3	2.0	4.060	0.36	未确定	49.6%
W18251	89.4	1.4	4.4	4.067	0.40	蛋白石-C	40.8%
W18252	84.6	4.3	8.1	4.066	0.42	未确定	35.9%
W18253	93.8	-0.3	1.8	4.060	0.37	方石英	49.0%
W18254	83.0	4.9	9.6	4.074	0.41	蛋白石-C	38.0%
W18258	90.3	1.0	3.9	4.060	0.39	未确定	43.9%

蛋白石-C的量化是基于XRD方法的。

实施例27：可吸入的二氧化硅相

[0184]　如前所述，可以通过计算确定块状粉末样品的可吸入含量(和其中的二氧化硅相)。通过XRD获得样品的细级分的二氧化硅相信息后，测定整个样品的粒径分布。CEN EN481基于颗粒尺寸和颗粒密度提供了颗粒可吸入可能性的统计计算，从而将其应用于测量分布以确定可吸入分数。然后将可吸入分数乘以二氧化硅相量以确定该特定二氧化硅相的可吸入量。

[0185] 使用这种方法分析了两个样品。图31和32表示它们的粒径分布，表16包括可吸入分析的结果。

表16：可吸入分析的结果(SWeFF)

样品	18188-4	FP-3/B17E2
蛋白石-C负25um的级分(wt%)	9.1	17.2
方石英和石英含量(wt%)	0.0	0.0
可吸入分数-EN481(wt%)	0.1	1.8
可吸入蛋白石-C(wt%)	0.0	0.3
可吸入方石英和石英(wt%)	0.0	0.0

实施例28：改进的二氧化硅文档-助熔煅烧样品

[0186] 利用传统方法(错误地将蛋白石-C鉴定为方石英)和LH方法，制作样品18188-9的二氧化硅文档。表17是在美国境内销售的SDS信息，其使用通过用于确定助熔煅烧硅藻土产品中的方石英含量的传统方法生成的数据来制作。表18是利用由LH方法生成的数据修正的SDS信息。与表17所示的SDS信息相比，对第2部分(危害)、第3部分(组成)、第8部分(暴露控制)、第11部分(毒理学信息)和第15部分(法规信息)作了显著改变。

表17：具有基于传统方法的数据的样品18188-9的SDS信息

第 1 部分：产品和公司标识	
产品标识符	具有传统的结晶二氧化硅定量的 18188-9
化学品名称	硅藻土、助熔煅烧
化学品	二氧化硅
材料用途	助滤剂
使用限制	尚未知
制造商	EP Minerals, LLC., 9875 Gateway Dr., Reno, NV 89521
电话号码	(775) 824 7600 (周一至周五， 8:00 am PST – 5:00 pm PST)
紧急电话号码	(775) 824 7600 (周一至周五，8:00 am PST – 5:00 pm PST)
SDS 制作日期	2014 年 1 月 31 日
第 2 部分：危害标识	
OSHA GHS 危害分类	致癌物质类别 1A 特定靶器官毒性，重复暴露类别 1
未分类的其他危害	无

标签要素	危险 吸入可能导致癌症。 长时间或反复暴露会对肺造成损害。 **使用前应获得特别指示。** **在阅读和理解所有安全措施之前，请勿处理。** 请勿吸入粉尘。 请佩戴护眼装置。 若暴露或担忧：请获取医疗建议。 **按照当地、州和联邦的规定处理。**

第 3 部分：组成/成分信息

成分标识	近似浓度（%）	C.A.S.号
硅藻土、助熔煅烧(砂藻土)(含 35-50%的结晶二氧化硅-方石英）	100%	68855-54-9 14464-46-1

第 4 部分：急救措施

眼睛	用大量水或眼部冲洗液冲洗眼睛。如果刺激持续存在，请咨询医师。
皮肤	如果发生干燥，请使用保湿更新乳液。
食入	喝大量的水以降低主要和干燥效应。
吸入	移至新鲜空气中。擤鼻子以清除粉尘。
最重要的症状/效应，急性的和迟发的	粉尘可能会对眼睛造成磨蚀性刺激。长时间的皮肤接触可能导致干燥。粉尘可能会导致鼻腔、喉咙和上呼吸道的刺激。长时间吸入含二氧化硅的可吸入粉尘可能会导致进行性肺部疾病、硅肺病和肺癌。更多信息请参见第 11 部分。
如有必要，指示立即就医和特殊治疗	通常不需要立即就医。如果粉尘刺激眼睛，请就医。

材料名称	具有传统的结晶二氧化硅定量的 18188-9	2/4 页

第 5 部分：消防措施

灭火介质	不适用，材料不易燃。

由该化学品引起的特殊危害	不适用，材料不易燃。
消防人员专用防护设备和预防措施	不适用，材料不易燃。
第 6 部分：意外泄露措施	
个人预防措施	如有粉尘，请按照第 8 部分的规定使用配有颗粒过滤器的呼吸器。请用护目镜保护眼睛。请勿吸入粉尘。
环境预防措施	该材料不会引起重大的环境问题。
用于控制和清洁的方法和材料	真空清洗溢出或湿扫。避免产生气载粉尘。放入容器中使用或处置。
第 7 部分：操作与储存	
安全操作注意事项	尽量减少粉尘的产生。避免与眼睛接触。请勿吸入粉尘。修理或处理破损的袋子。遵守所有标签上的注意事项和警告。
安全储存条件	存放在干燥处以保持包装完整性和产品质量。请勿靠近氢氟酸或浓碱溶液储存。
第 8 部分：暴露控制/个人防护	
暴露指南	

组分	OSHA PEL	ACGIH TLV	MSHA PEL	NIOSH REL

硅藻土、助熔煅烧（砂藻土）	5 mg/m^3 可吸入粉尘 15 mg/m^3 总粉尘	未建立	5 mg/m^3 可吸入粉尘 15 mg/m^3 总粉尘	未建立
结晶二氧化硅（方石英）	$\frac{1}{2}$ x $\frac{30\ mg/m^3}{\%\ SiO_2+2}$ 总粉尘 $\frac{1}{2}$ x $\frac{10\ mg/m^3}{\%\ SiO_2+2}$ 可吸入粉尘	0.025 mg/m^3 可吸入粉尘	$\frac{1}{2}$ x $\frac{30\ mg/m^3}{\%\ SiO_2+2}$ 总粉尘 $\frac{1}{2}$ x $\frac{10\ mg/m^3}{\%\ SiO_2+2}$ 可吸入粉尘	0.05 mg/ m^3 可吸入粉尘

工程控制	使用一般或局部排气通风将粉尘控制在建议暴露限值内。关于通风系统的设计，请参阅 ACGIH 出版物“工业通风”或类似的出版物。	
个人防护设备：		
眼睛/面部防护	佩戴护目镜以防止粉尘	
皮肤防护	不需要特殊设备。	
呼吸系统防护	当存在粉尘时，应佩戴带有符合标准 42CFR84 的 N95 系列的过滤器的呼吸器。如果粉尘浓度低于允许暴露限值（PEL）的十（10）倍，则使用带有 N95 防尘过滤器的四分之一或半面罩呼吸器或 N95 的一次性防尘面罩。如果粉尘浓度大于 PEL 的十（10）倍且小于五十（50）倍，则建议使用装有可更换 N95 过滤器的全面罩呼吸器。如果粉尘浓度大于 PEL 的五十（50）倍且小于二百（200）倍，则使用带有可更换 N95 过滤器的动力空气净化（正压）呼吸器。如果粉尘浓度大于 PEL 的二百（200）倍，则使用带有全面罩、头罩或头盔的 C 型供气呼吸器（持续气流，正压）。	
一般卫生	避免吸入粉尘。避免与眼睛接触。处理后以及进食或饮用前洗手。	
材料名称	具有传统的结晶二氧化硅定量的 18188-9	3/4 页
第 9 部分：物理和化学性能		

外观，颜色	深粉色到灰白色粉末	**气味**	无味
物理状态	固体	**气味阈值**	不适用
蒸汽压	不适用	**蒸汽密度**	不适用
沸点	不适用	**熔点**	> 1300° C
闪点	不适用	**pH (10%悬浮液)**	10
可燃极限	不适用	**蒸发速度**	不适用
分解温度	> 1300°C	**规定重力/相对密度**	2.3
自燃温度	不适用	**分配系数-正辛醇/水**	不适用
可燃性（固体/气体）	不适用	**溶解度-水**	<1%
		粘度	不适用

第 10 部分：稳定性和反应性

反应性	材料不会发生反应。
化学稳定性	材料稳定。
危害反应的可能性	在正常的处理条件下，材料不会发生反应，除非与以下不相容物质混合。
应避免的条件	不适用
不相容材料	氢氟酸和浓碱溶液可能与该产品发生剧烈反应。
危害分解产物	不适用

第 11 部分：毒理学信息

潜在健康影响	
可能的暴露途径	如下
眼睛	如果粉尘进入眼睛，可能会引起刺激(形成眼泪和发红)。
皮肤	不被皮肤吸收，但如果长时间暴露可能会造成干燥。
食入	小量食入不认为是有害的，但可能会引起口腔、喉咙和胃的刺激。
吸入	急性吸入会导致鼻腔通道干燥、肺部充血、咳嗽和一般的咽喉刺激。急性吸入高浓度的可吸入结晶二氧化硅可能导致急性硅肺病。
慢性影响	本产品含有结晶二氧化硅。如果吸入较长时间，可吸入的结晶二氧化硅可能会导致肺癌和肺部疾病（硅肺病）。硅肺病的症状包括气喘、咳嗽和气短。

致癌性	助熔煅烧的硅藻土（砂藻土）由非晶和结晶二氧化硅构成。 IARC 和 NTP 将可吸入结晶二氧化硅（方石英）归类为已知的人类致癌物。仅已知以可吸入形式吸入结晶二氧化硅会导致癌症。尚不知通过任何其他暴露途径引起癌症。	
NTP	可吸入的结晶二氧化硅(方石英)归类为已知的人类致癌物。	
IARC	可吸入的结晶二氧化硅(方石英)归类为已知的人类致癌物。	
毒性的数值测量	无可用数据	
腐蚀性、敏感性、刺激性	不适用	
材料名称	具有传统的结晶二氧化硅定量的 18188-9	4/4 页
生殖毒性	无	
致畸性、致突变性	无	
第 12 部分：生态学信息		
生态毒性：	硅藻土产品作为天然杀虫剂已经显示出一些功效，但在水生或陆生生物方面没有表现出毒性。	
持久性和降解性	不可生物降解，惰性。	
生物累积的潜在可能性	生物累积的潜在可能性很小	
土壤中的流动性	无流动性	
其它不利影响	尚未知	
第 13 部分：废弃考虑		
废物处置	如果所提供的材料成为废物，则使用垃圾填埋式操作中常见的固体废物处置，或在污水坑内处理。根据 RCRA（4OCFR 第261 部分）不被视为危害废物。	
包装处置	根据适用的法律法规进行处置，通常是垃圾填埋式操作中常见的固体废物处置。	
第 14 部分：运输信息		
基本的运输信息	DOT 运输分类 55（无限制）。技术名称是“硅藻土”。	
附加信息	无特殊要求或不必张贴危险告示。	
第 15 部分：法规信息		
美国联邦：		

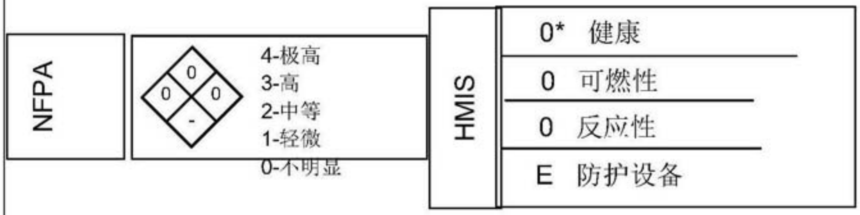
TSCA	硅藻土和方石英出现在EPA TSCA库存清单上。
CERCLA	根据美国“综合环境响应、赔偿和责任法”（CERCLA）40 CFR 302的规定，硅藻土不被列为有害物质。
SARA TITLE III	未列出。
加州65号提案	本产品含有结晶二氧化硅，这是加州已知可导致癌症的化学物质。
国际组织：	
WHMIS分类	级别D-2-A
WHMIS成分披露清单	二氧化硅、晶体、方石英
第16部分：其他信息	
	
原始发行日期	不适用
修订日期	不适用
修订号	实施例

表18：利用来自LH方法的数据制作的样品18188-9的SDS信息

第1部分：产品和公司标识	
产品标识符	具有根据LH方法定量的二氧化硅含量的18188-9
化学品名称	硅藻土、助熔煅烧
化学族	二氧化硅
材料用途	助滤剂
使用限制	尚未知
制造商	EP Minerals, LLC., 9875 Gateway Dr., Reno, NV 89521
电话号码	(775) 824 7600 （周一至周五，8:00 am PST – 5:00 pm）

紧急电话号码	(775) 824 7600 （周一至周五，8:00 am PST – 5:00 pm）	
SDS 制作日期	2014 年 1 月 31 日	
第 2 部分：危害标识		
OSHA GHS 危害分类	未归类为有危害	
未分类的其他危害	无	
标签要素	不需要 GHS 标签	
第 3 部分：组成/成分信息		
成分标识	近似浓度（%）	C.A.S.号
硅藻土、助熔煅烧（砂藻土）	100%	68855-54-9
第 4 部分：急救措施		
眼睛	用大量水或眼部冲洗液冲洗眼睛。如果刺激持续存在，请咨询医师。	
皮肤	如果发生干燥，请使用保湿更新乳液。	
食入	喝大量的水以降低主要和干燥效应。	
吸入	移至新鲜空气中。擤鼻子以清除粉尘。	
最重要的症状/效应，急性的和迟发的	粉尘可能会对眼睛造成磨蚀性刺激。长时间的皮肤接触可能导致干燥。粉尘可能会导致鼻腔、喉咙和上呼吸道的刺激。长时间吸入高浓度的粉尘可能会导致影响肺部。	
如有必要，指示立即就医和特殊治疗	通常不需要立即就医。如果粉尘刺激眼睛，请就医。	
材料名称	具有根据 LH 方法定量的二氧化硅含量的 18188-9	2/4 页
第 5 部分：消防措施		

<table>
<tr><td>灭火介质</td><td colspan="4">不适用，材料不易燃。</td></tr>
<tr><td>由该化学品引起的特殊危害</td><td colspan="4">不适用，材料不易燃。</td></tr>
<tr><td>消防人员专用防护设备和预防措施</td><td colspan="4">不适用，材料不易燃。</td></tr>
<tr><td colspan="5">第 6 部分：意外泄露措施</td></tr>
<tr><td>个人预防措施</td><td colspan="4">如有粉尘，请按照第 8 部分的规定使用配有颗粒过滤器的呼吸器。请用护目镜保护眼睛。请勿吸入粉尘。</td></tr>
<tr><td>环境预防措施</td><td colspan="4">该材料不会引起重大的环境问题。</td></tr>
<tr><td>用于控制和清洁的方法和材料</td><td colspan="4">真空清洗溢出或湿扫。避免产生气载粉尘。放入容器中使用或处置。</td></tr>
<tr><td colspan="5">第 7 部分：操作与储存</td></tr>
<tr><td>安全操作注意事项</td><td colspan="4">尽量减少粉尘的产生。避免与眼睛接触。请勿吸入粉尘。修理或处理破损的袋子。遵守所有标签上的注意事项和警告。</td></tr>
<tr><td>安全储存条件</td><td colspan="4">存放在干燥处以保持包装完整性和产品质量。请勿靠近氢氟酸或浓碱溶液储存。</td></tr>
<tr><td colspan="5">第 8 部分：暴露控制/个人防护</td></tr>
<tr><td>暴露指南</td><td colspan="4"></td></tr>
<tr><td>组分</td><td>OSHA PEL</td><td>ACGIH TLV</td><td>MSHA PEL</td><td>NIOSH REL</td></tr>
<tr><td>硅藻土、助熔煅烧（砂藻土）</td><td>5 mg/m^3 可吸入粉尘
15 mg/m^3 总粉尘</td><td>未建立</td><td>5 mg/m^3 可吸入粉尘
15 mg/m^3 总粉尘</td><td>未建立</td></tr>
<tr><td>工程控制</td><td colspan="4">使用一般或局部排气通风将粉尘控制在建议暴露限值内。关于通风系统的设计，请参阅 ACGIH 出版物“工业通风”或类似的出版物。</td></tr>
</table>

个人防护设备：		
眼睛/面部防护	佩戴护目镜以防止粉尘	
皮肤防护	不需要特殊设备。	
呼吸系统防护	当存在粉尘时，应佩戴带有符合标准 42CFR84 的 N95 系列的过滤器的呼吸器。如果粉尘浓度低于允许暴露限值（PEL）的十（10）倍，则使用带有 N95 防尘过滤器的四分之一或半面罩呼吸器或 N95 的一次性防尘面罩。如果粉尘浓度大于 PEL 的十（10）倍且小于五十（50）倍，则建议使用装有可更换 N95 过滤器的全面罩呼吸器。必须根据 OSHA 1910.134 和良好的工业卫生习惯选择和使用呼吸设备。	
一般卫生	避免吸入粉尘。避免与眼睛接触。处理后以及进食或饮用前洗手。	
材料名称	具有根据 LH 方法定量的二氧化硅含量的 18188-9	3/4 页

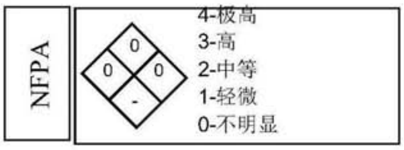
第 9 部分：物理和化学性能

外观，颜色	深粉色到灰白色粉末	**气味**	无味
物理状态	固体	**气味阈值**	不适用
蒸汽压	不适用	**蒸汽密度**	不适用
沸点	不适用	**熔点**	＞1300° C
闪点	不适用	**pH (10%悬浮液)**	10
可燃极限	不适用	**蒸发速度**	不适用
分解温度	＞1300°C	**规定重力/相对密度**	2.3
自燃温度	不适用	**分配系数-正辛醇/水**	不适用
可燃性（固体/气体）	不适用	**溶解度-水**	＜1%
		粘度	不适用

第 10 部分：稳定性和反应性

反应性	材料不会发生反应。
化学稳定性	材料稳定。
危害反应的可能性	在正常的处理条件下，材料不会发生反应，除非与以下不相容物质混合。
应避免的条件	不适用

不相容材料	氢氟酸和浓碱溶液可能与该产品发生剧烈反应。
危害分解产物	不适用
第 11 部分：毒理学信息	
潜在健康影响	
可能的暴露途径	如下
眼睛	如果粉尘进入眼睛，可能会引起刺激(形成眼泪和发红)。
皮肤	不被皮肤吸收，但如果长时间暴露可能会造成干燥。
食入	小量食入不认为是有害的，但可能会引起口腔、喉咙和胃的刺激。
吸入	急性吸入会导致鼻腔通道干燥、肺部充血、咳嗽和一般的咽喉刺激。应避免粉尘的长期吸入。
慢性影响	在长达数年内长期吸入超过 OSHA 确定的允许暴露限值（PEL）的粉尘可能会导致肺部变化。
NTP	不含结晶二氧化硅的硅藻土不列为致癌物质。
IARC	不含结晶二氧化硅的硅藻土不归类为人类致癌性（第 3 组）
毒性的数值测量	无可用数据
腐蚀性、敏感性、刺激性	不适用
材料名称	具有根据 LH 方法定量的二氧化硅含量的 18188-9 4/4 页
生殖毒性	无
致畸性、致突变性	无
第 12 部分：生态学信息	
生态毒性:	硅藻土产品作为天然杀虫剂已经显示出一些功效，但在水生或陆生生物方面没有表现出毒性。
持久性和降解性	不可生物降解，惰性。
生物累积的潜在可能性	生物累积的潜在可能性很小
土壤中的流动性	无流动性
其它不利影响	尚未知

第 13 部分：废弃考虑	
废物处置	如果所提供的材料成为废物，则使用垃圾填埋式操作中常见的固体废物处置，或在污水坑内处理。根据 RCRA（4OCFR 第 261 部分）不被视为危害废物。
包装处置	根据适用的法律法规进行处置，通常是垃圾填埋式操作中常见的固体废物处置。
第 14 部分：运输信息	
基本的运输信息	DOT 运输分类 55（无限制）。技术名称是“硅藻土”。
附加信息	无特殊要求或不必张贴危险告示。
第 15 部分：法规信息	
U.S.FEDERAL:	
TSCA	硅藻土出现在 EPA TSCA 库存清单上。
CERCLA	根据美国“综合环境响应、赔偿和责任法”（CERCLA）40 CFR 302 的规定，硅藻土不被列为有害物质。
SARA TITLE III	未列出。
国际组织:	
WHMIS 分类	本产品不受 WHMIS 的管制
WHMIS 成分披露清单	无可报告的成分
第 16 部分：其他信息	
	 HMIS 0* 健康 0 可燃性 0 反应性 E 防护设备
原始发行日期	不适用
修订日期	不适用
修订号	实施例

实施例29:改进的二氧化硅文档-直接煅烧样品

[0187] 也为类似于表6和表7中描述的一些产品的直接煅烧产品制作了二氧化硅文档信

息。表19是用于在美国境内销售的SDS信息，其利用通过用于确定该直煅硅藻土产品(含有一些石英和被错误鉴定为方石英的蛋白石-C)中的结晶二氧化硅含量的传统方法产生的数据制作。表20是利用由LH方法生成的数据修正的SDS信息。在这种情况下，对二氧化硅文档的更改没有在实施例28中那么重要。然而，在第3、8和11部分中已经作了有意义的改变。

表19：具有基于传统方法的数据的、含有石英的直接煅烧产品的SDS信息

第 1 部分：产品和公司标识	
产品标识符	直接煅烧-传统结晶二氧化硅含量确定。
化学品名称	硅藻土、煅烧的
化学族	二氧化硅
材料用途	助滤剂、功能性填料
使用限制	尚未知
制造商	EP Minerals, LLC., 9875 Gateway Dr., Reno, NV 89521
电话号码	(775) 824 7600（周一至周五，8:00 am PST – 5:00 pm）
紧急电话号码	(775) 824 7600 （周一至周五，8:00 am PST – 5:00 pm）
SDS 制作日期	2016 年
第 2 部分：危害标识	
OSHA GHS 危害分类	致癌物质类别 1A 特定靶器官毒性，重复暴露类别 1
未分类的其他危害	无

标签要素	危险 吸入可能导致癌症。 长时间或反复暴露会对肺造成损害。 **使用前应获得特别指示。** **在阅读和理解所有安全措施之前，请勿处理。** 请勿吸入粉尘。 请佩戴护眼装置。 若暴露或担忧：请获取医疗建议。 **按照当地、州和联邦的规定处理。**

第 3 部分：组成/成分信息

成分标识	近似浓度（%）	C.A.S.号
硅藻土、煅烧（砂藻土）（含有 2-30%的结晶二氧化硅-方石英和 0.1 至 5%的结晶二氧化硅-石英）	100%	91053-39-3 14464-46-1 14808-60-7

第 4 部分：急救措施

眼睛	用大量水或眼部冲洗液冲洗眼睛。如果刺激持续存在，请咨询医师。
皮肤	如果发生干燥，请使用保湿更新乳液。
食入	喝大量的水以降低主要和干燥效应。
吸入	移至新鲜空气中。擤鼻子以清除粉尘。
最重要的症状/效应，急性的和迟发的	粉尘可能会对眼睛造成磨蚀性刺激。长时间的皮肤接触可能导致干燥。粉尘可能会导致鼻腔、喉咙和上呼吸道的刺激。长时间吸入含二氧化硅的可吸入粉尘可能会导致进行性肺部疾病、硅肺病和肺癌。更多信息请参见第 11 部分。

