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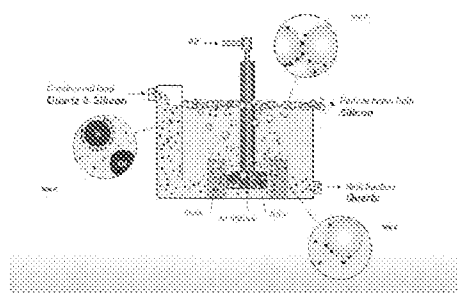
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(71)	Applicant	Norwegian University of Science and Technology (NTNU), Sem Sælandsvei 14, 7491 TRONDHEIM, Norge			
(72)	Inventor	Erik Larsen, c/o Norwegian University of Science and Technology (NTNU), Sem Sælands vei 14, 7491 TRONDHEIM, Norge Rolf Arne Kleiv, c/o Norwegian University of Science and Technology (NTNU), Sem Sælands vei 14, 7491 TRONDHEIM, Norge			
(74)	Agent or Attorney	OSLO PATENTKONTOR AS, Hoffsvæien 1A, 0275 OSLO, Norge			

(54) Title **SILICON AND SILICA PRODUCTION PROCESS**

(57) Abstract

A process for the purification of silicon metal and/or silica from a plurality of particles comprising silica and silicon metal, said process comprising: (I) fragmenting a population of particles comprising silicon metal and silica to obtain a fragmented flotation feed comprising liberated particles, preferably liberated silicon metal particles and liberated silica particles such that at least 90 wt% of the particles have a diameter of 10 to 500 μm ; (II) contacting the fragmented flotation feed with an aqueous solution comprising fluoride ions and a frother to create a suspension and introducing gas bubbles to said suspension to form a froth on top of the suspension to which liberated silicon metal particle adhere; and (III) removing the froth.



This invention relates to a new process for the separation of silica (SiO_2) and silicon metal (Si) to obtain a high purity grade silicon product and/or a high purity silica product. In particular, the invention relates to a multi-step process of primary fragmenting, sorting, secondary fragmenting and floating silicon metal particles to
5 recover highly pure silicon and/or silica.

The invention uses a flotation process in which silicon particles float and silica particles remain in the flotation cell, in combination with a discovery that fragmentation of a silica/silicon feedstock allows the formation of silica and/or silicon particles that are suitable for automatic sensor based or manual sorting and
10 ultimately for providing single phase particles as the feed for the flotation process.

Background of the Invention

Quartz (a form of silica) is an important industrial mineral with a number of uses, spanning from foundry sand, abrasives, and filter media to its use as a raw material in the production of glass and silicon carbide. Accompanying the span in uses and
15 applications, there is a corresponding span in the mineralogical and chemical purity of the respective quartz products.

The highest quality demands are put on quartz for the production of electronic grade silicon, but also quartz for solar grade silicon requires high quality concentrates consisting of pure quartz with a minimum of impurities in the crystal
20 lattice. Hence, concentrates for such uses are highly priced commodities. However, chemical processing of pure quartz is costly and energy-intensive.

Silicon is also an important industrial metalloid used in the production of ferrosilicon and aluminium alloys, fumed silica, silanes, silicones, and high purity silicon metal products used in poly- and monocrystalline solar cells and microelectronics.
25 Accompanying the span in applications, there is a corresponding span in the chemical purity of the respective silicon products. High quality demands are put on silicon used in the electronics and photovoltaic industries, and again therefore processing of these materials is costly and energy intensive. This invention seeks to provide high purity silicon and silica whilst minimising cost and energy usage.

30 Flotation is an indispensable tool in the production of high purity quartz and silicon concentrates for high purity uses. The present inventors have devised a process in which high purity silicon metal is isolated via flotation leaving a high purity silica in

the flotation cell containing a reduced silicon phase. In one process therefore, the present inventors provide two highly valuable, high purity concentrates for applications such as those discussed above. Moreover, this process can make use of solar grade silicon scrap or scrap from other high purity silicon production processes.

The flotation of silicon and silica is not however new. In Minerals Engineering 83 (2015) 13-18, Larsen reports that quartz can be floated in solutions of hydrofluoric acid (HF) simply by the aid of frothers alone. The quartz that is recovered in this process is purer than the starting material.

In Mineral Engineering 98 (2016) 49-51, flotation is the selected method for the separation of quartz and feldspar.

More recently, in Flotation of Metallurgical Grade Silicon and Silicon Metal from Slag by Selective Hydrogen Fluoride-Assisted Flotation, The Minerals, Metals & Materials Society and ASM International 2017, (pub 24/8/17), flotation experiments performed on metallurgical grade silicon have demonstrated that silicon (Si) can be