如有必要，指示立即就医和特殊治疗	通常不需要立即就医。如果粉尘刺激眼睛，请就医。	
材料名称	直接煅烧-传统结晶二氧化硅含量确定。	2/4 页
第 5 部分：消防措施		
灭火介质	不适用，材料不易燃。	
由该化学品引起的特殊危害	不适用，材料不易燃。	
消防人员专用防护设备和预防措施	不适用，材料不易燃。	
第 6 部分：意外泄露措施		
个人预防措施	如有粉尘，请按照第 8 部分的规定使用配有颗粒过滤器的呼吸器。请用护目镜保护眼睛。请勿吸入粉尘。	
环境预防措施	该材料不会引起重大的环境问题。	
用于控制和清洁的方法和材料	真空清洗溢出或湿扫。避免产生气载粉尘。放入容器中使用或处置。	
第 7 部分：操作与储存		
安全操作注意事项	尽量减少粉尘的产生。避免与眼睛接触。请勿吸入粉尘。修理或处理破损的袋子。遵守所有标签上的注意事项和警告。	
安全储存条件	存放在干燥处以保持包装完整性和产品质量。请勿靠近氢氟酸或浓碱溶液储存。	
第 8 部分：暴露控制/个人防护		

暴露指南				
组分	OSHA PEL	ACGIH TLV	MSHA PEL	NIOSH REL

硅藻土、煅烧（砂藻土）	5 mg/m^3 可吸入粉尘 15 mg/m^3 总粉尘	未建立	5 mg/m^3 可吸入粉尘 15 mg/m^3 总粉尘	未建立
结晶二氧化硅（方石英）	$\frac{1}{2}$ x $\frac{30\ mg/m^3}{\%\ SiO_2+2}$ 总粉尘 $\frac{1}{2}$ x $\frac{10\ mg/m^3}{\%\ SiO_2+2}$ 可吸入粉尘	0.025 mg/m^3 可吸入粉尘	$\frac{1}{2}$ x $\frac{30\ mg/m^3}{\%\ SiO_2+2}$ 总粉尘 $\frac{1}{2}$ x $\frac{10\ mg/m^3}{\%\ SiO_2+2}$ 可吸入粉尘	0.05 mg/m^3 可吸入粉尘
结晶二氧化硅（石英）	$\frac{30\ mg/m^3}{\%\ SiO_2+2}$ 总粉尘 $\frac{10\ mg/m^3}{\%\ SiO_2+2}$ 可吸入粉尘	0.025 mg/m^3 可吸入粉尘	$\frac{30\ mg/m^3}{\%\ SiO_2+2}$ 总粉尘 $\frac{10\ mg/m^3}{\%\ SiO_2+2}$ 可吸入粉尘	0.05 mg/m^3 可吸入粉尘

工程控制	使用一般或局部排气通风将粉尘控制在建议暴露限值内。关于通风系统的设计，请参阅 ACGIH 出版物“工业通风”或类似的出版物。
个人防护设备：	
眼睛/面部防护	佩戴护目镜以防止粉尘
皮肤防护	不需要特殊设备。

呼吸系统防护	当存在粉尘时，应佩戴带有符合标准 42CFR84 的 N95 系列的过滤器的呼吸器。如果粉尘浓度低于允许暴露限值（PEL）的十（10）倍，则使用带有 N95 防尘过滤器的四分之一或半面罩呼吸器或 N95 的一次性防尘面罩。如果粉尘浓度大于 PEL 的十（10）倍且小于五十（50）倍，则建议使用装有可更换 N95 过滤器的全面罩呼吸器。如果粉尘浓度大于 PEL 的五十（50）倍且小于二百（200）倍，则使用带有可更换 N95 过滤器的动力空气净化（正压）呼吸器。如果粉尘浓度大于 PEL 的二百（200）倍，则使用带有全面罩、头罩或头盔的 C 型供气呼吸器（持续气流，正压）。		
一般卫生	避免吸入粉尘。避免与眼睛接触。处理后以及进食或饮用前洗手。		
材料名称	直接煅烧-传统结晶二氧化硅含量确定。	3/4 页	
第 9 部分：物理和化学性能			
外观，颜色	浅黄色至粉红色粉末	**气味**	无味
物理状态	固体	**气味阈值**	不适用
蒸汽压	不适用	**蒸汽密度**	不适用
沸点	不适用	**熔点**	> 1300° C
闪点	不适用	**pH (10%悬浮液)**	7
可燃极限	不适用	**蒸发速度**	不适用
分解温度	> 1300°C	**规定重力/相对密度**	2.2
自燃温度	不适用	**分配系数-正辛醇/水**	不适用
可燃性（固体/气体）	不适用	**溶解度-水**	< 1%
		粘度	不适用
第 10 部分：稳定性和反应性			
反应性	材料不会发生反应。		
化学稳定性	材料稳定。		
危害反应的可能性	在正常的处理条件下，材料不会发生反应，除非与以下不相容物质混合。		
应避免的条件	不适用		
不相容材料	氢氟酸和浓碱溶液可能与该产品发生剧烈反应。		
危害分解产物	不适用		
第 11 部分：毒理学信息			

潜在健康影响		
可能的暴露途径	如下	
眼睛	如果粉尘进入眼睛，可能会引起刺激(形成眼泪和发红)。	
皮肤	不被皮肤吸收，但如果长时间暴露可能会造成干燥。	
食入	小量食入不认为是有害的，但可能会引起口腔、喉咙和胃的刺激。	
吸入	急性吸入会导致鼻腔通道干燥、肺部充血、咳嗽和一般的咽喉刺激。急性吸入高浓度的可吸入结晶二氧化硅可能导致急性硅肺病。	
慢性影响	本产品含有结晶二氧化硅。如果吸入较长时间，可吸入的结晶二氧化硅可能会导致肺癌和肺部疾病（硅肺病）。硅肺病的症状包括气喘、咳嗽和气短。	
致癌性	煅烧的硅藻土（砂藻土）包含非晶和结晶二氧化硅。IARC 和 NTP 将可吸入结晶二氧化硅（石英和方石英）归类为已知的人类致癌物。仅已知以可吸入形式吸入结晶二氧化硅会导致癌症。尚不知通过任何其他暴露途径引起癌症。	
NTP	可吸入的结晶二氧化硅（石英和方石英）归类为已知的人类致癌物。	
IARC	可吸入的结晶二氧化硅（石英和方石英）归类为已知的人类致癌物。	
毒性的数值测量	无可用数据	
腐蚀性、敏感性、刺激性	不适用	
材料名称	直接煅烧-传统结晶二氧化硅含量确定。	4/4 页
生殖毒性	无	
致畸性、致突变性	无	
第 12 部分：生态学信息		
生态毒性:	硅藻土产品作为天然杀虫剂已经显示出一些功效，但在水生或陆生生物方面没有表现出毒性。	
持久性和降解性	不可生物降解，惰性。	
生物累积的潜在可能性	生物累积的潜在可能性很小	
土壤中的流动性	无流动性	
其它不利影响	尚未知	

第 13 部分：废弃考虑	
废物处置	如果所提供的材料成为废物，则使用垃圾填埋式操作中常见的固体废物处置，或在污水坑内处理。根据 RCRA（4OCFR 第 261 部分）不被视为危害废物。
包装处置	根据适用的法律法规进行处置，通常是垃圾填埋式操作中常见的固体废物处置。
第 14 部分：运输信息	
基本的运输信息	DOT 运输分类 55（无限制）。技术名称是“硅藻土”。
附加信息	无特殊要求或不必张贴危险告示。
第 15 部分：法规信息	
美国联邦:	
TSCA	硅藻土、石英和方石英出现在 EPA TSCA 库存清单上。
CERCLA	根据美国“综合环境响应、赔偿和责任法”（CERCLA）40 CFR 302 的规定，硅藻土不被列为有害物质。
SARA TITLE III	未列出。
加州 65 号提案	本产品含有结晶二氧化硅，这是加州已知可导致癌症的化学物质。
国际组织:	
WHMIS 分类	Class D-2-A
WHMIS 成分披露清单	二氧化硅、晶体、方石英、和二氧化硅、晶体、石英
第 16 部分：其他信息	

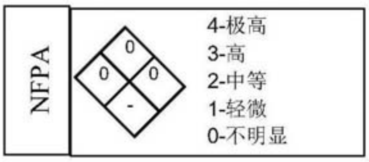
	 
原始发行日期	不适用
修订日期	不适用
修订号	

表20:利用来自LH方法的数据制作的含有石英的直接煅烧产品的SDS信息

第 1 部分：产品和公司标识	
产品标识符	根据 LH 方法的直接煅烧-二氧化硅含量确定
化学品名称	硅藻土、煅烧的
化学族	二氧化硅
材料用途	助滤剂、功能性填料
使用限制	尚未知
制造商	EP Minerals, LLC., 9875 Gateway Dr., Reno, NV 89521
电话号码	(775) 824 7600 （周一至周五，8:00 am PST – 5:00 pm）
紧急电话号码	(775) 824 7600（周一至周五，8:00 am PST – 5:00 pm）
SDS 制作日期	2016 年
第 2 部分：危害标识	
OSHA GHS 危害分类	致癌物质类别 1A 特定靶器官毒性，重复暴露类别 1
未分类的其他危害	无

标签要素	危险 吸入可能导致癌症。 长时间或反复暴露会对肺造成损害。 **使用前应获得特别指示。** **在阅读和理解所有安全措施之前，请勿处理。** **请勿吸入粉尘。** 请佩戴护眼装置。 若暴露或担忧：请获取医疗建议。 **按照当地、州和联邦的规定处理。**

第 3 部分：组成/成分信息

成分标识	近似浓度（%）	C.A.S.号
硅藻土，煅烧(砂藻土)(含有 0.1%至5%的结晶二氧化硅-石英）	100%	91053-39-3 14808-60-7

第 4 部分：急救措施

眼睛	用大量水或眼部冲洗液冲洗眼睛。如果刺激持续存在，请咨询医师。
皮肤	如果发生干燥，请使用保湿更新乳液。
食入	喝大量的水以降低主要和干燥效应。
吸入	移至新鲜空气中。擤鼻子以清除粉尘。
最重要的症状/效应，急性的和迟发的	粉尘可能会对眼睛造成磨蚀性刺激。长时间的皮肤接触可能导致干燥。粉尘可能会导致鼻腔、喉咙和上呼吸道的刺激。长时间吸入含二氧化硅的可吸入粉尘可能会导致进行性肺部疾病、硅肺病和肺癌。更多信息请参见第 11 部分。
如有必要，指示立即就医和特殊治疗	通常不需要立即就医。如果粉尘刺激眼睛，请就医。

<table>
<tr><td>材料名称</td><td colspan="3">根据LH方法的直接煅烧-二氧化硅含量确定</td><td>2/4 页</td></tr>
<tr><td colspan="5">第5部分：消防措施</td></tr>
<tr><td>灭火介质</td><td colspan="4">不适用，材料不易燃。</td></tr>
<tr><td>由该化学品引起的特殊危害</td><td colspan="4">不适用，材料不易燃。</td></tr>
<tr><td>消防人员专用防护设备和预防措施</td><td colspan="4">不适用，材料不易燃。</td></tr>
<tr><td colspan="5">第6部分：意外泄露措施</td></tr>
<tr><td>个人预防措施</td><td colspan="4">如有粉尘，请按照第8部分的规定使用配有颗粒过滤器的呼吸器。请用护目镜保护眼睛。请勿吸入粉尘。</td></tr>
<tr><td>环境预防措施</td><td colspan="4">该材料不会引起重大的环境问题。</td></tr>
<tr><td>用于控制和清洁的方法和材料</td><td colspan="4">真空清洗溢出或湿扫。避免产生气载粉尘。放入容器中使用或处置。</td></tr>
<tr><td colspan="5">第7部分：操作与储存</td></tr>
<tr><td>安全操作注意事项</td><td colspan="4">尽量减少粉尘的产生。避免与眼睛接触。请勿吸入粉尘。修理或处理破损的袋子。遵守所有标签上的注意事项和警告。</td></tr>
<tr><td>安全储存条件</td><td colspan="4">存放在干燥处以保持包装完整性和产品质量。请勿靠近氢氟酸或浓碱溶液储存。</td></tr>
<tr><td colspan="5">第8部分：暴露控制/个人防护</td></tr>
<tr><td>暴露指南</td><td colspan="4"></td></tr>
<tr><td>组分</td><td>OSHA PEL</td><td>ACGIH TLV</td><td>MSHA PEL</td><td>NIOSH REL</td></tr>
</table>

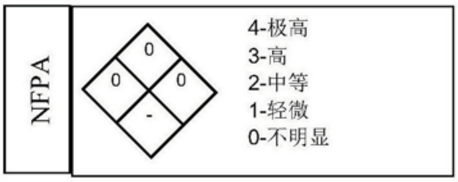
硅藻土、煅烧（砂藻土）	5 mg/m^{3}可吸入粉尘 15 mg/m^{3}总粉尘	未建立	5 mg/m^3 可吸入粉尘 15 mg/m^{3}总粉尘	未建立
结晶二氧化硅（石英）	$\frac{30\ mg/m^3}{\%\ SiO_2+2}$ 总粉尘 $\frac{10\ mg/m^3}{\%\ SiO_2+2}$ 可吸入粉尘	0.025 mg/ m^3 可吸入粉尘	$\frac{30\ mg/m^3}{\%\ SiO_2+2}$ 总粉尘 $\frac{10\ mg/m^3}{\%\ SiO_2+2}$ 可吸入粉尘	0.05 mg/m^3 可吸入粉尘

工程控制	使用一般或局部排气通风将粉尘控制在建议暴露限值内。关于通风系统的设计，请参阅 ACGIH 出版物“工业通风”或类似的出版物。
个人防护设备：	
眼睛/面部防护	佩戴护目镜以防止粉尘
皮肤防护	不需要特殊设备。
呼吸系统防护	当存在粉尘时，应佩戴带有符合标准 42CFR84 的 N95 系列的过滤器的呼吸器。如果粉尘浓度低于允许暴露限值（PEL）的十（10）倍，则使用带有 N95 防尘过滤器的四分之一或半面罩呼吸器或 N95 的一次性防尘面罩。如果粉尘浓度大于 PEL 的十（10）倍且小于五十（50）倍，则建议使用装有可更换 N95 过滤器的全面罩呼吸器。如果粉尘浓度大于 PEL 的五十（50）倍且小于二百（200）倍，则使用带有可更换 N95 过滤器的动力空气净化（正压）呼吸器。如果粉尘浓度大于 PEL 的二百（200）倍，则使用带有全面罩、头罩或头盔的 C 型供气呼吸器（持续气流，正压）。
一般卫生	避免吸入粉尘。避免与眼睛接触。处理后以及进食或饮用前洗手。

材料名称	根据 LH 方法的直接煅烧-二氧化硅含量确定	3/4 页
第 9 部分：物理和化学性能		

外观，颜色	浅黄色至粉红色粉末	**气味**	无味
物理状态	固体	**气味阈值**	不适用
蒸汽压	不适用	**蒸汽密度**	不适用
沸点	不适用	**熔点**	> 1300° C
闪点	不适用	**pH (10%悬浮液)**	7
可燃极限	不适用	**蒸发速度**	不适用
分解温度	> 1300℃	**规定重力/相对密度**	2.2
自燃温度	不适用	**分配系数-正辛醇/水**	不适用
可燃性（固体/气体）	不适用	**溶解度-水**	< 1%
		粘度	不适用
第 10 部分：稳定性和反应性			
反应性	材料不会发生反应。		
化学稳定性	材料稳定。		
危害反应的可能性	在正常的处理条件下，材料不会发生反应，除非与以下不相容物质混合。		
应避免的条件	不适用		
不相容材料	氢氟酸和浓碱溶液可能与该产品发生剧烈反应。		
危害分解产物	不适用		
第 11 部分：毒理学信息			
潜在健康影响			
可能的暴露途径	如下		
眼睛接触	如果粉尘进入眼睛，可能会引起刺激(形成眼泪和发红)。		
皮肤接触	不被皮肤吸收，但如果长时间暴露可能会造成干燥。		
食入	小量食入不认为是有害的，但可能会引起口腔、喉咙和胃的刺激。		
吸入	急性吸入会导致鼻腔通道干燥、肺部充血、咳嗽和一般的咽喉刺激。急性吸入高浓度的可吸入结晶二氧化硅可能导致急性硅肺病。		

慢性影响	该产品含有一种天然形式的结晶二氧化硅(石英)。如果吸入较长时间，可吸入的结晶二氧化硅可能会导致肺癌和肺部疾病（硅肺病）。硅肺病的症状包括气喘、咳嗽和气短。	
致癌性	煅烧硅藻土（砂藻土）主要由非晶二氧化硅组成，但也可含有石英形式的结晶二氧化硅。IARC 和 NTP 将可吸入结晶二氧化硅（石英）归类为已知的人类致癌物。仅已知以可吸入形式吸入结晶二氧化硅会导致癌症。尚不知通过任何其他暴露途径引起癌症。	
NTP	可吸入的结晶二氧化硅(石英)归类为已知的人类致癌物。	
IARC	可吸入的结晶二氧化硅(石英)归类为已知的人类致癌物。	
毒性的数值测量	无可用数据	
腐蚀性、敏感性、刺激性	不适用	
材料名称	根据 LH 方法的直接煅烧-二氧化硅含量确定	4/4 页
生殖毒性	无	
致畸性、致突变性	无	
第 12 部分：生态学信息		
生态毒性：	硅藻土产品作为天然杀虫剂已经显示出一些功效，但在水生或陆生生物方面没有表现出毒性。	
持久性和降解性	不可生物降解，惰性。	
生物累积的潜在可能性	生物累积的潜在可能性很小	
土壤中的流动性	无流动性	
其它不利影响	尚未知	
第 13 部分：废弃考虑		
废物处置	如果所提供的材料成为废物，则使用垃圾填埋式操作中常见的固体废物处置，或在污水坑内处理。根据 RCRA（4OCFR 第 261 部分）不被视为危害废物。	
包装处置	根据适用的法律法规进行处置，通常是垃圾填埋式操作中常见的固体废物处置。	
第 14 部分：运输信息		
基本的运输信息	DOT 运输分类 55（无限制）。技术名称是“硅藻土”。	
附加信息	无特殊要求或不必张贴危险告示。	

第 15 部分：法规信息	
美国联邦:	
TSCA	硅藻土和石英出现在 EPA TSCA 库存清单上。
CERCLA	根据美国“综合环境响应、赔偿和责任法”（CERCLA）40 CFR 302 的规定，硅藻土不被列为有害物质。
SARA TITLE III	未列出。
加州 65 号提案	本产品含有结晶二氧化硅，这是加州已知可导致癌症的化学物质。
国际组织:	
WHMIS 分类	级别 D-2-A
WHMIS 成分披露清单	二氧化硅、晶体、石英
第 16 部分：其他信息	
	 
原始发行日期	不适用
修订日期	不适用
修订号	

[0188] 图33示出了产品4的一个示例性实施例。产品4包括(产品4的)物理组分6和数据组分9。数据组分9包括新二氧化硅文档8。在图33示的实施例中，二氧化硅文档8包括产品标签8a、条形码8b和SDS 8c。这并不意味着所有这三种类型的二氧化硅文档8都必须与给定的产品4相关。图33仅用于示例性目的。在其他实施例中，如前所述，二氧化硅文档8可以包括一个或多个法规支持文件、危害披露、安全数据表、标签、产品标签、产品条形码、分析证书或其他记录或公开产品4的结晶二氧化硅含量或不存在结晶二氧化硅的电子或印刷形式的数据。在图33所示的实施例中，根据LH方法确定、测定或量化，二氧化硅文档8(与产品4相关)

公开了物理组分6中存在的结晶二氧化硅含量(或不存在结晶二氧化硅)。如前所述,通过明确声明或二氧化硅文档8所鉴定的产品含量中结晶二氧化硅的不存在,来公开不存在结晶二氧化硅(例如方石英、石英、鳞石英)。

[0189] 以下引用的出版物的公开内容在此通过引用全部并入本发明。Eichhubl,P,and R.J.Behl,1998.“Diagenesis,Deformation,and Fluid Flow in the Miocene Monterey Formation”:Special Publication,Pacific Section,SEPM,V83,p.5-13.J.M.Elzea,I.E.Odom,W.J.Miles,“Distinguishing well-ordered opal-CT and opal-C from high temperature cristobalite by x-ray diffraction”,Anal.Chim.Acta 286(1994)107-116.Hillier,S.,and D.G.Lumsdon.“Distinguishing opaline silica from cristobalite in bentonites:a practical procedure and perspective based on NaOH dissolution”,Clay Minerals(2008)43,477-486.Damby,David E.,Llewellin,Edward W.,Horwell,Claire J.,Williamson,Ben J.,Najorka,Jens,Cressey,Gordon,Carpenter,Michael,2014,“The α-βphase transition in volcanic cristobalite”,Journal of Applied Crystallography,47,1205-1215.Chao,Chin-Hsiao,Lu,Hong-Yang,2002,“Stress-inducedβtoα-cristobalite phase transformation in(Na_2O+Al_2O_3)-codoped silica”,Materials Science and Engineering,A328,267-276.Klug,H.P.,&Alexander,L.E.,1974,“X-ray Diffraction Procedures”,John Wiley and Sons,Inc.Silica,Crystalline,by XRD 7500,NIOSH Manual of Analytical Methods,Fourth Edition,2003.

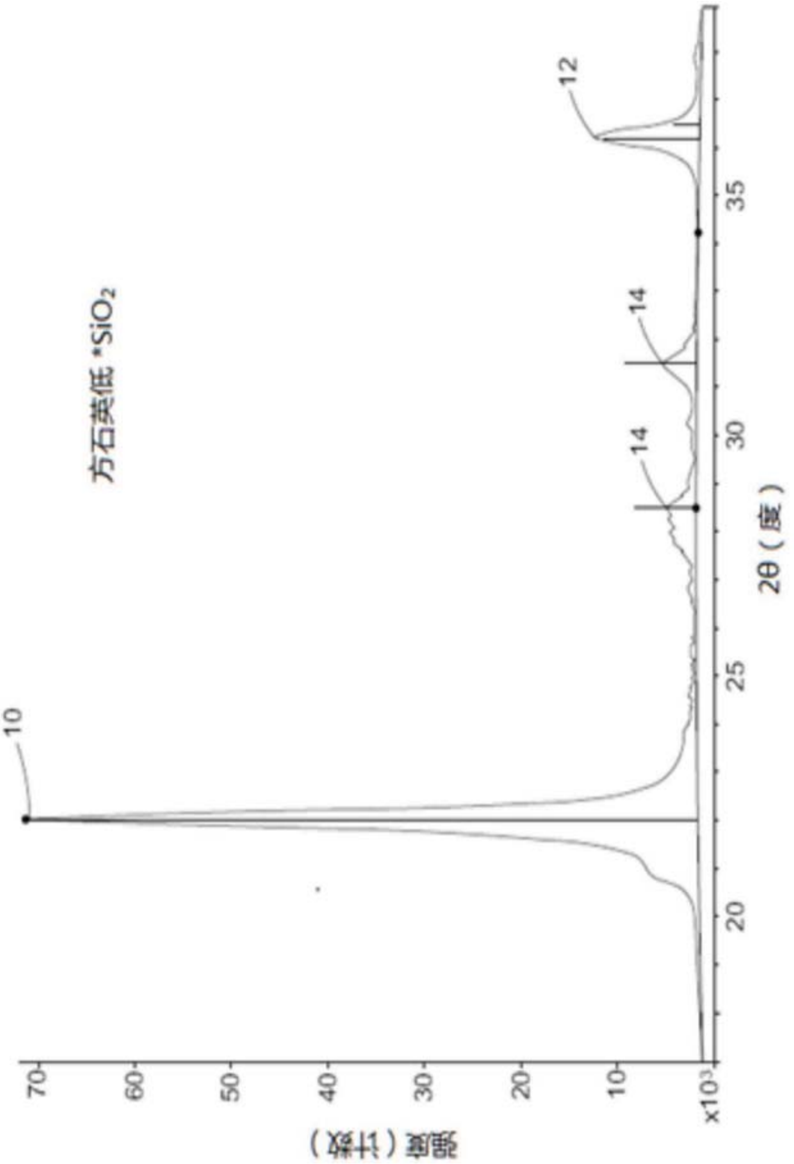
工业应用性

[0190] 本发明的教导包括,包含粉末状硅藻土和新二氧化硅文档的产品,以及相关的用于确定和量化该产品的二氧化硅含量(例如,蛋白石-C(和/或蛋白石-CT)、方石英、石英或鳞石英含量)的新的LH方法。通过基于LH方法的二氧化硅文档进行适当表征的该产品,对分析潜在产品危害提供益处,并为包括硅藻土在内的产品生产商提供适当的激励措施,以开发并推出新产品,该新产品包含降低水平的结晶二氧化硅和关于工人和消费者对结晶二氧化硅和可吸入结晶二氧化硅的潜在暴露的改进信息。此外,本文公开的用于确定和量化包含硅藻土的产品的蛋白石-C(和/或蛋白石-CT)和结晶二氧化硅(方石英、石英、鳞石英)含量的新的LH方法,和本文公开的加工控制方法,在该产品的制造过程中提供有效和新颖的质量控制。

[0191] 此外,本发明的教导可以在工业规模上实施,用于提供包含低水平或不可检测水平的结晶二氧化硅的新过滤介质、载体、吸收剂和功能性填料等。该新产品以及生产该产品的方法,通过减少对结晶二氧化硅的暴露而使用户、处理者和制造商受益。

[0192] 本文中数值范围的叙述仅仅意在作为一种速记方法,其分别指代落入该范围内的每个单独数值,除非本文另有说明,每个单独数值都被并入本说明书中,如其在本文中分别列举一样。除非本文另有说明或与上下文明显地矛盾,本文描述的所有方法都可以以任何合适的顺序完成。

[0193] 因此,本发明包括由适用法律所允许的所附权利要求中列举的主题的所有修改和等同物。另外,除非本文另有说明或与上下文明显地矛盾,在其所有可能的变体中的上述要素的任何组合都包含在本发明中。



具有方石英相加少量（1至2%）长石的Celite® 501（样品#18362）的XRD图谱

图1

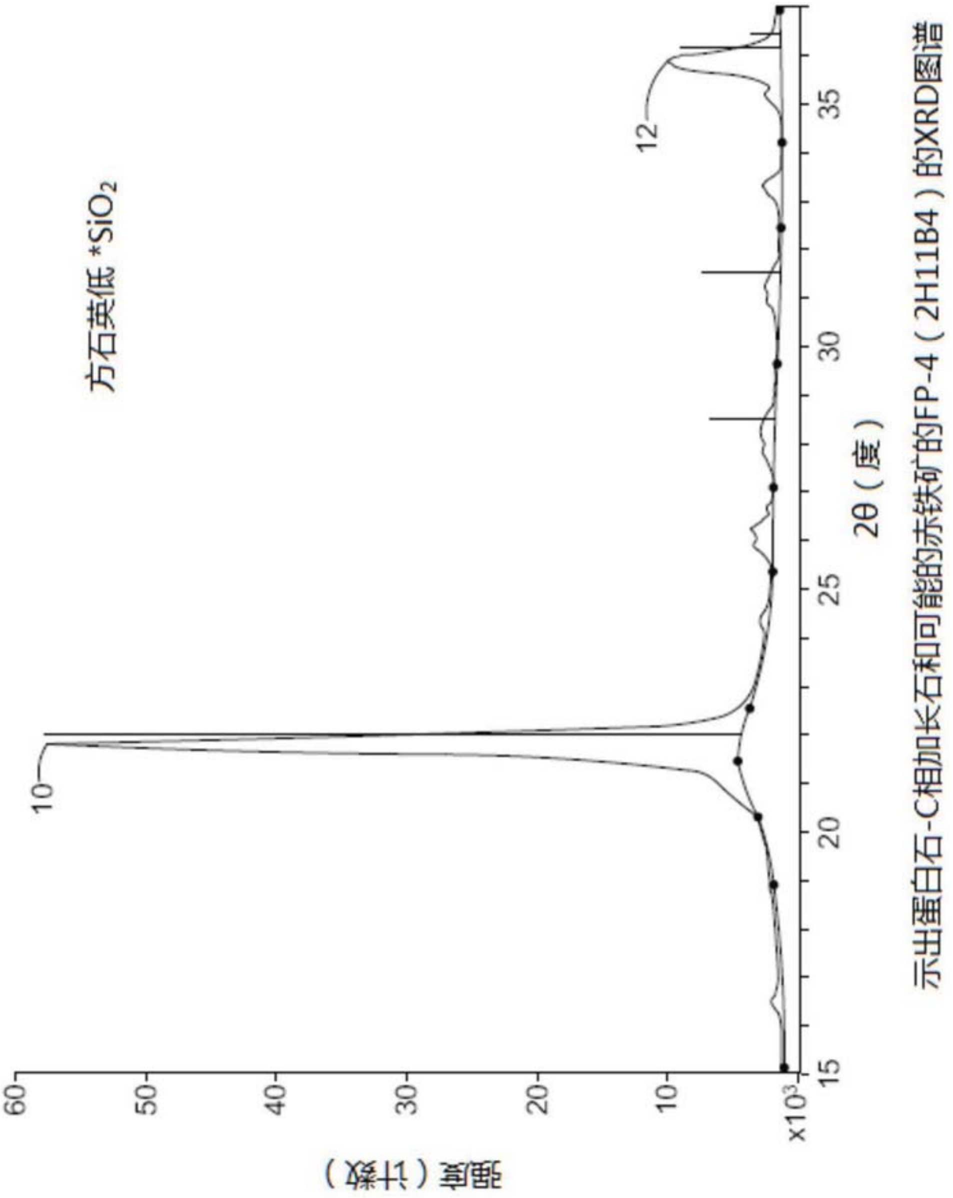

方石英低 *SiO_2
10
12
强度（计数）
$\times10^3$
60
50
40
30
20
10
15
20
25
30
35
2θ（度）
示出蛋白石-C相加长石和可能的赤铁矿的FP-4（2H11B4）的XRD图谱

图2

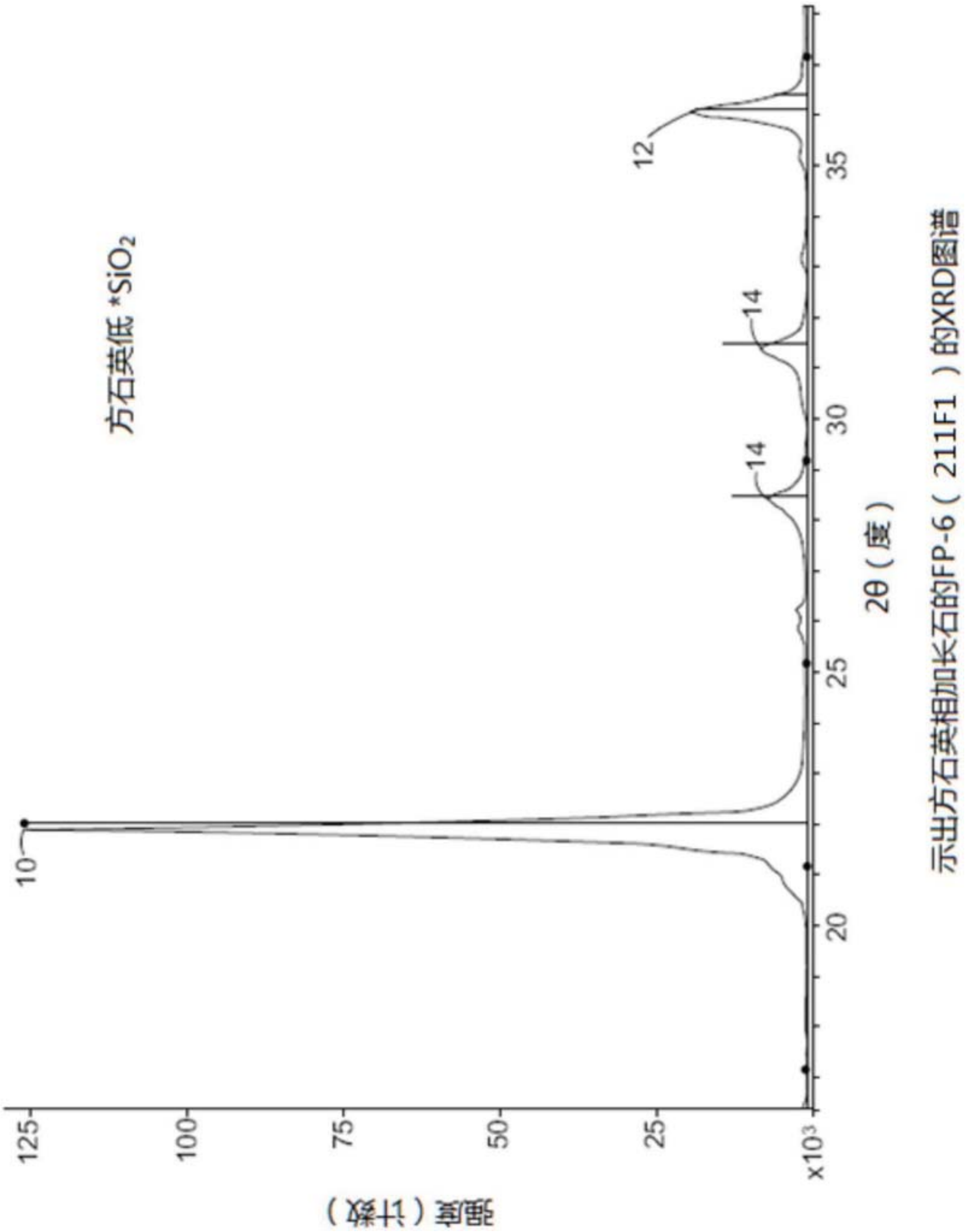

方石英低 *SiO$_2$
强度（计数）
125
100
75
50
25
x10³
20
25
30
35
2θ（度）
10
12
14
14
示出方石英相加长石的FP-6（211F1）的XRD图谱

图3

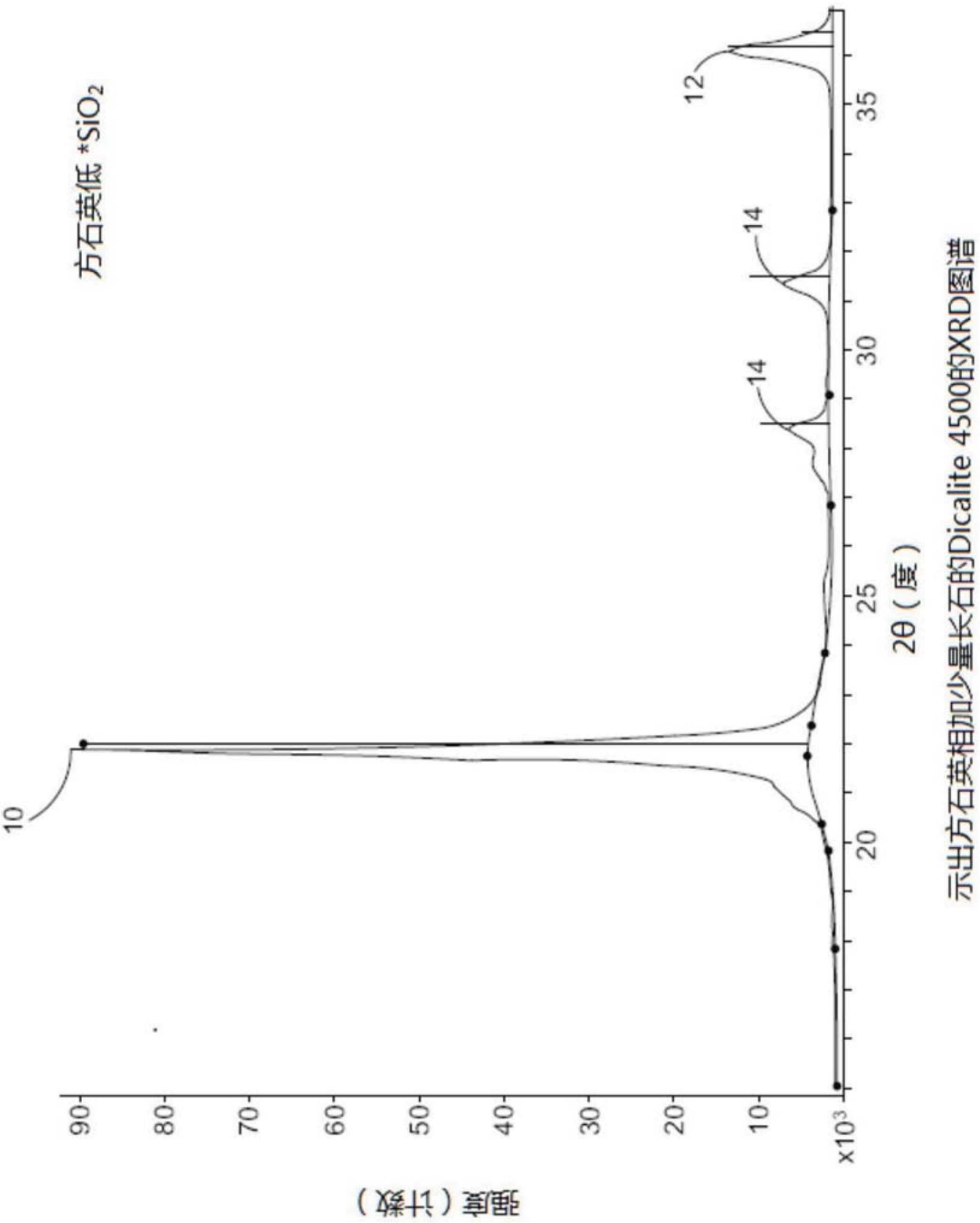

方石英低 *SiO₂
10
12
14
14
强度（计数）
90
80
70
60
50
40
30
20
10
x10³
20
25
30
35
2θ（度）
示出方石英相加少量长石的Dicalite 4500的XRD图谱

图4

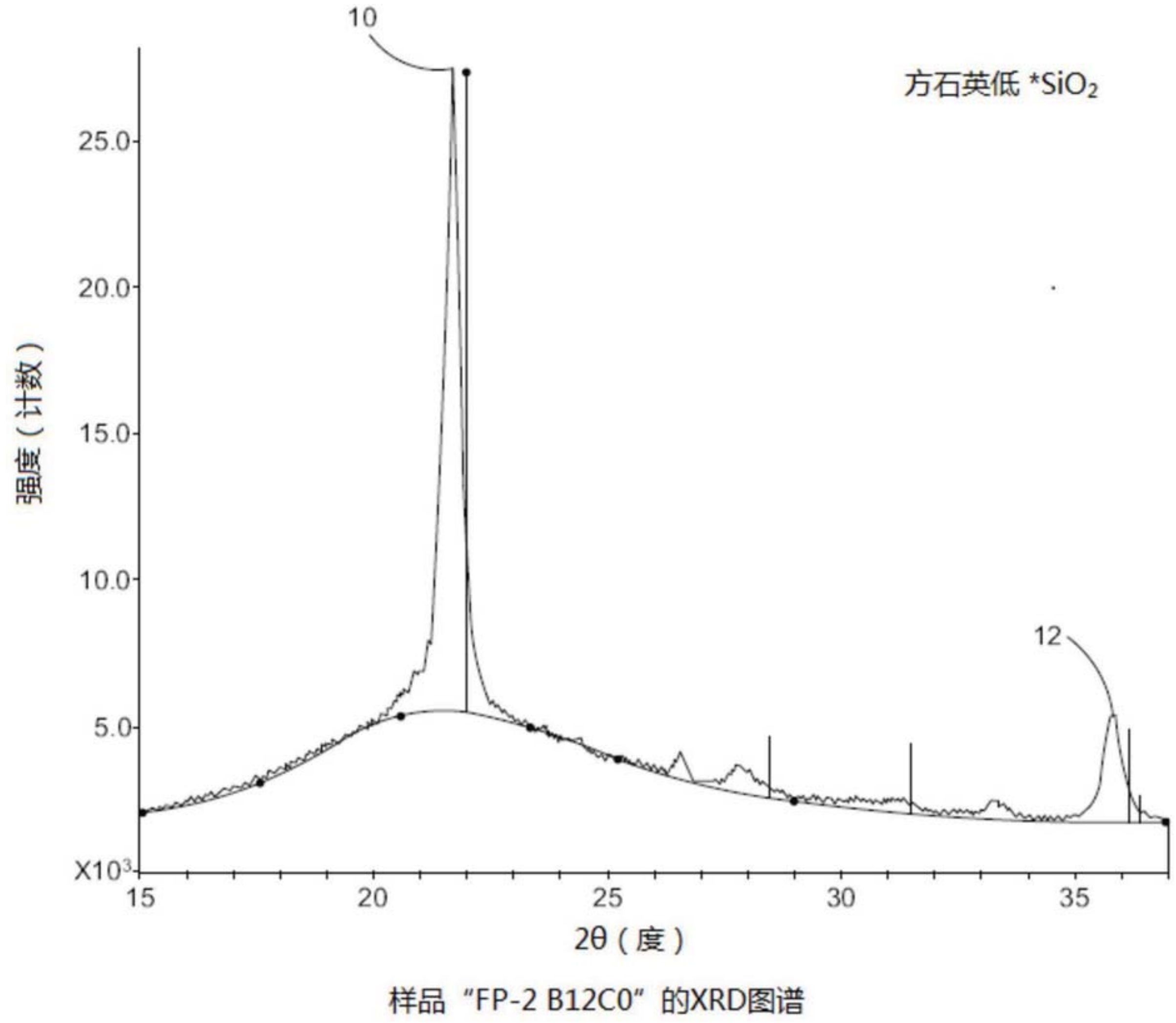

方石英低 *SiO₂
10
12
强度（计数）
25.0
20.0
15.0
10.0
5.0
X10³
15
20
25
30
35
2θ（度）
样品“FP-2 B12C0”的XRD图谱

图5

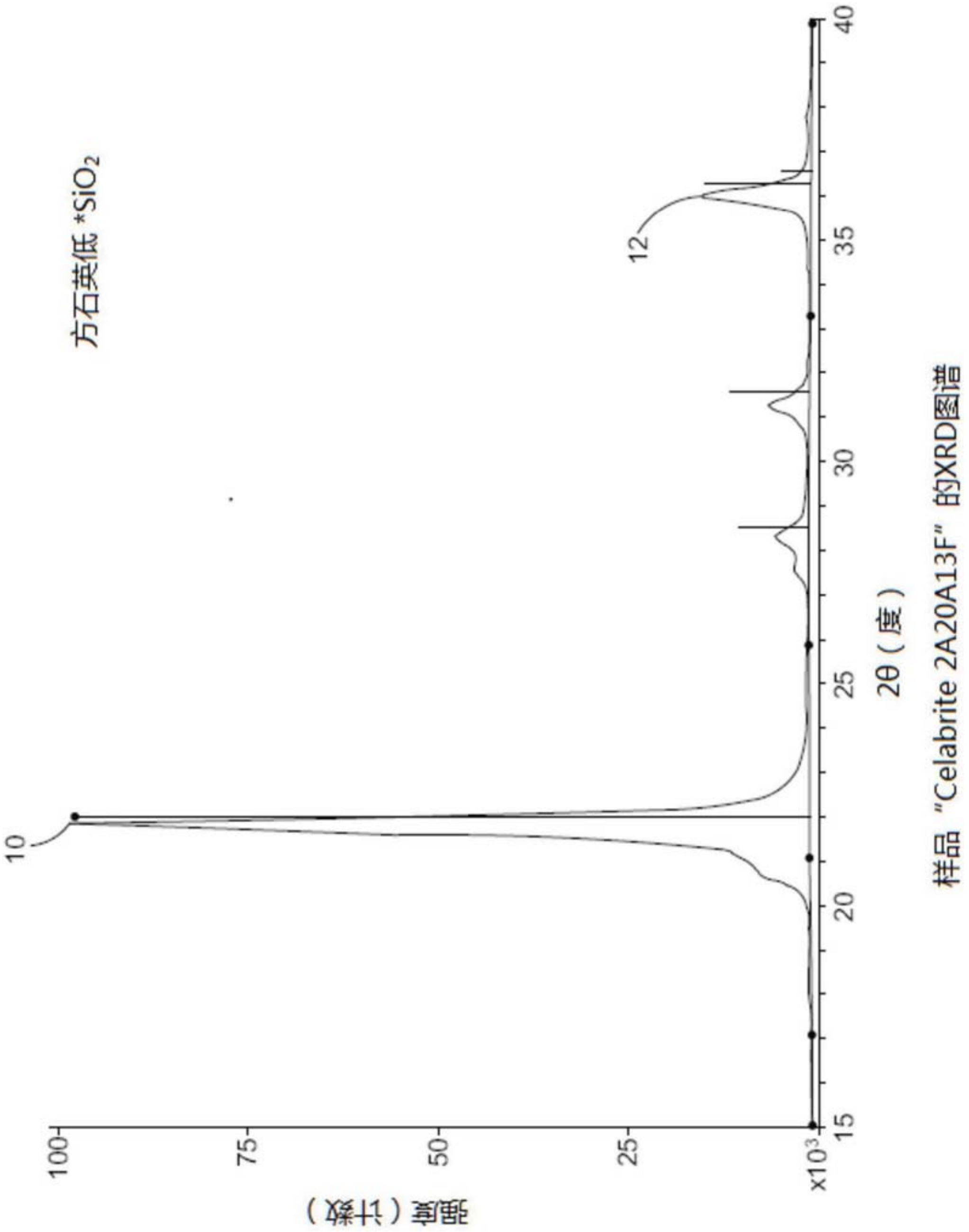

方石英低 *SiO₂
10
12
100
75
50
25
x10³
15
20
25
30
35
40
2θ（度）
强度（计数）
样品 "Celabrite 2A20A13F" 的XRD图谱

图6

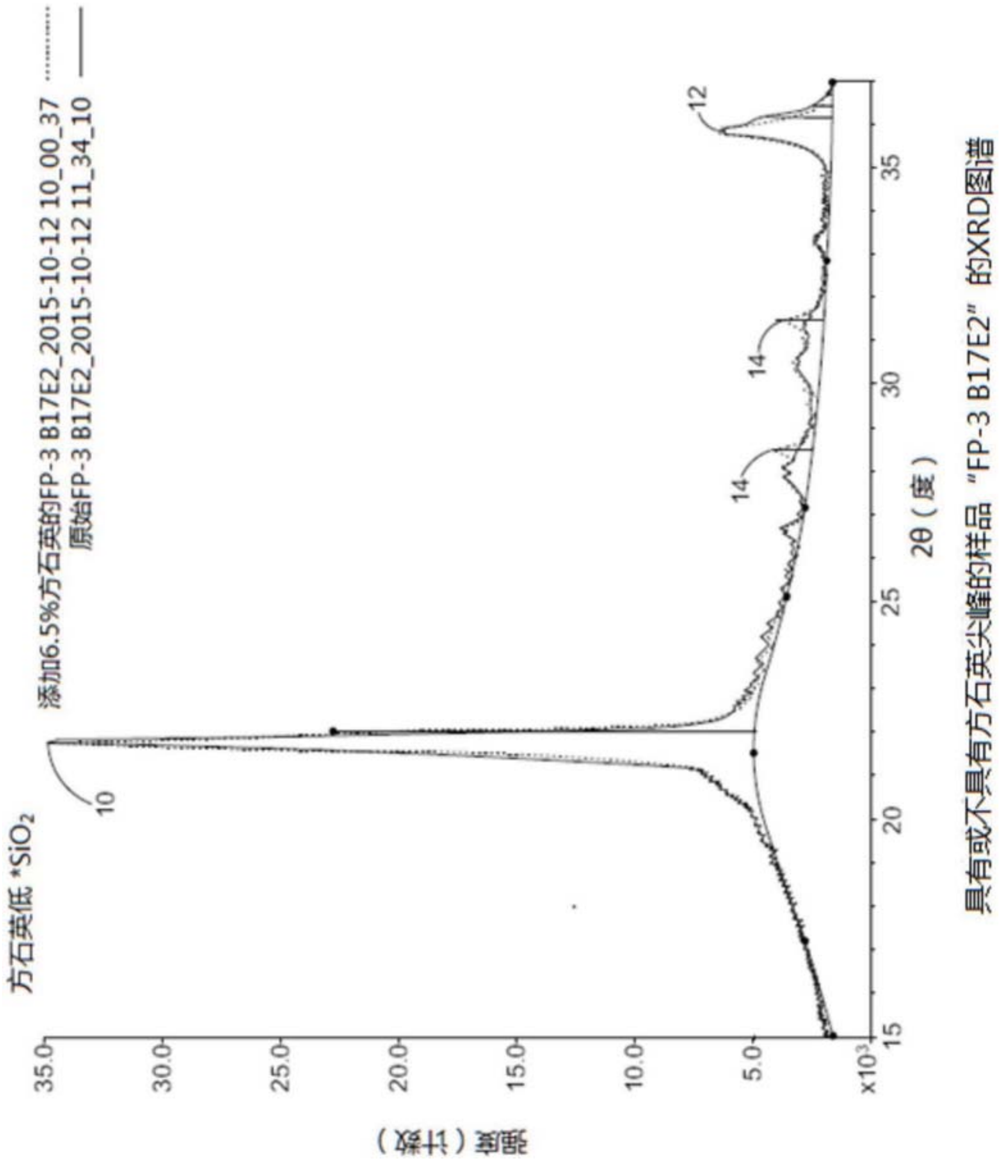

添加6.5%方石英的FP-3 B17E2_2015-10-12 10_00_37
原始FP-3 B17E2_2015-10-12 11_34_10
方石英低 *SiO$_2$
10
12
14
14
强度（计数）
35.0
30.0
25.0
20.0
15.0
10.0
5.0
x10^3
15
20
25
30
35
2θ（度）
具有或不具有方石英尖峰的样品“FP-3 B17E2”的XRD图谱

图7

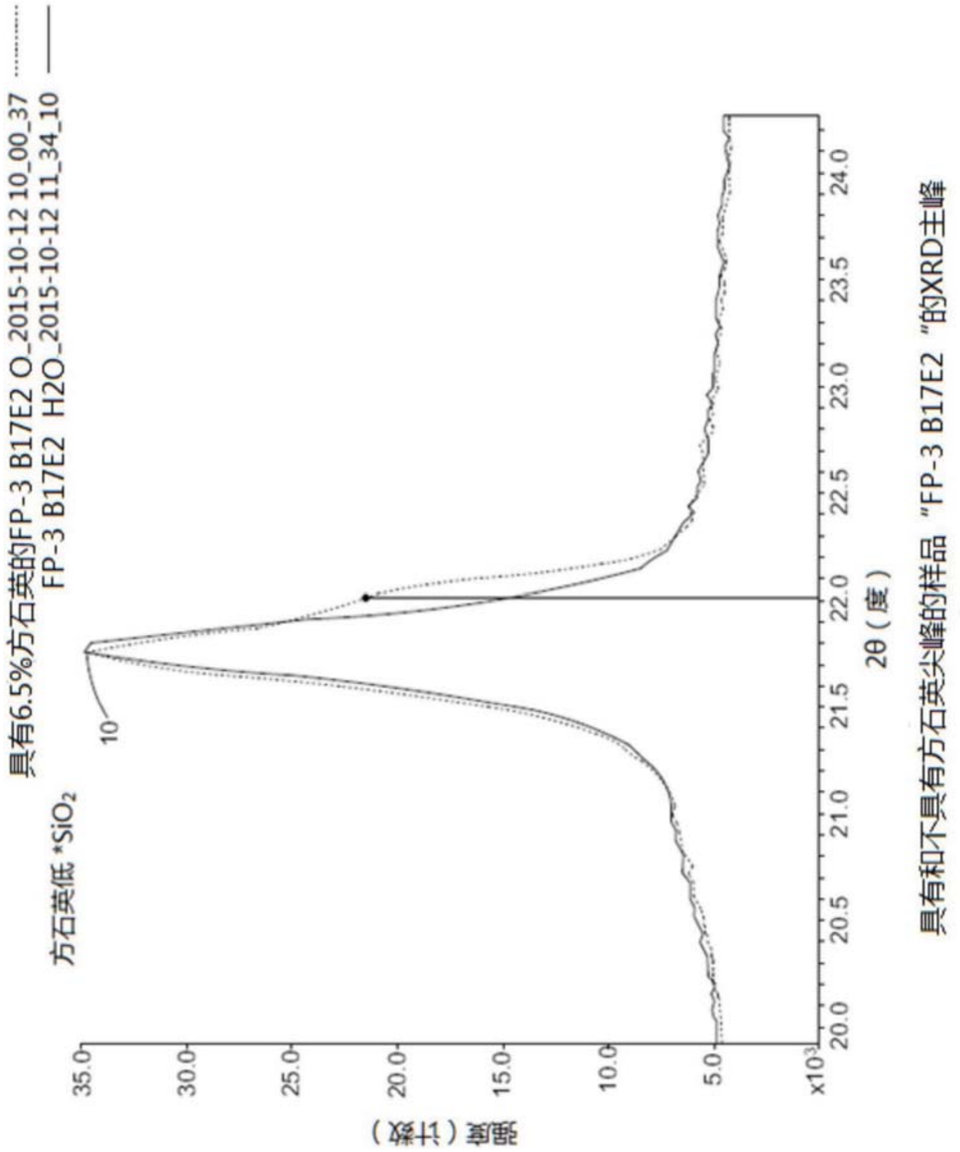

具有6.5%方石英的FP-3 B17E2 O_2015-10-12 10_00_37
FP-3 B17E2 H2O_2015-10-12 11_34_10
方石英低 *SiO₂
10
35.0
30.0
25.0
20.0
15.0
10.0
5.0
x10³
强度（计数）
20.0
20.5
21.0
21.5
22.0
22.5
23.0
23.5
24.0
2θ（度）
具有和不具有方石英尖峰的样品 "FP-3 B17E2 "的XRD主峰

图8

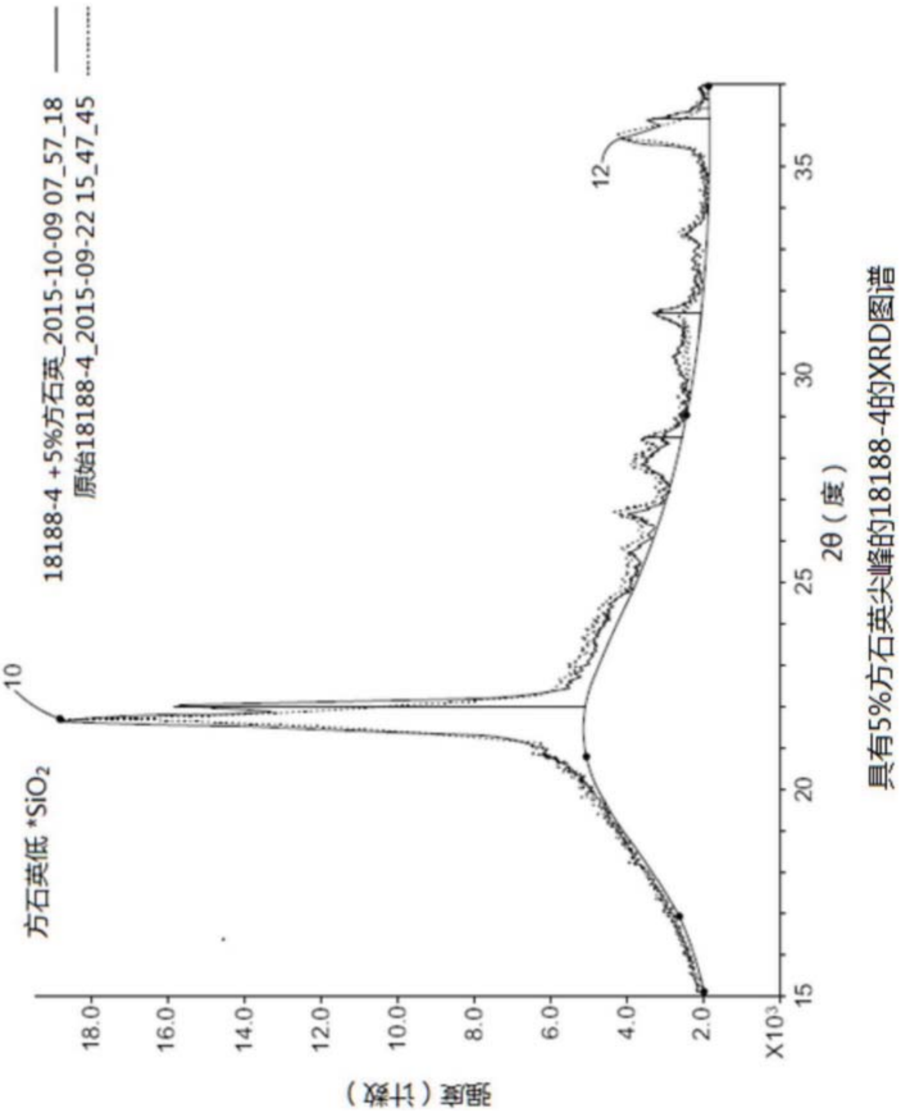

18188-4 +5%方石英_2015-10-09 07_57_18
原始18188-4_2015-09-22 15_47_45
方石英低 *SiO₂
10
12
强度（计数）
X10³
18.0
16.0
14.0
12.0
10.0
8.0
6.0
4.0
2.0
15
20
25
30
35
2θ（度）
具有5%方石英尖峰的18188-4的XRD图谱

图9

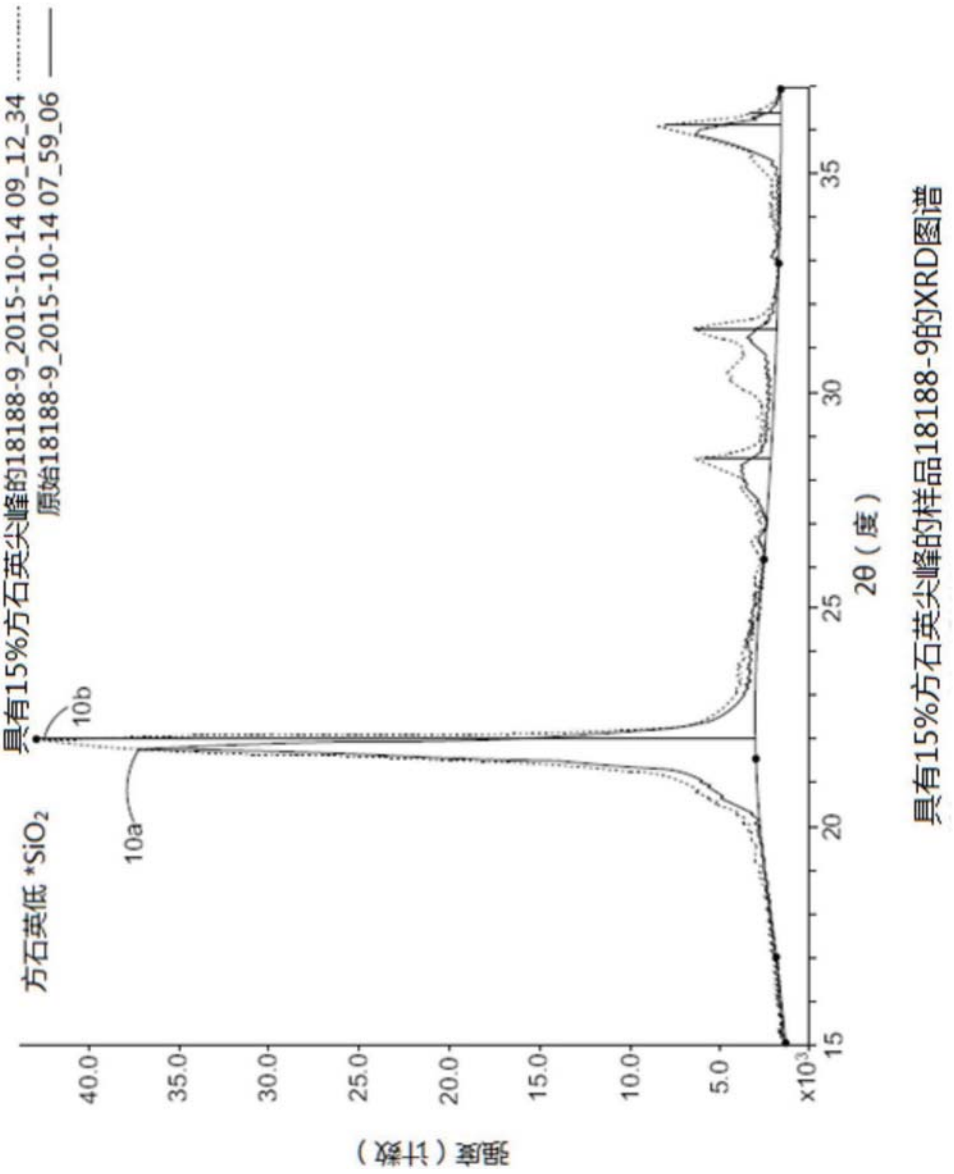

具有15%方石英尖峰的18188-9_2015-10-14 09_12_34
原始18188-9_2015-10-14 07_59_06
方石英低 *SIO$_2$
10a
10b
强度（计数）
x10^3
40.0
35.0
30.0
25.0
20.0
15.0
10.0
5.0
15
20
25
30
35
2θ（度）
具有15%方石英尖峰的样品18188-9的XRD图谱

图10

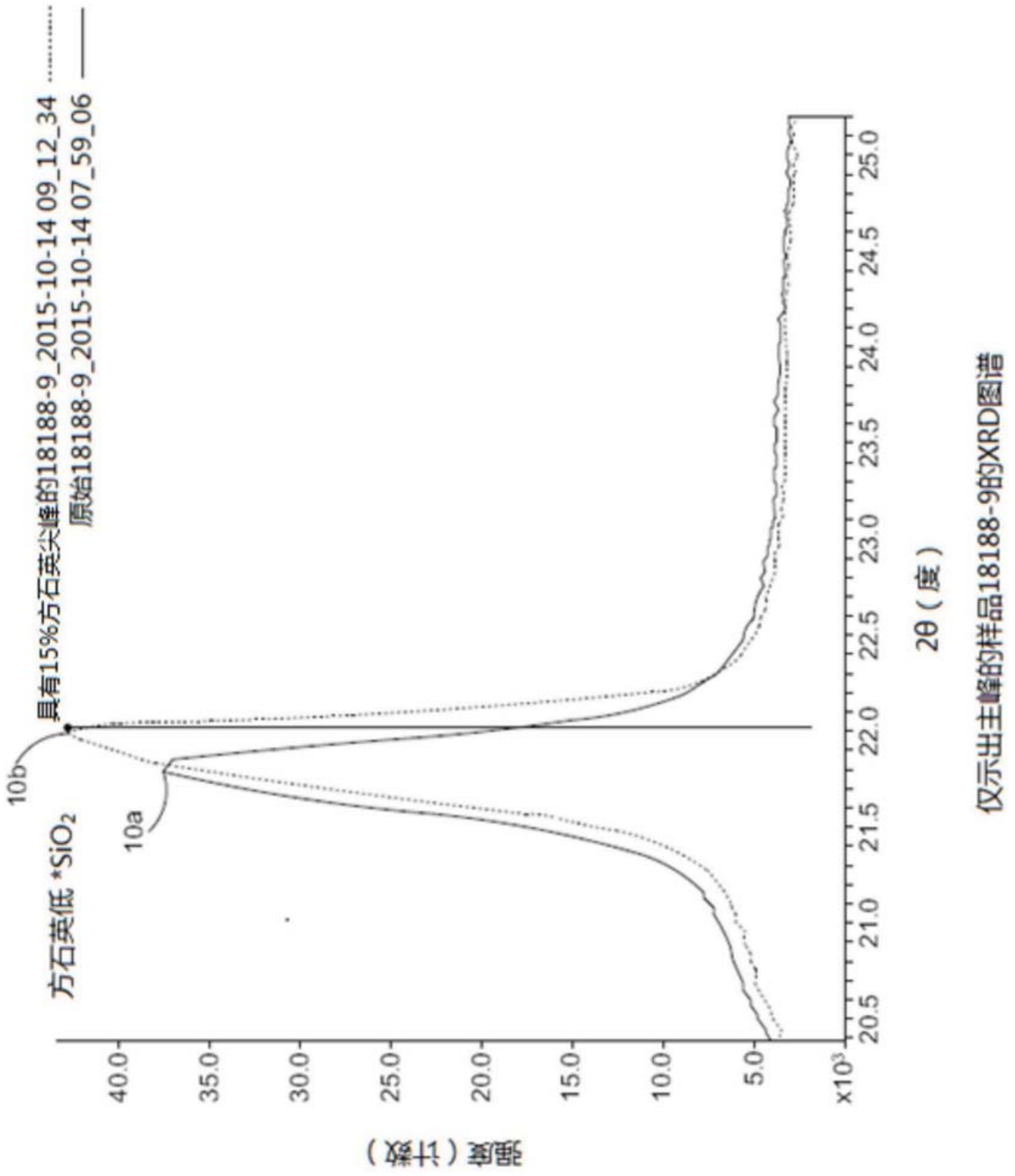

具有15%方石英尖峰的18188-9_2015-10-14 09_12_34
原始18188-9_2015-10-14 07_59_06
方石英低 *SiO$_2$
10b
10a
强度（计数）
40.0
35.0
30.0
25.0
20.0
15.0
10.0
5.0
x10^3
20.5
21.0
21.5
22.0
22.5
23.0
23.5
24.0
24.5
25.0
2θ（度）
仅示出主峰的样品18188-9的XRD图谱

图11

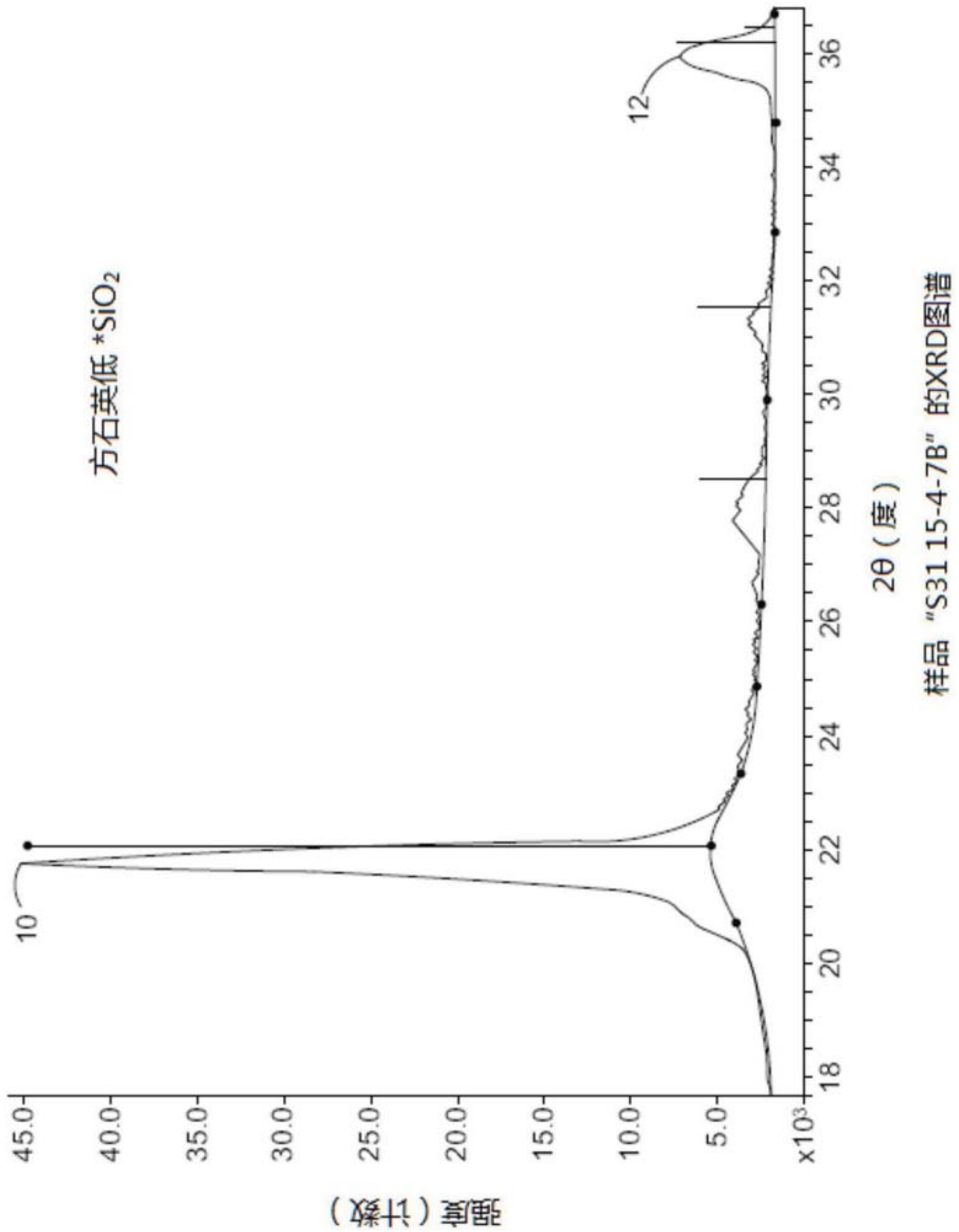

方石英低 *SiO₂
样品 "S31 15-4-7B" 的XRD图谱
2θ（度）
强度（计数）
x10³
45.0
40.0
35.0
30.0
25.0
20.0
15.0
10.0
5.0
18
20
22
24
26
28
30
32
34
36
10
12

图12

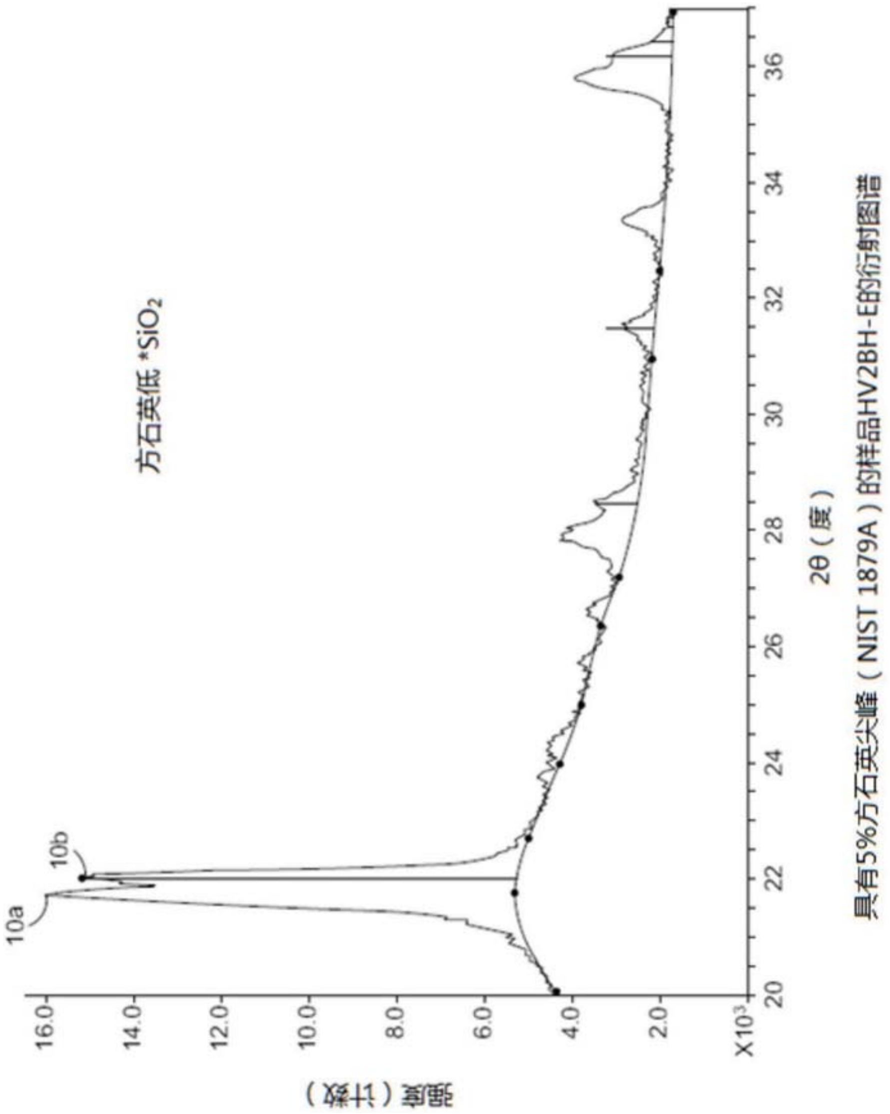

方石英低 *SiO₂
10a
10b
强度（计数）
16.0
14.0
12.0
10.0
8.0
6.0
4.0
2.0
X10³
20
22
24
26
28
30
32
34
36
2θ（度）
具有5%方石英尖峰（NIST 1879A）的样品HV2BH-E的衍射图谱

图13

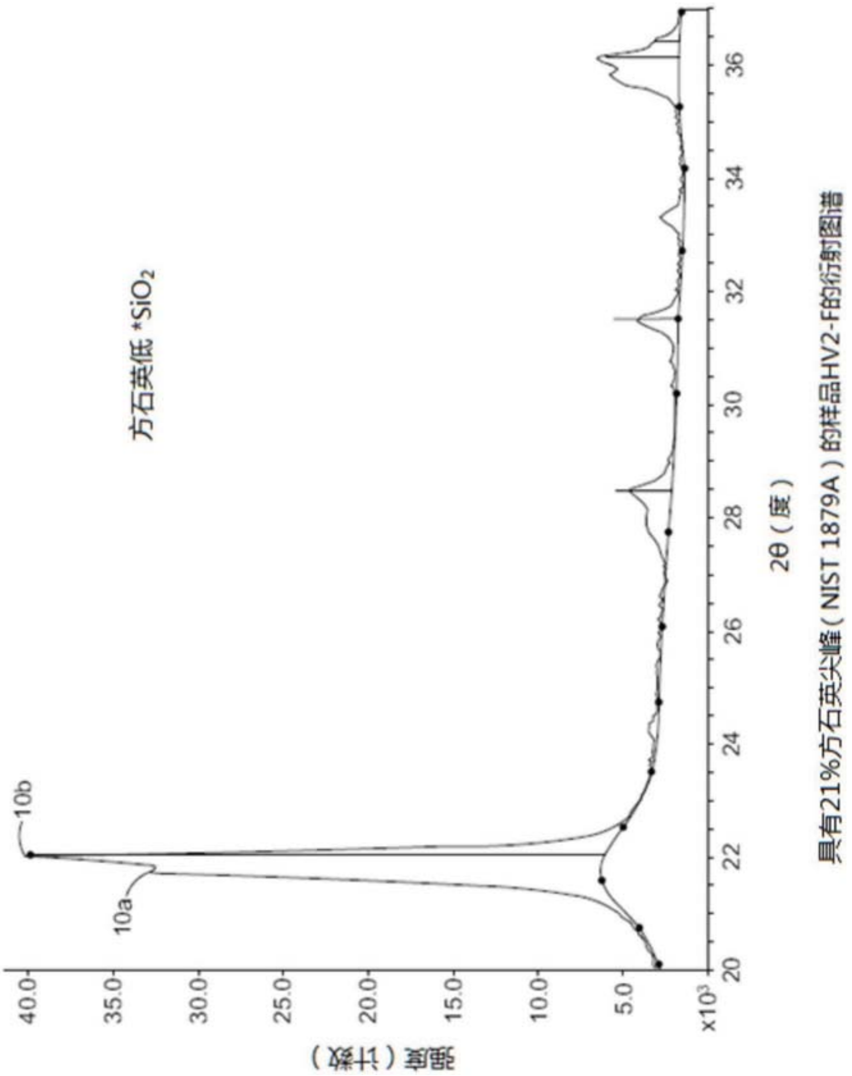

方石英低 *SiO$_2$
10b
10a
强度（计数）
x10³
40.0
35.0
30.0
25.0
20.0
15.0
10.0
5.0
20
22
24
26
28
30
32
34
36
2θ（度）
具有21%方石英尖峰（NIST 1879A）的样品HV2-F的衍射图谱

图14

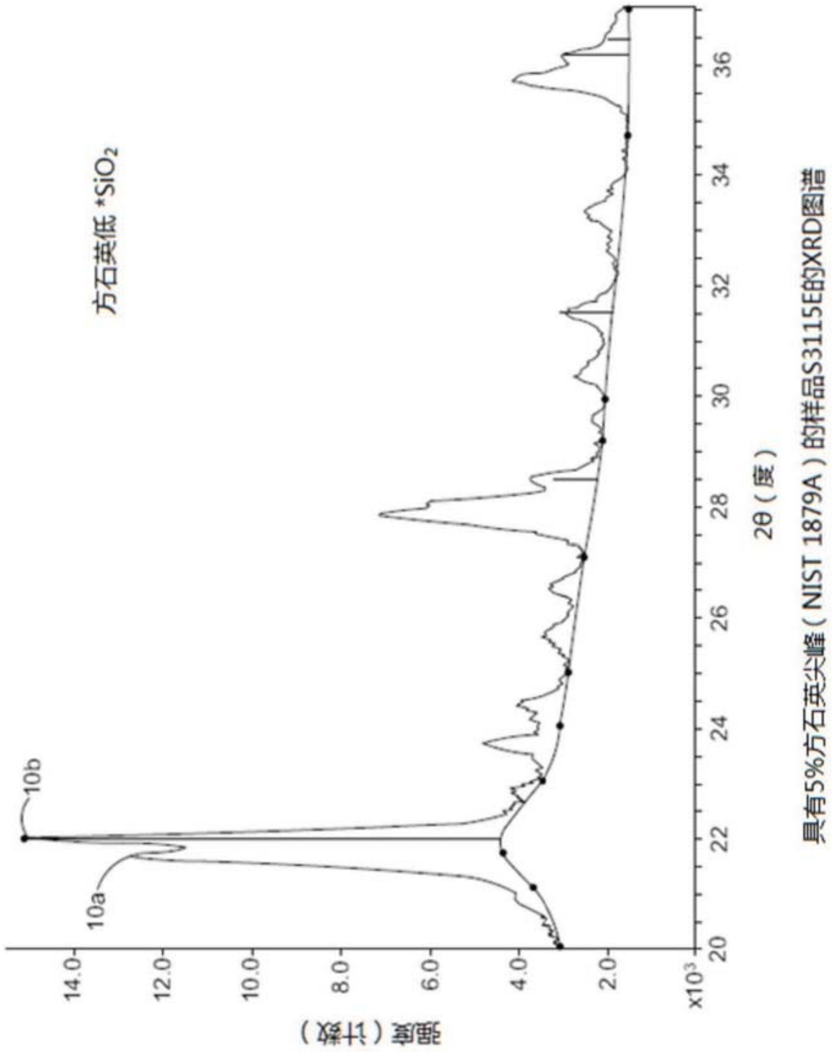

方石英低 *SiO2
10b
10a
14.0
12.0
10.0
8.0
6.0
4.0
2.0
x10³
强度（计数）
20
22
24
26
28
30
32
34
36
2θ（度）
具有5%方石英尖峰（NIST 1879A）的样品S3115E的XRD图谱

图15

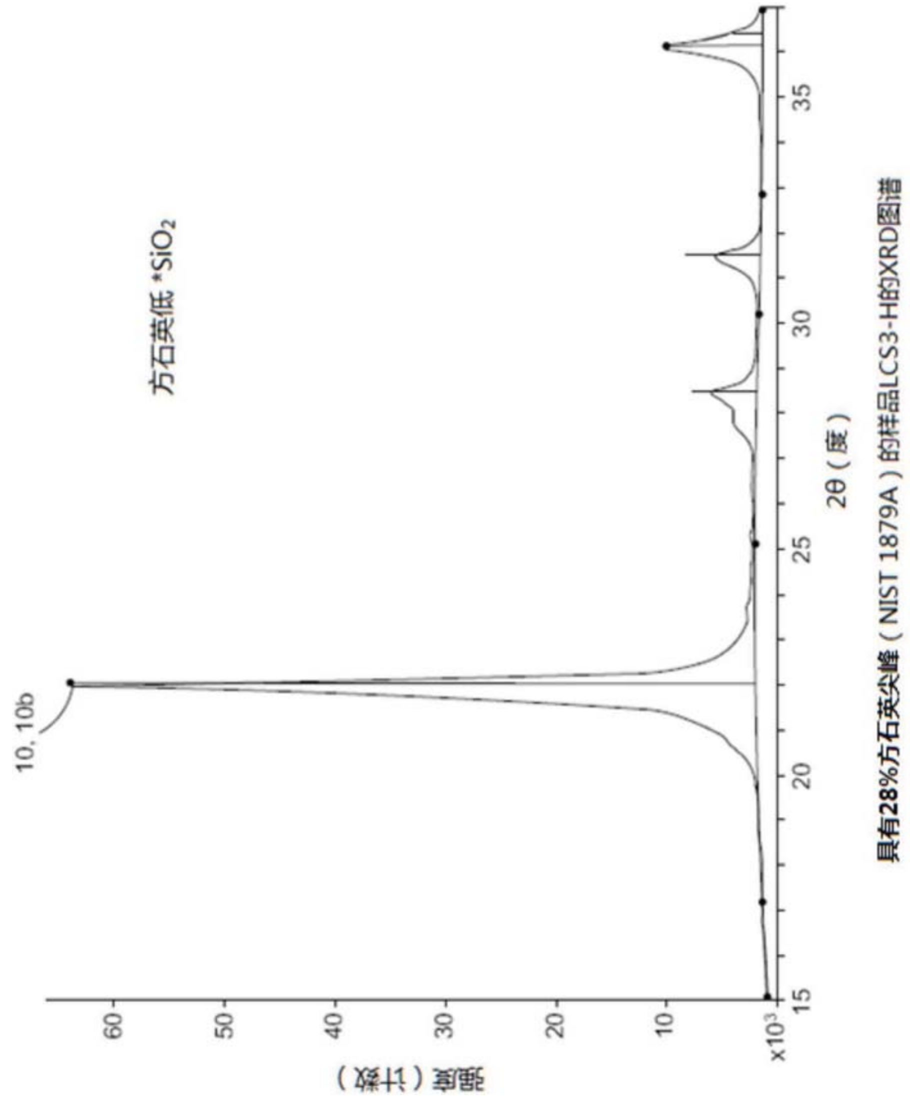

方石英低 *SiO$_2$
10, 10b
强度（计数）
x10^3
60
50
40
30
20
10
15
20
25
30
35
2θ（度）
具有28%方石英尖峰（NIST 1879A）的样品LCS3-H的XRD图谱

图16

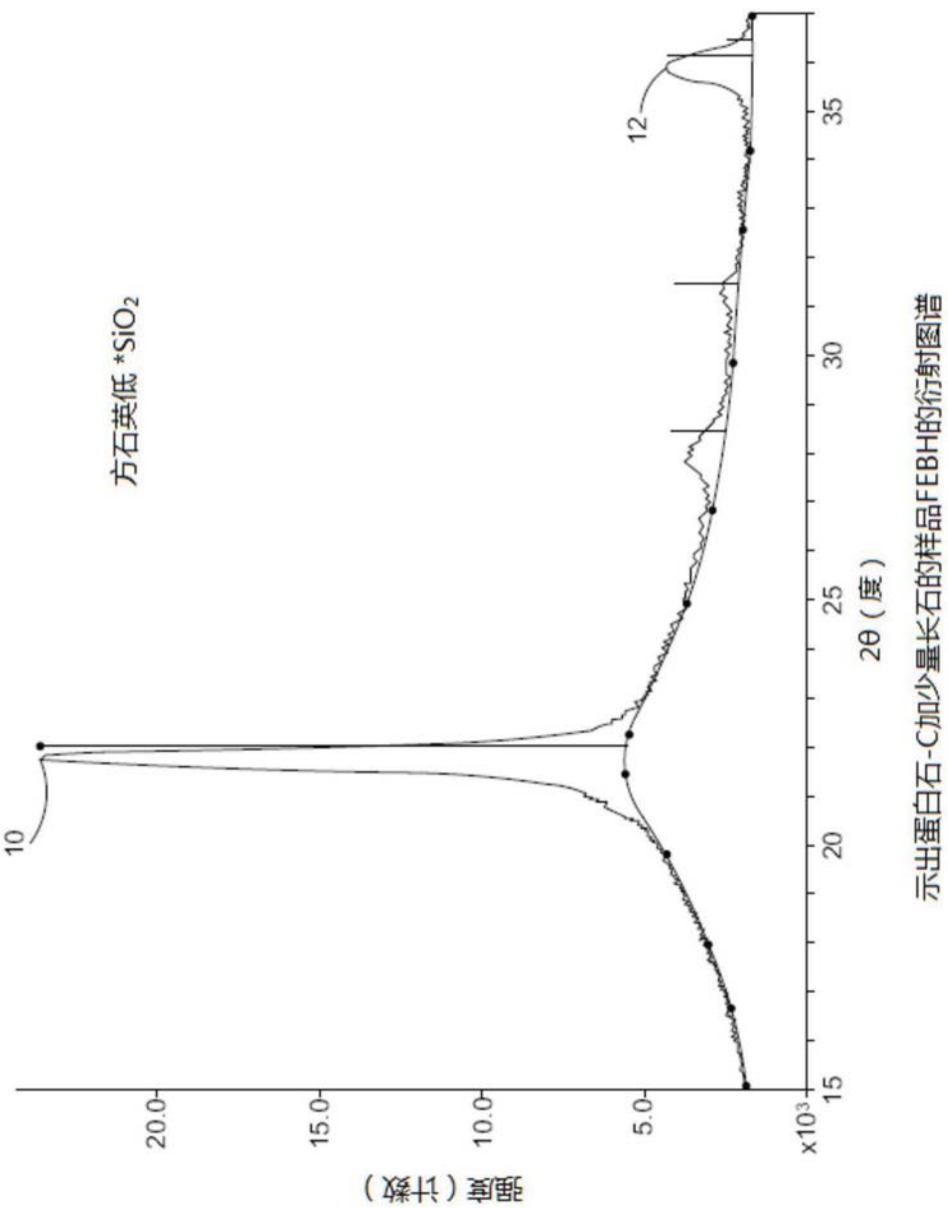

方石英低 *SiO$_2$
10
12
强度（计数）
20.0
15.0
10.0
5.0
x10^3
15
20
25
30
35
2θ（度）
示出蛋白石-C加少量长石的样品FEBH的衍射图谱

图17

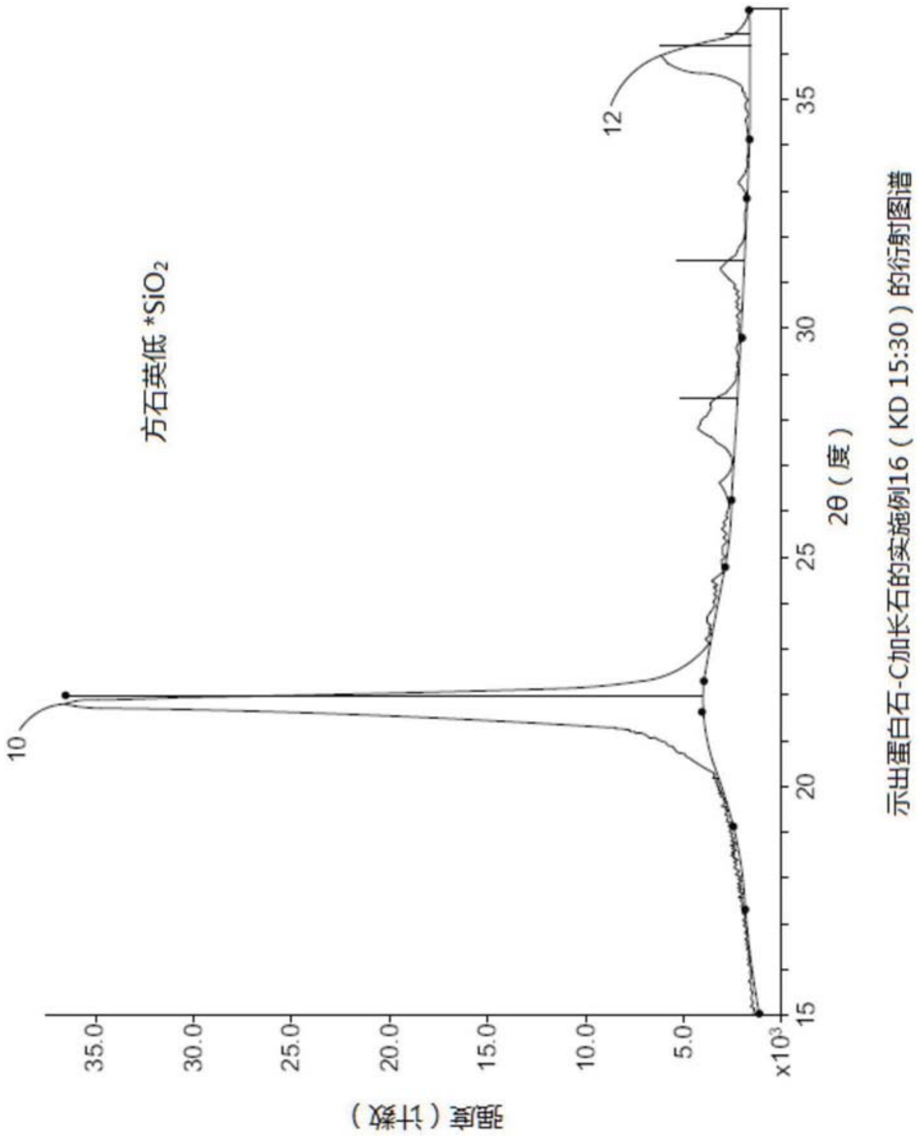
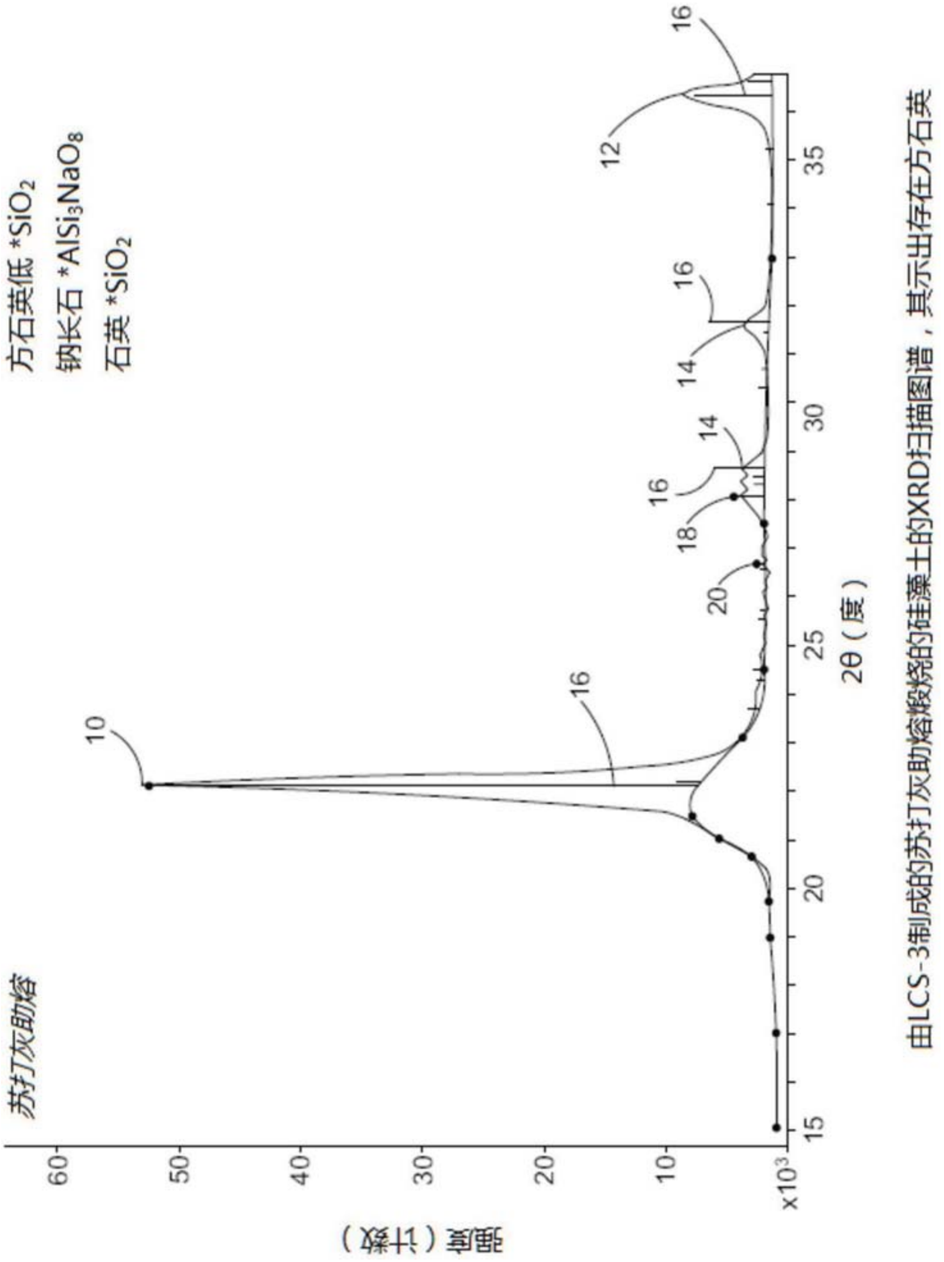
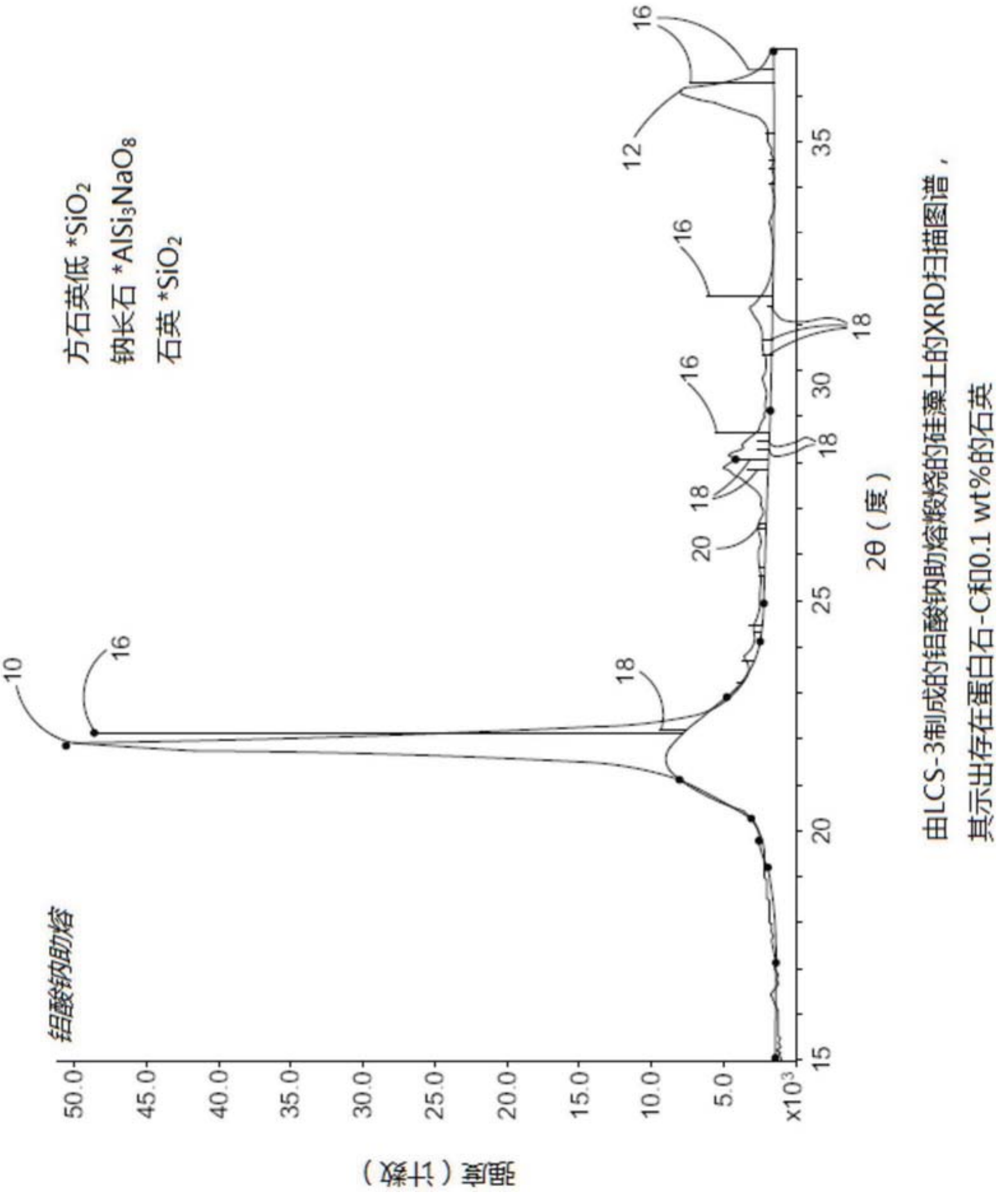

方石英低 *SiO$_2$
10
12
强度（计数）
35.0
30.0
25.0
20.0
15.0
10.0
5.0
x10^3
15
20
25
30
35
2θ（度）
示出蛋白石-C加长石的实施例16（KD 15:30）的衍射图谱

图18



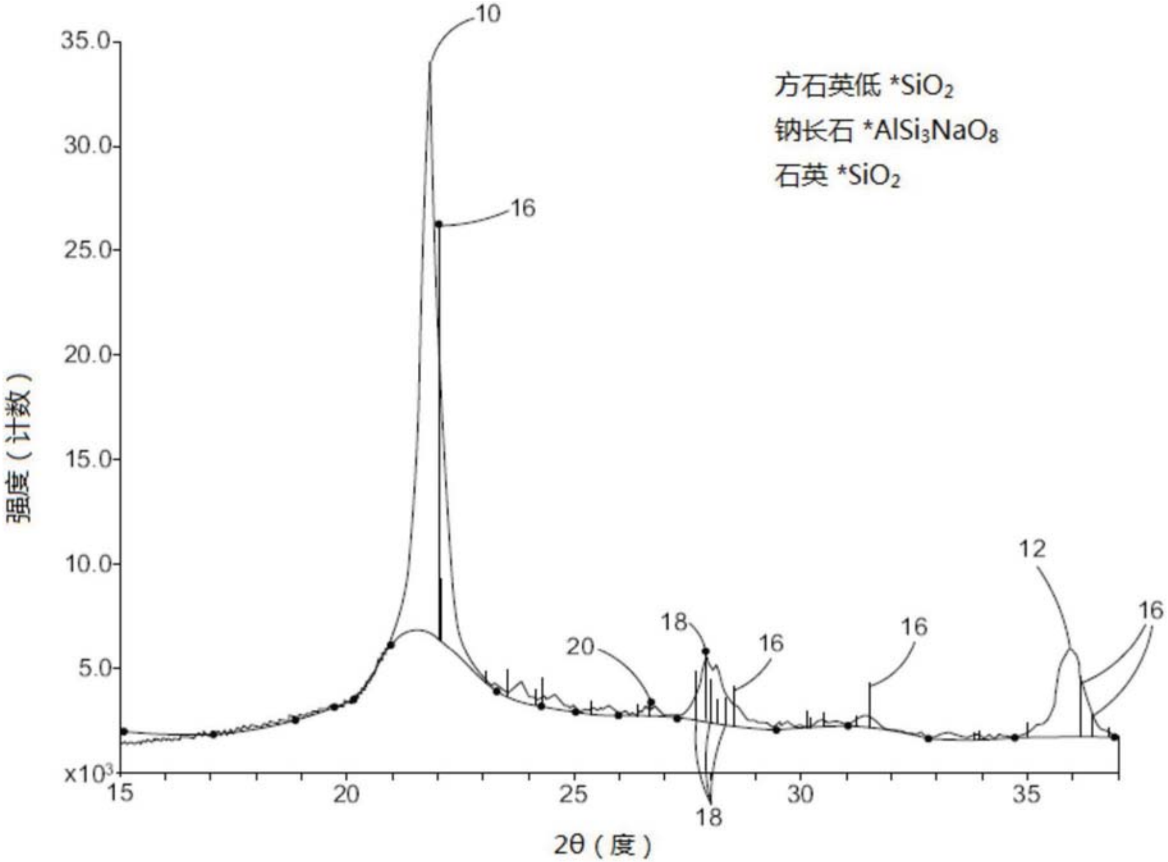
由LCS-3制成的苏打灰助熔煅烧的硅藻土的XRD扫描图谱，其示出存在方石英

图19



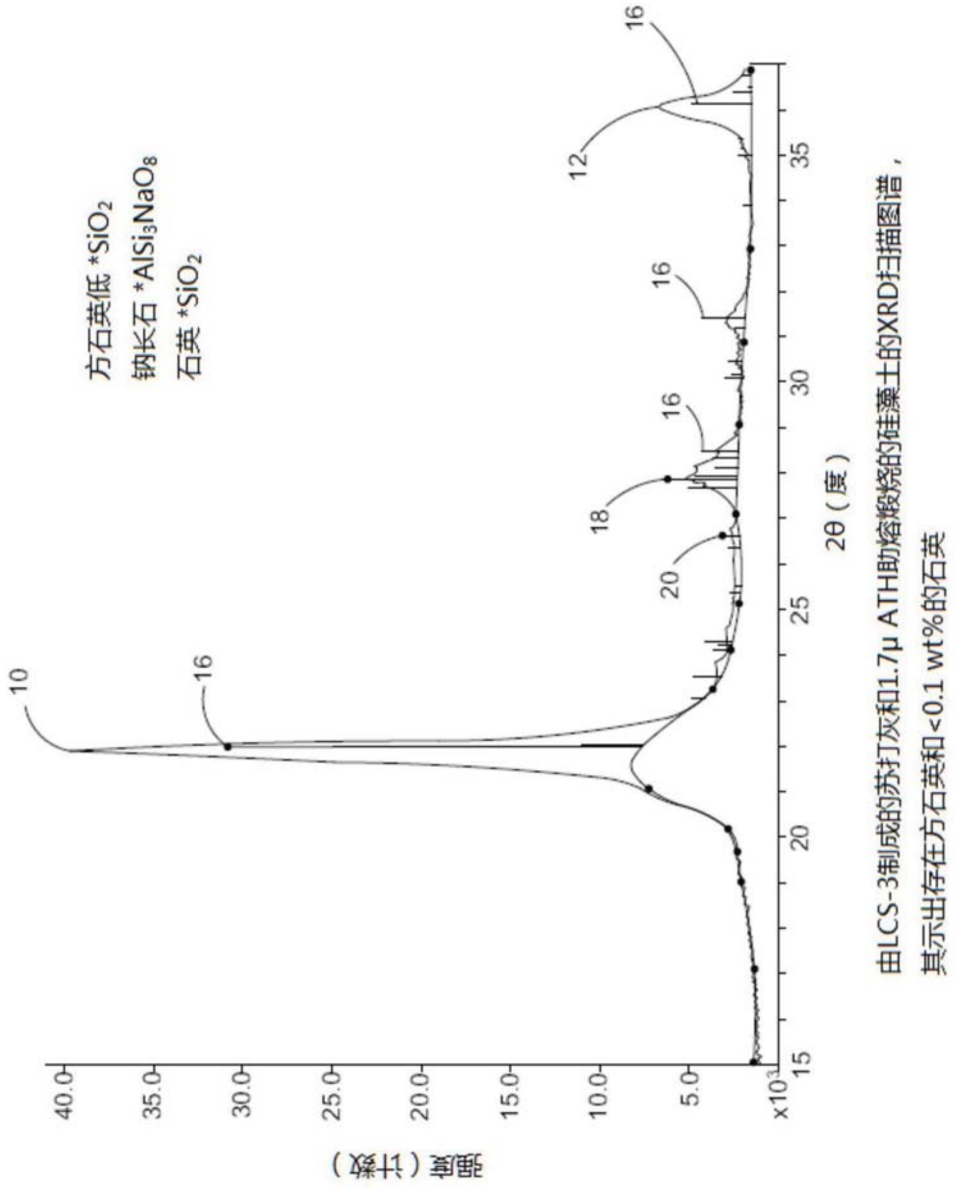
由LCS-3制成的铝酸钠助熔煅烧的硅藻土的XRD扫描图谱，其示出存在蛋白石-C和0.1 wt%的石英

图20



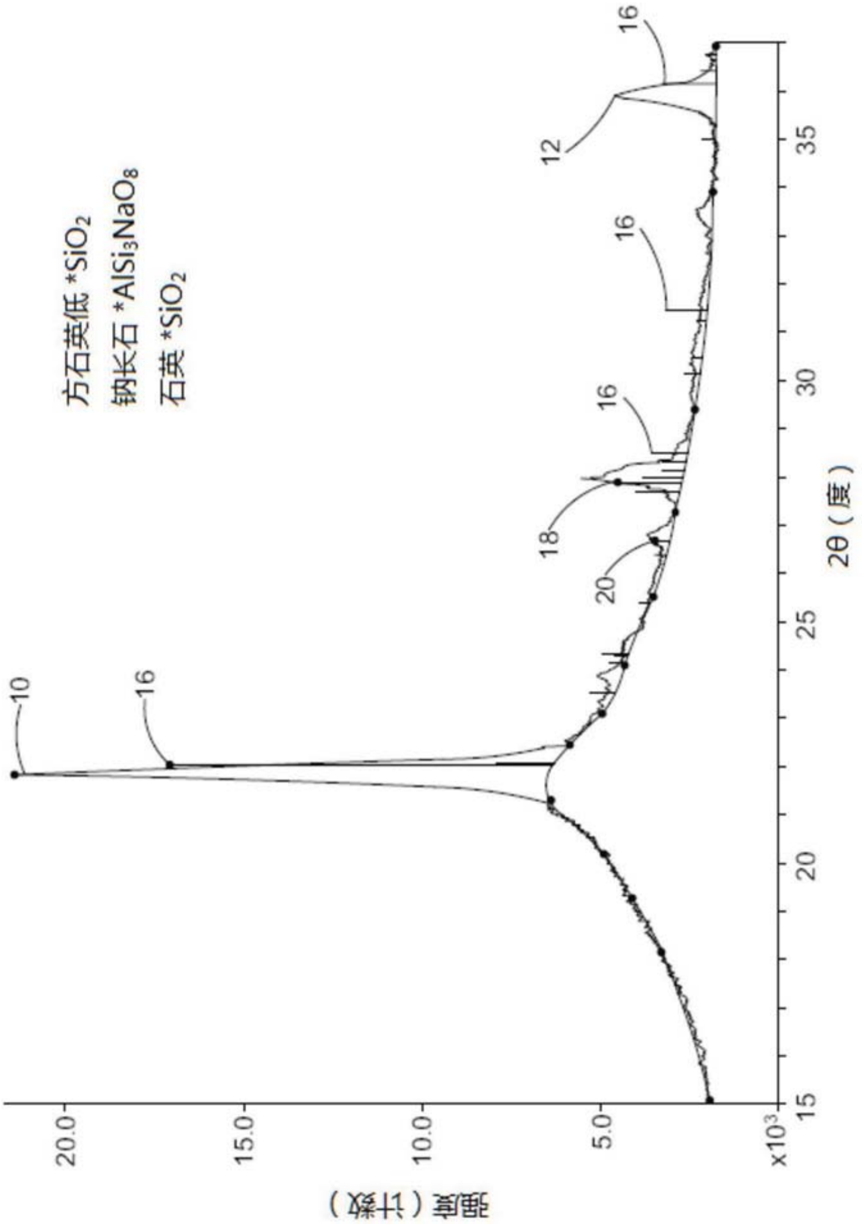
由LCS-3制成的苏打灰和0.3μ氧化铝助熔煅烧的硅藻土的XRD扫描图谱，其示出存在蛋白石-C和0.3 wt%的石英

图21



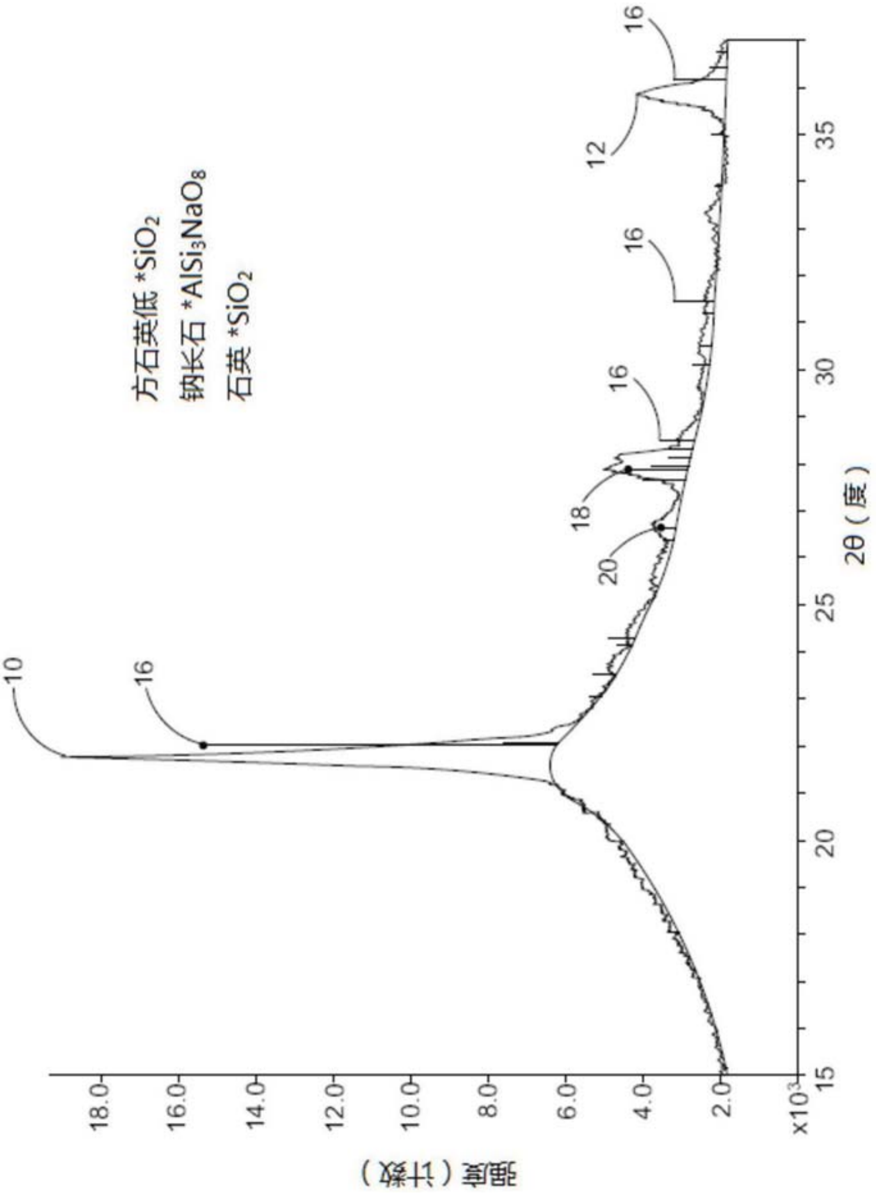
由LCS-3制成的苏打灰和1.7μ ATH助熔煅烧的硅藻土的XRD扫描图谱，其示出存在方石英和<0.1 wt%的石英

图22



由LCS-3制成的助熔煅烧的硅藻土的XRD扫描图谱，其示出存在蛋白石-C和0.2 wt%的石英

图23



由LCS-3加入ATH添加剂制成的助熔煅烧的硅藻土的XRD扫描图谱，其示出存在蛋白石-C和0.25 wt%的石英

图24

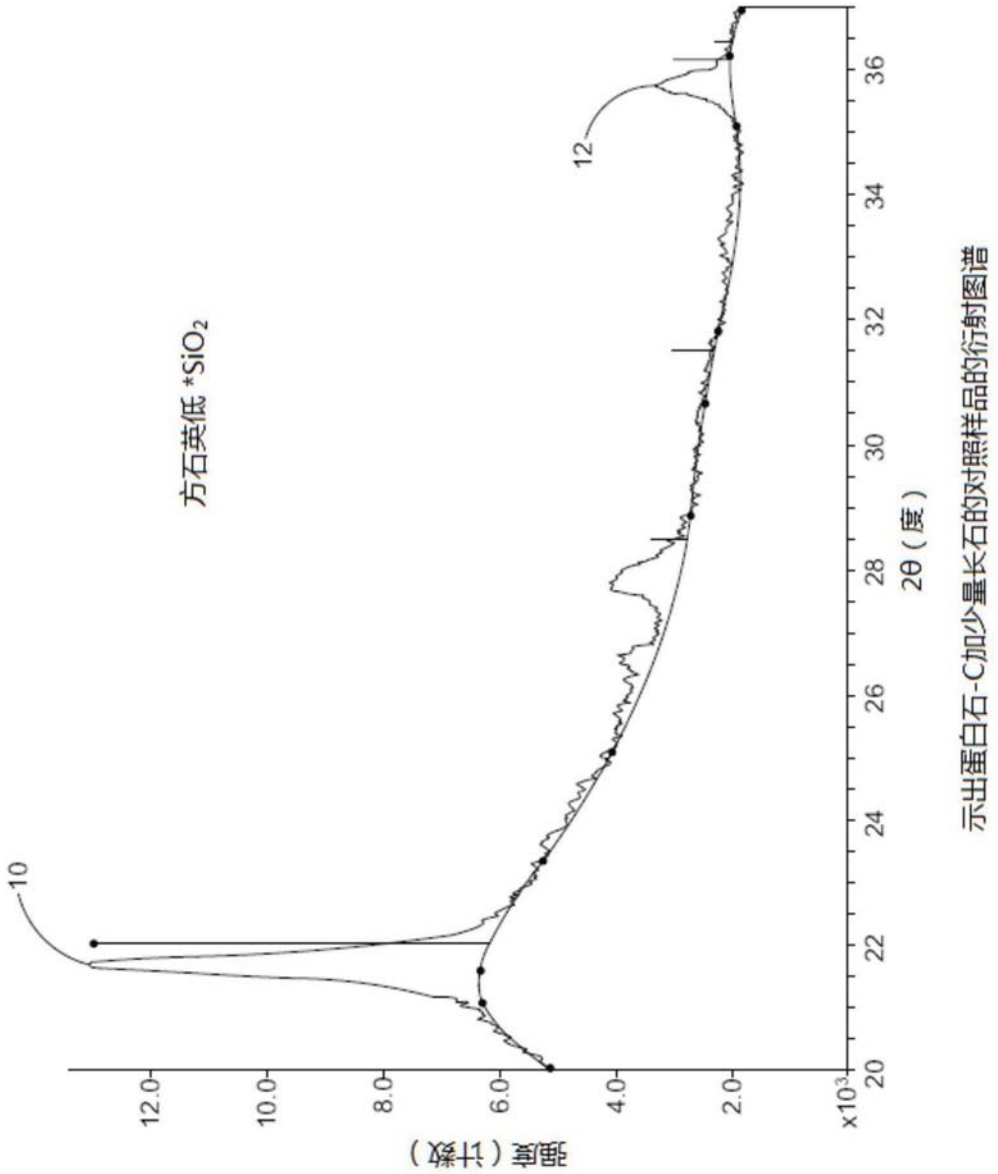

方石英低 *SiO_2
10
12
12.0
10.0
8.0
6.0
4.0
2.0
x10^3
强度（计数）
20
22
24
26
28
30
32
34
36
2θ（度）
示出蛋白石-C加少量长石的对照样品的衍射图谱

图25

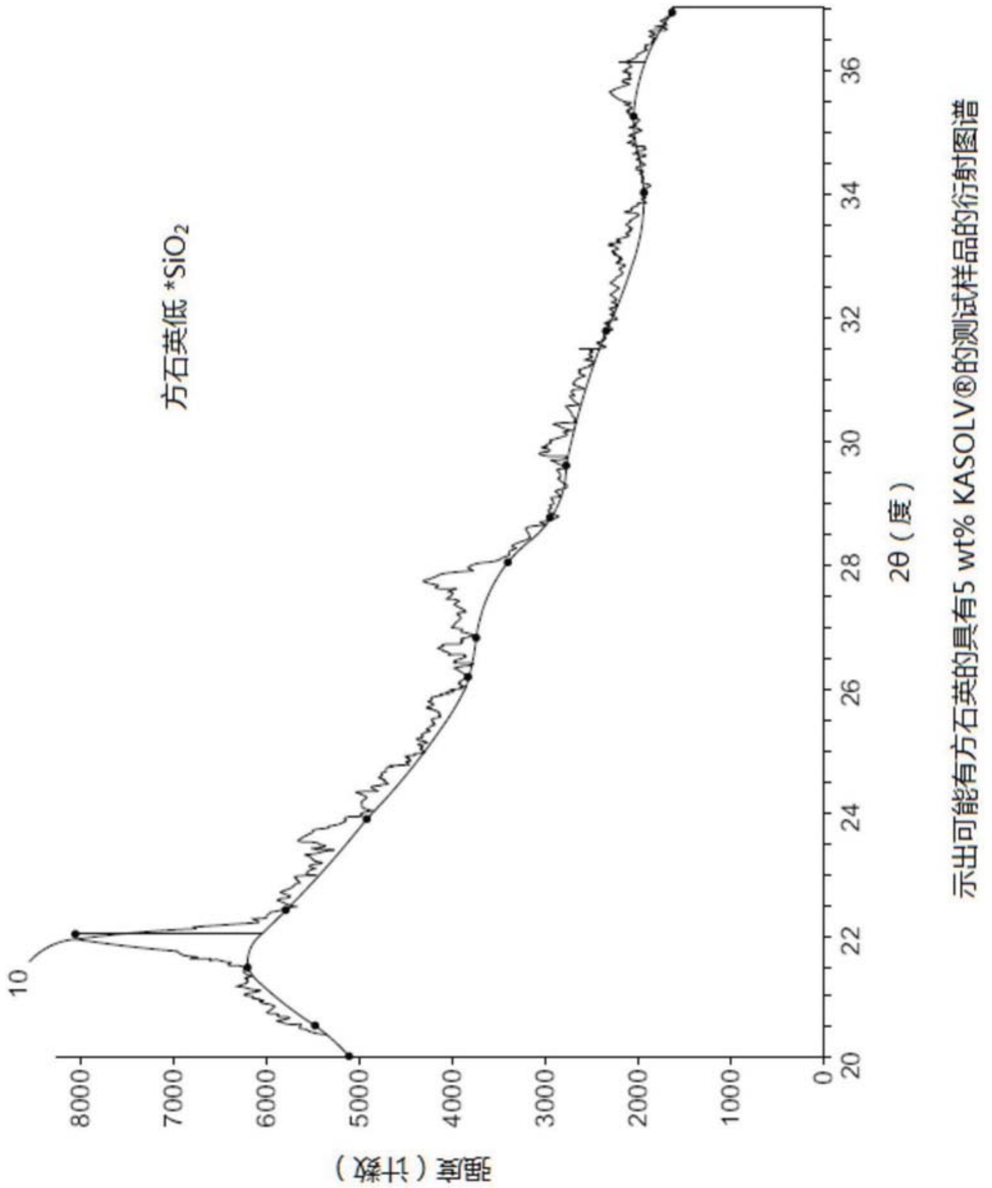
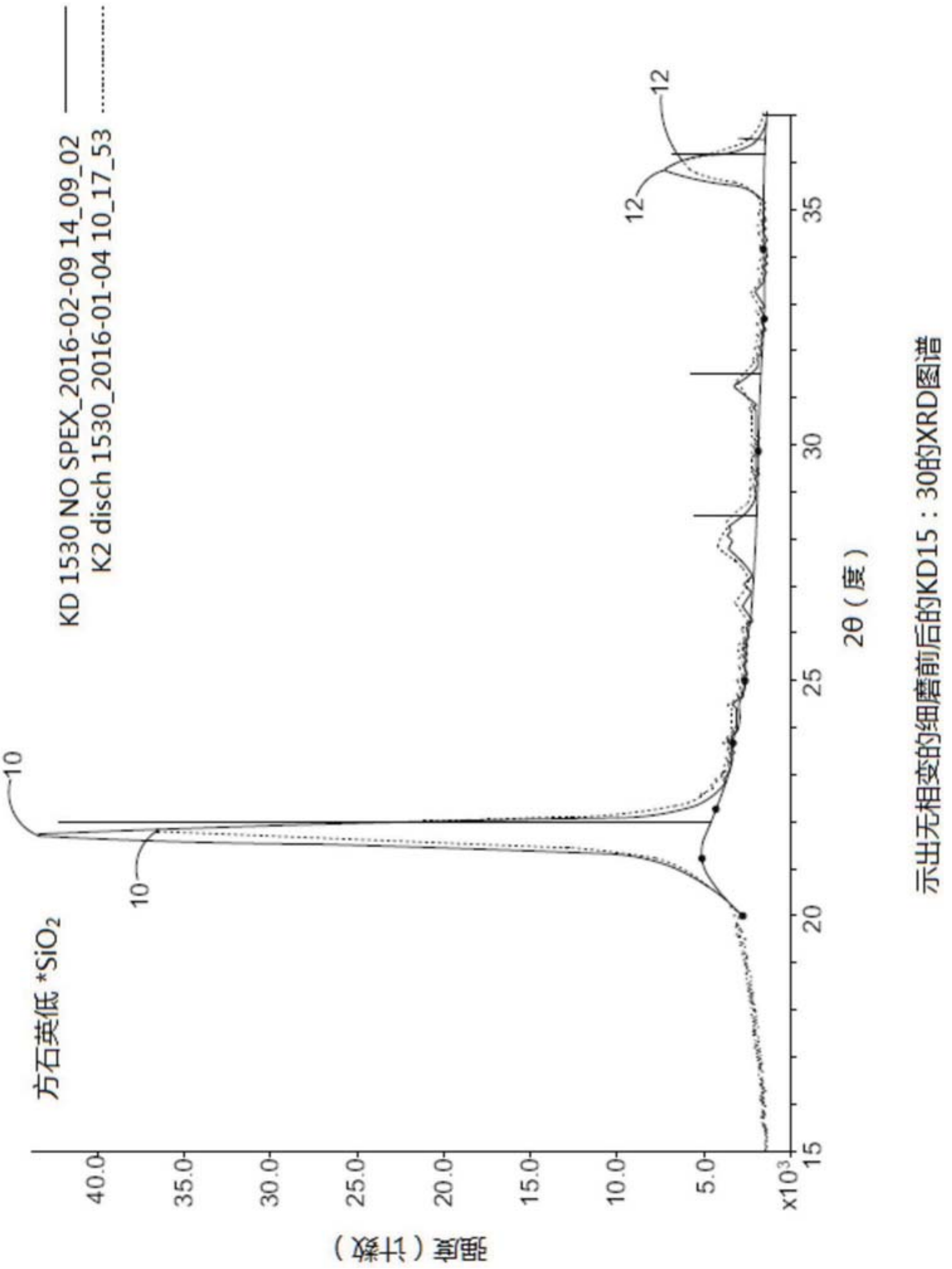

方石英低 *SiO₂
10
强度（计数）
8000
7000
6000
5000
4000
3000
2000
1000
0
20
22
24
26
28
30
32
34
36
2θ（度）
示出可能有方石英的具有5 wt% KASOLV®的测试样品的衍射图谱

图26



示出无相变的细磨前后的KD15：30的XRD图谱

图27

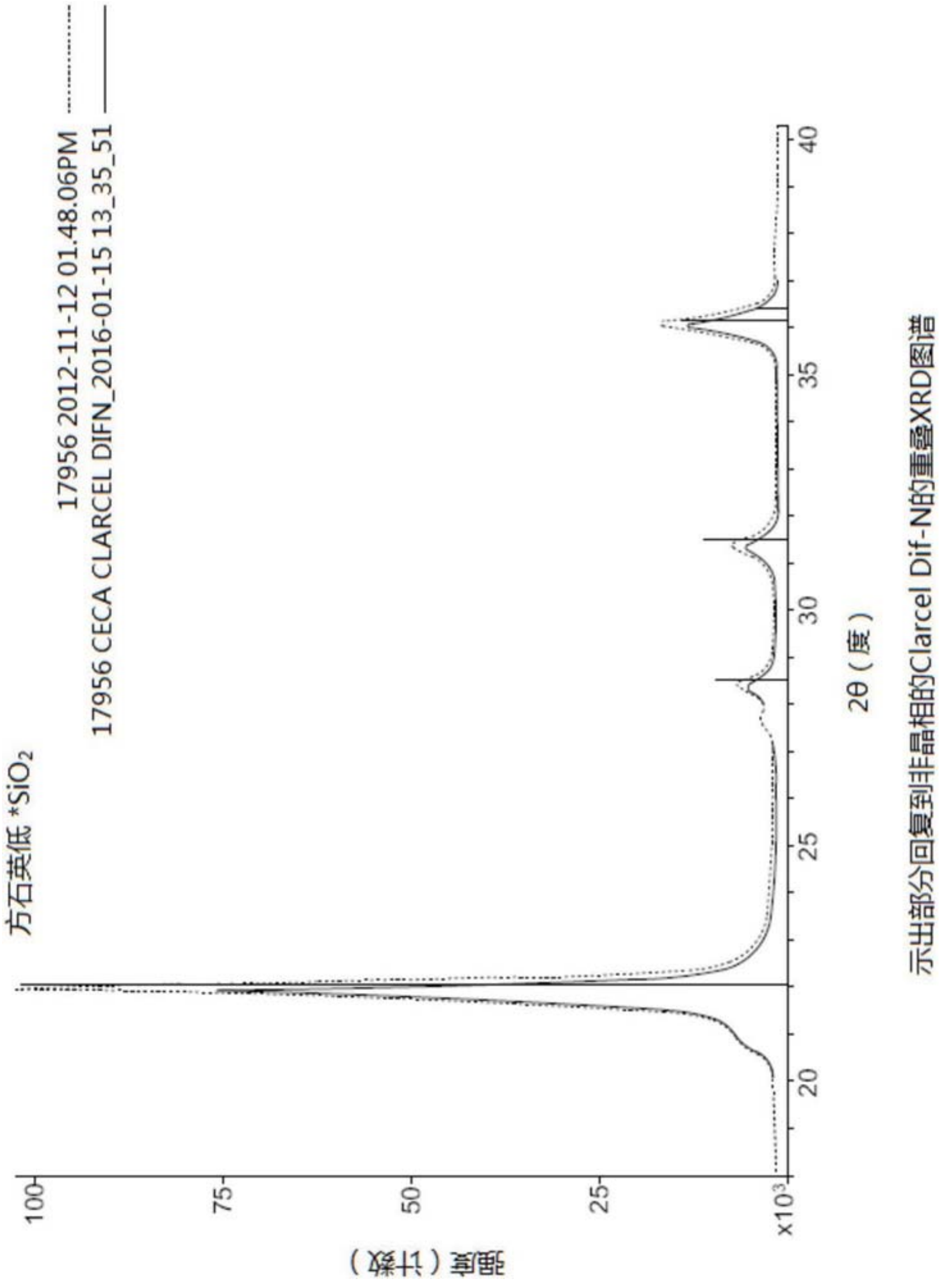
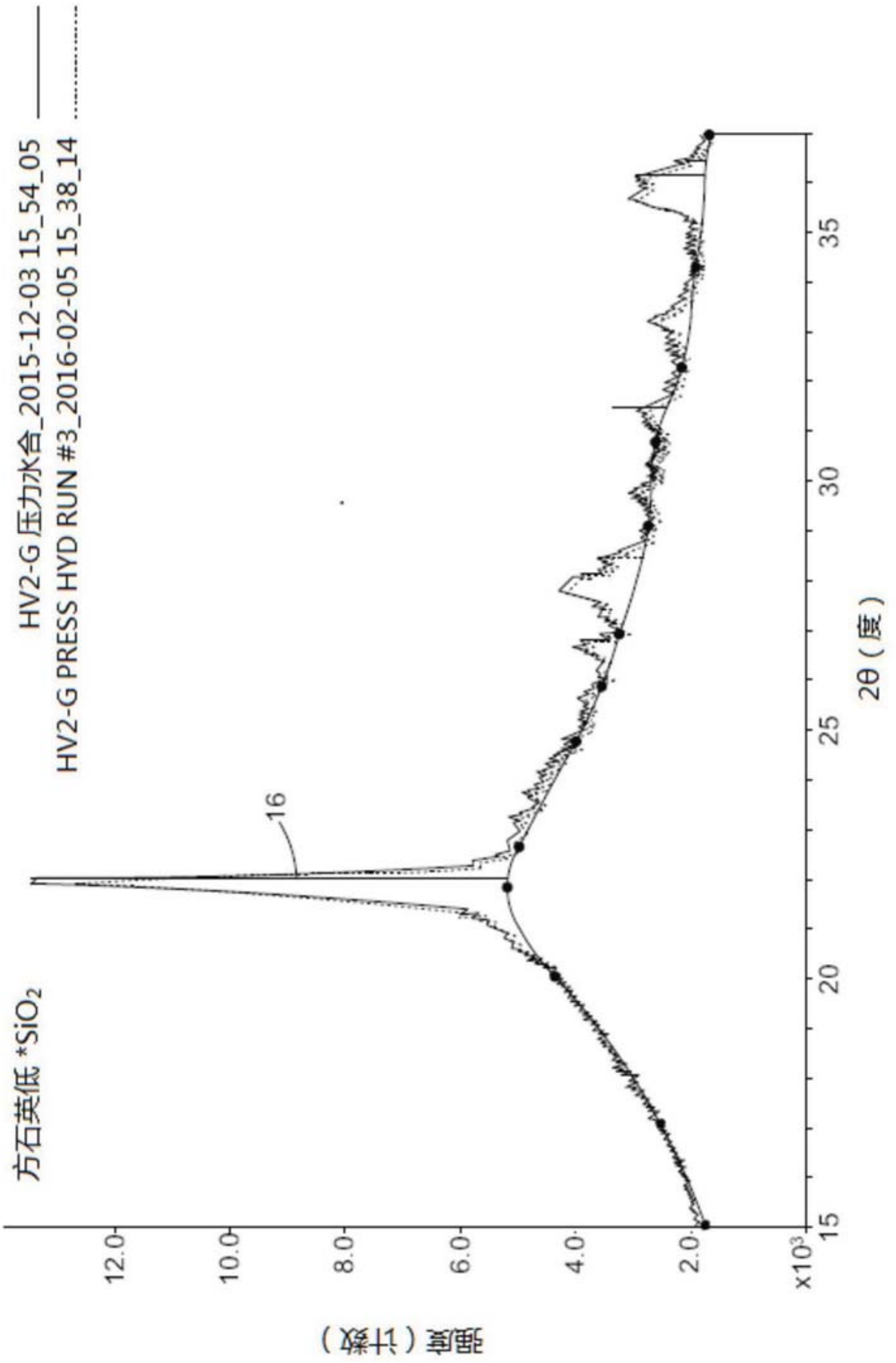

17956 2012-11-12 01.48.06PM
17956 CECA CLARCEL DIFN_2016-01-15 13_35_51
方石英低 *SiO₂
强度（计数）
100
75
50
25
x10³
20
25
30
35
40
2θ（度）
示出部分回复到非晶相的Clarcel Dif-N的重叠XRD图谱

图28



示出蛋白石-C部分回复到非晶相的HV2-G的重叠XRD图谱

图29

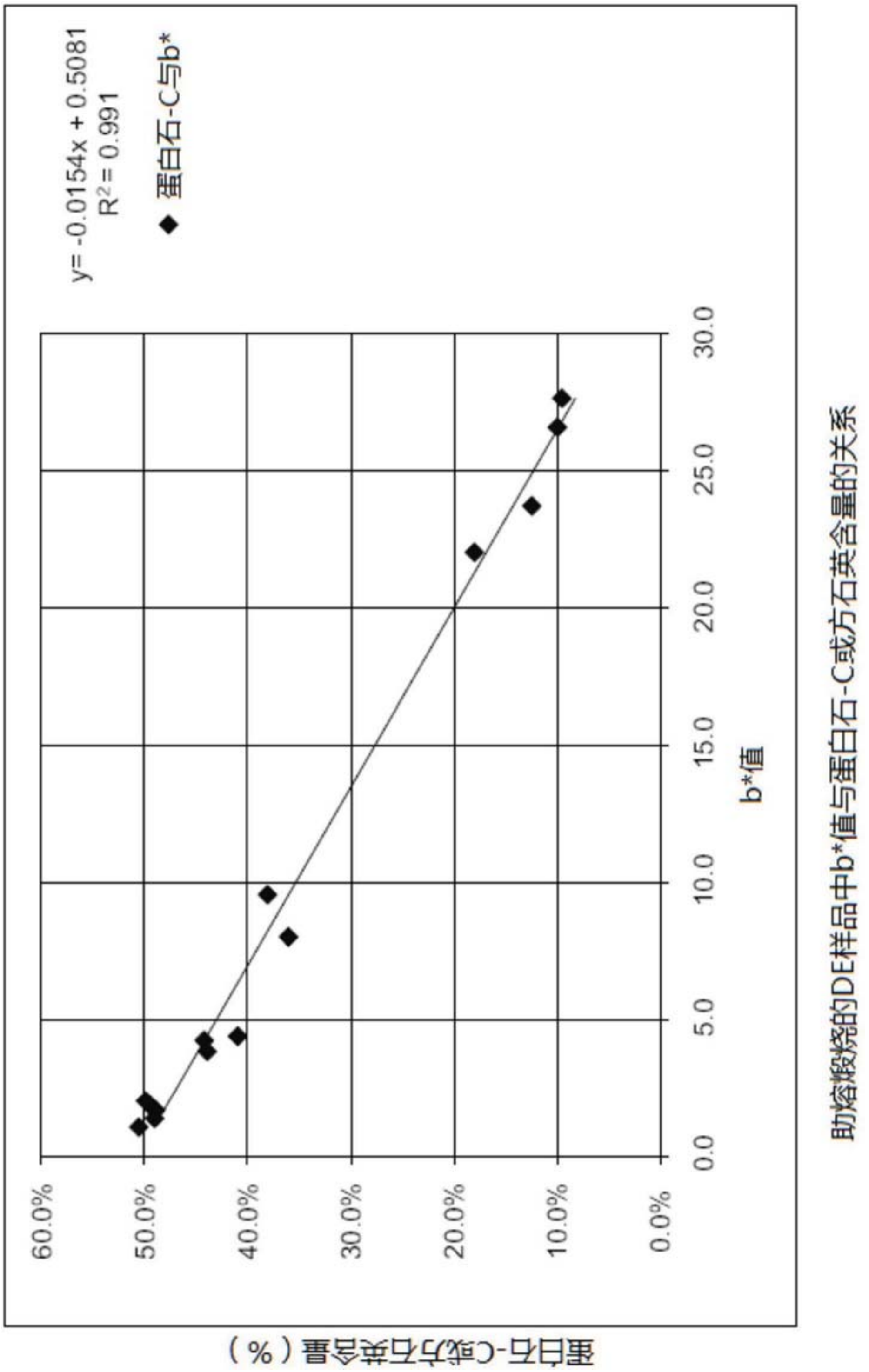
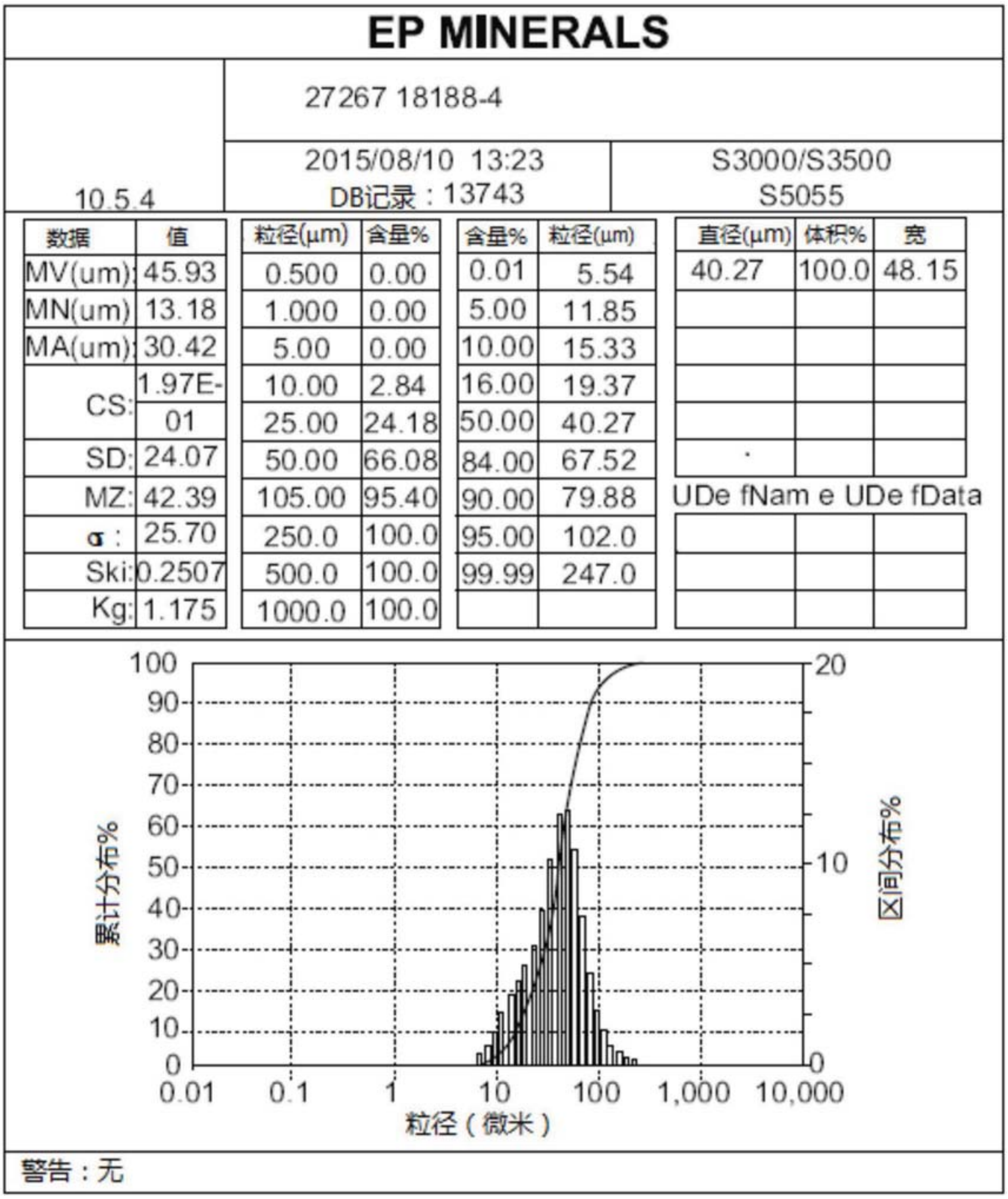

y= -0.0154x + 0.5081
R² = 0.991
◆ 蛋白石-C与b*
60.0%
50.0%
40.0%
30.0%
20.0%
10.0%
0.0%
蛋白石-C或方石英含量（%）
0.0
5.0
10.0
15.0
20.0
25.0
30.0
b*值
助熔煅烧的DE样品中b*值与蛋白石-C或方石英含量的关系

图30



EP MINERALS

27267 18188-4

10.5.4

2015/08/10 13:23
DB记录：13743

S3000/S3500
S5055

数据	值
MV(um):	45.93
MN(um)	13.18
MA(um):	30.42
CS:	1.97E- 01
SD:	24.07
MZ:	42.39
σ :	25.70
Ski:	0.2507
Kg:	1.175

粒径(μm)	含量%
0.500	0.00
1.000	0.00
5.00	0.00
10.00	2.84
25.00	24.18
50.00	66.08
105.00	95.40
250.0	100.0
500.0	100.0
1000.0	100.0

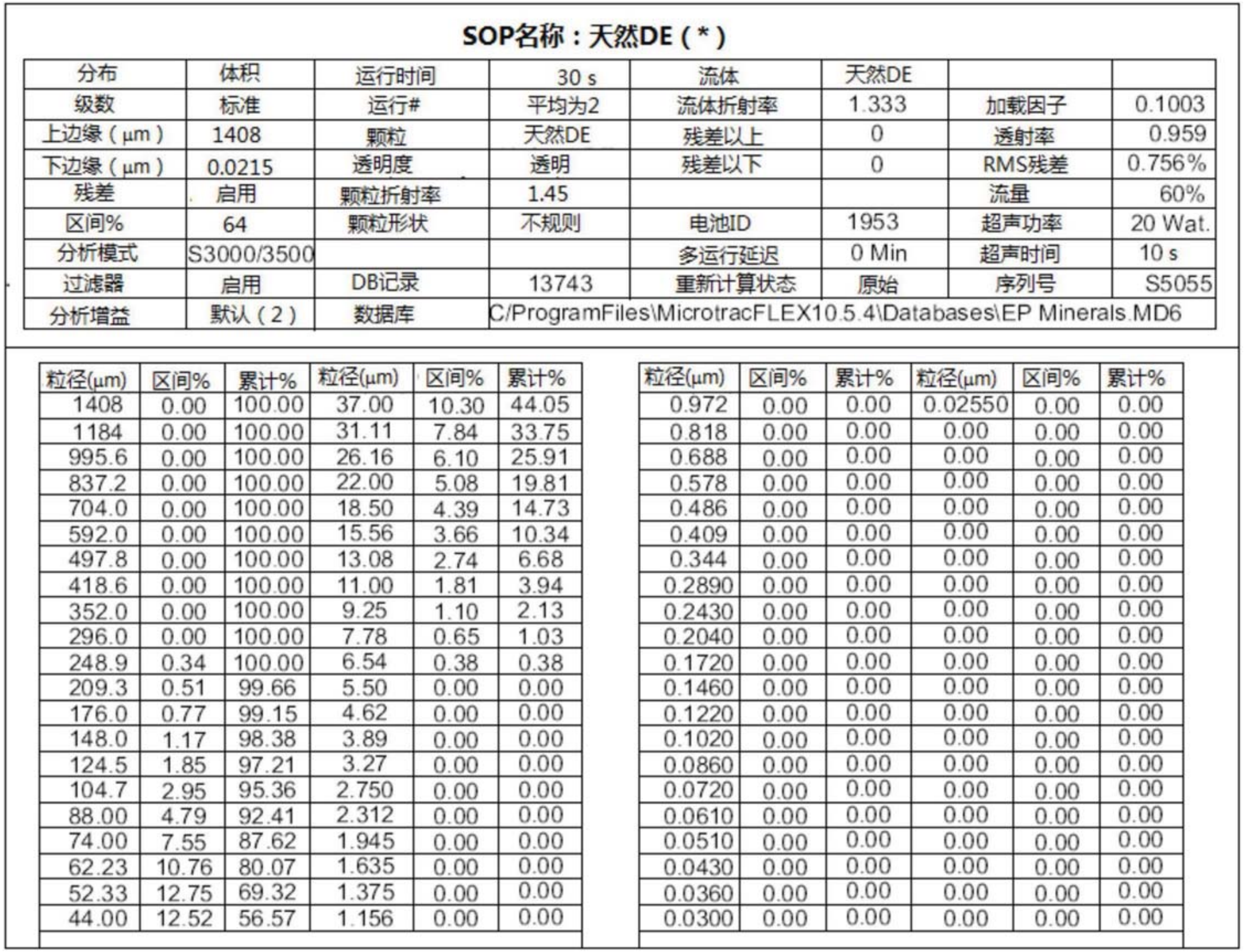
含量%	粒径(μm)
0.01	5.54
5.00	11.85
10.00	15.33
16.00	19.37
50.00	40.27
84.00	67.52
90.00	79.88
95.00	102.0
99.99	247.0

直径(μm)	体积%	宽
40.27	100.0	48.15

UDe fNam e UDe fData

警告：无

图31a



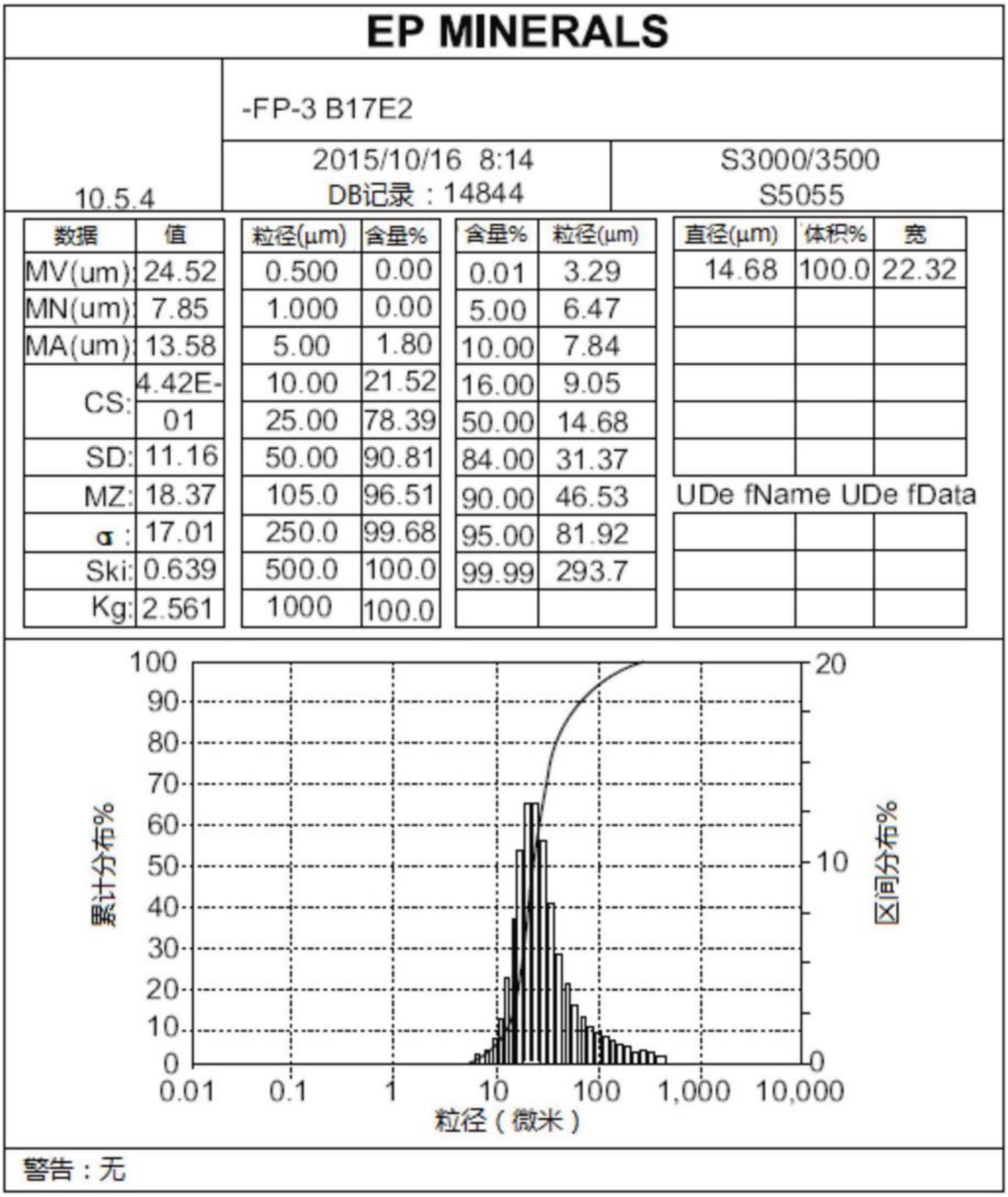
SOP名称：天然DE（*）

分布	体积	运行时间	30 s	流体	天然DE		
级数	标准	运行#	平均为2	流体折射率	1.333	加载因子	0.1003
上边缘（µm）	1408	颗粒	天然DE	残差以上	0	透射率	0.959
下边缘（µm）	0.0215	透明度	透明	残差以下	0	RMS残差	0.756%
残差	启用	颗粒折射率	1.45			流量	60%
区间%	64	颗粒形状	不规则	电池ID	1953	超声功率	20 Wat.
分析模式	S3000/3500			多运行延迟	0 Min	超声时间	10 s
过滤器	启用	DB记录	13743	重新计算状态	原始	序列号	S5055
分析增益	默认（2）	数据库	C/ProgramFiles\MicrotracFLEX10.5.4\Databases\EP Minerals.MD6				

粒径(µm)	区间%	累计%	粒径(µm)	区间%	累计%
1408	0.00	100.00	37.00	10.30	44.05
1184	0.00	100.00	31.11	7.84	33.75
995.6	0.00	100.00	26.16	6.10	25.91
837.2	0.00	100.00	22.00	5.08	19.81
704.0	0.00	100.00	18.50	4.39	14.73
592.0	0.00	100.00	15.56	3.66	10.34
497.8	0.00	100.00	13.08	2.74	6.68
418.6	0.00	100.00	11.00	1.81	3.94
352.0	0.00	100.00	9.25	1.10	2.13
296.0	0.00	100.00	7.78	0.65	1.03
248.9	0.34	100.00	6.54	0.38	0.38
209.3	0.51	99.66	5.50	0.00	0.00
176.0	0.77	99.15	4.62	0.00	0.00
148.0	1.17	98.38	3.89	0.00	0.00
124.5	1.85	97.21	3.27	0.00	0.00
104.7	2.95	95.36	2.750	0.00	0.00
88.00	4.79	92.41	2.312	0.00	0.00
74.00	7.55	87.62	1.945	0.00	0.00
62.23	10.76	80.07	1.635	0.00	0.00
52.33	12.75	69.32	1.375	0.00	0.00
44.00	12.52	56.57	1.156	0.00	0.00

粒径(µm)	区间%	累计%	粒径(µm)	区间%	累计%
0.972	0.00	0.00	0.02550	0.00	0.00
0.818	0.00	0.00	0.00	0.00	0.00
0.688	0.00	0.00	0.00	0.00	0.00
0.578	0.00	0.00	0.00	0.00	0.00
0.486	0.00	0.00	0.00	0.00	0.00
0.409	0.00	0.00	0.00	0.00	0.00
0.344	0.00	0.00	0.00	0.00	0.00
0.2890	0.00	0.00	0.00	0.00	0.00
0.2430	0.00	0.00	0.00	0.00	0.00
0.2040	0.00	0.00	0.00	0.00	0.00
0.1720	0.00	0.00	0.00	0.00	0.00
0.1460	0.00	0.00	0.00	0.00	0.00
0.1220	0.00	0.00	0.00	0.00	0.00
0.1020	0.00	0.00	0.00	0.00	0.00
0.0860	0.00	0.00	0.00	0.00	0.00
0.0720	0.00	0.00	0.00	0.00	0.00
0.0610	0.00	0.00	0.00	0.00	0.00
0.0510	0.00	0.00	0.00	0.00	0.00
0.0430	0.00	0.00	0.00	0.00	0.00
0.0360	0.00	0.00	0.00	0.00	0.00
0.0300	0.00	0.00	0.00	0.00	0.00

图31b



EP MINERALS

10.5.4	-FP-3 B17E2	
	2015/10/16 8:14 DB记录：14844	S3000/3500 S5055

数据	值
MV(um):	24.52
MN(um):	7.85
MA(um):	13.58
CS:	4.42E- 01
SD:	11.16
MZ:	18.37
σ :	17.01
Ski:	0.639
Kg:	2.561

粒径(μm)	含量%
0.500	0.00
1.000	0.00
5.00	1.80
10.00	21.52
25.00	78.39
50.00	90.81
105.0	96.51
250.0	99.68
500.0	100.0
1000	100.0

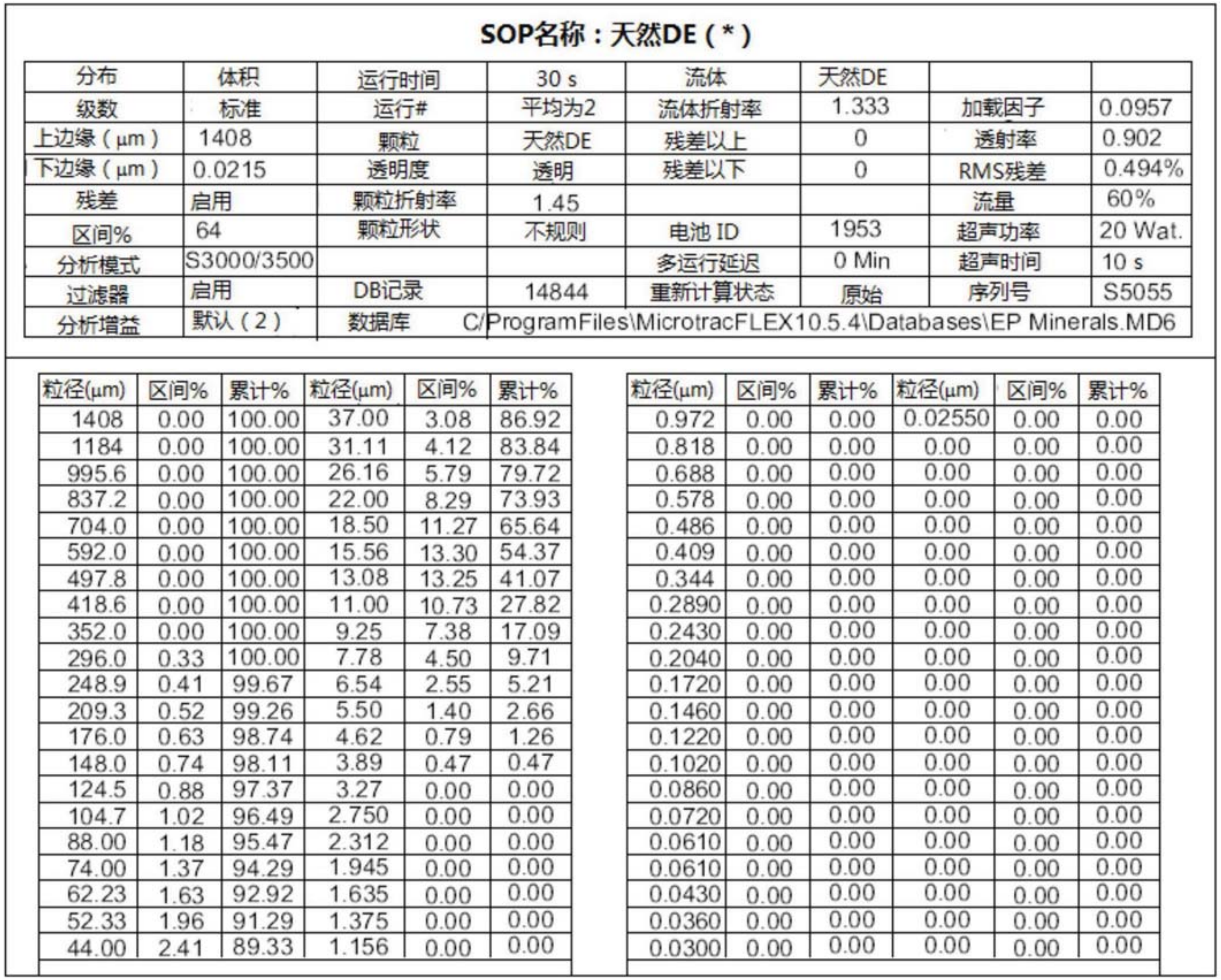
含量%	粒径(μm)
0.01	3.29
5.00	6.47
10.00	7.84
16.00	9.05
50.00	14.68
84.00	31.37
90.00	46.53
95.00	81.92
99.99	293.7

直径(μm)	体积%	宽
14.68	100.0	22.32

UDe fName UDe fData

警告：无

图32a



SOP名称：天然DE（*）

分布	体积	运行时间	30 s	流体	天然DE		
级数	标准	运行#	平均为2	流体折射率	1.333	加载因子	0.0957
上边缘（μm）	1408	颗粒	天然DE	残差以上	0	透射率	0.902
下边缘（μm）	0.0215	透明度	透明	残差以下	0	RMS残差	0.494%
残差	启用	颗粒折射率	1.45			流量	60%
区间%	64	颗粒形状	不规则	电池 ID	1953	超声功率	20 Wat.
分析模式	S3000/3500			多运行延迟	0 Min	超声时间	10 s
过滤器	启用	DB记录	14844	重新计算状态	原始	序列号	S5055
分析增益	默认（2）	数据库	C/ProgramFiles\MicrotracFLEX10.5.4\Databases\EP Minerals.MD6				

粒径(μm)	区间%	累计%	粒径(μm)	区间%	累计%
1408	0.00	100.00	37.00	3.08	86.92
1184	0.00	100.00	31.11	4.12	83.84
995.6	0.00	100.00	26.16	5.79	79.72
837.2	0.00	100.00	22.00	8.29	73.93
704.0	0.00	100.00	18.50	11.27	65.64
592.0	0.00	100.00	15.56	13.30	54.37
497.8	0.00	100.00	13.08	13.25	41.07
418.6	0.00	100.00	11.00	10.73	27.82
352.0	0.00	100.00	9.25	7.38	17.09
296.0	0.33	100.00	7.78	4.50	9.71
248.9	0.41	99.67	6.54	2.55	5.21
209.3	0.52	99.26	5.50	1.40	2.66
176.0	0.63	98.74	4.62	0.79	1.26
148.0	0.74	98.11	3.89	0.47	0.47
124.5	0.88	97.37	3.27	0.00	0.00
104.7	1.02	96.49	2.750	0.00	0.00
88.00	1.18	95.47	2.312	0.00	0.00
74.00	1.37	94.29	1.945	0.00	0.00
62.23	1.63	92.92	1.635	0.00	0.00
52.33	1.96	91.29	1.375	0.00	0.00
44.00	2.41	89.33	1.156	0.00	0.00

粒径(μm)	区间%	累计%	粒径(μm)	区间%	累计%
0.972	0.00	0.00	0.02550	0.00	0.00
0.818	0.00	0.00	0.00	0.00	0.00
0.688	0.00	0.00	0.00	0.00	0.00
0.578	0.00	0.00	0.00	0.00	0.00
0.486	0.00	0.00	0.00	0.00	0.00
0.409	0.00	0.00	0.00	0.00	0.00
0.344	0.00	0.00	0.00	0.00	0.00
0.2890	0.00	0.00	0.00	0.00	0.00
0.2430	0.00	0.00	0.00	0.00	0.00
0.2040	0.00	0.00	0.00	0.00	0.00
0.1720	0.00	0.00	0.00	0.00	0.00
0.1460	0.00	0.00	0.00	0.00	0.00
0.1220	0.00	0.00	0.00	0.00	0.00
0.1020	0.00	0.00	0.00	0.00	0.00
0.0860	0.00	0.00	0.00	0.00	0.00
0.0720	0.00	0.00	0.00	0.00	0.00
0.0610	0.00	0.00	0.00	0.00	0.00
0.0610	0.00	0.00	0.00	0.00	0.00
0.0430	0.00	0.00	0.00	0.00	0.00
0.0360	0.00	0.00	0.00	0.00	0.00
0.0300	0.00	0.00	0.00	0.00	0.00

图32b

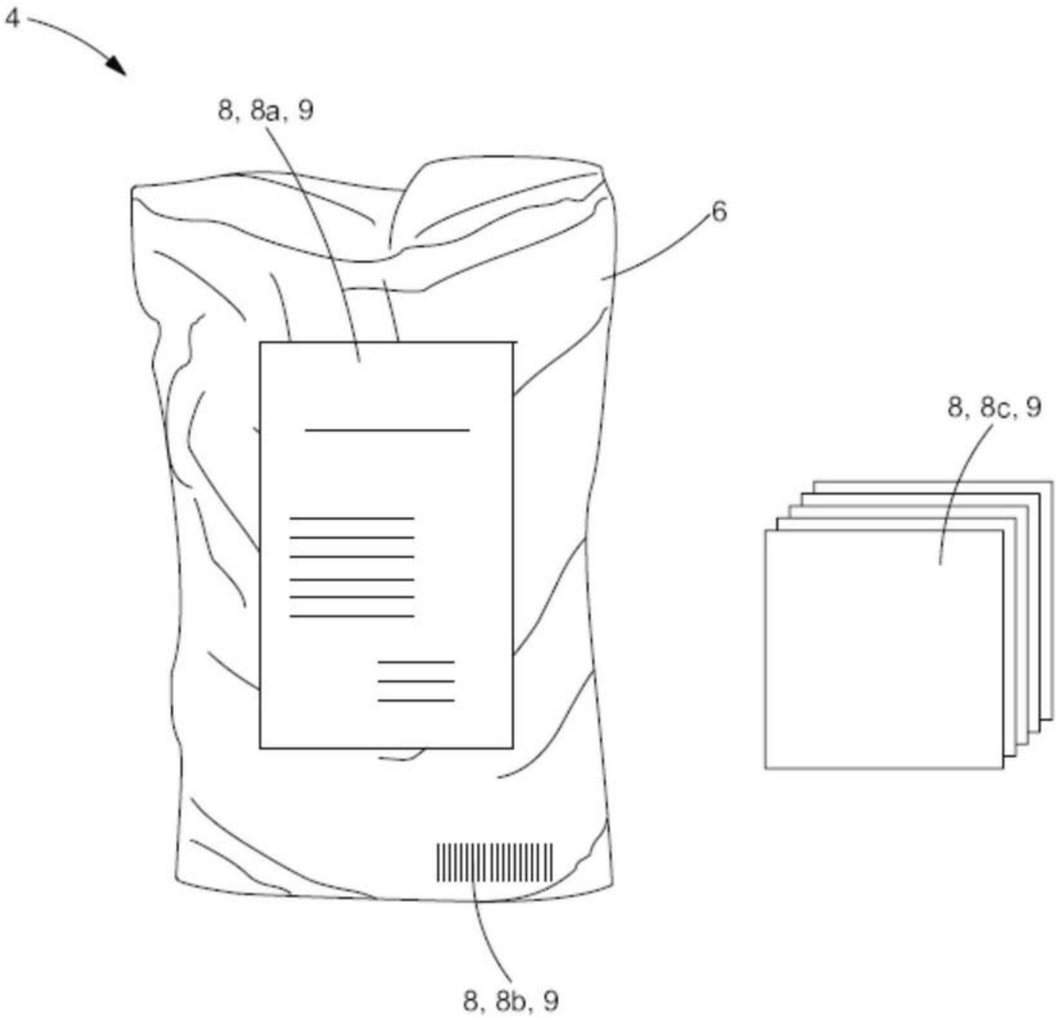


图33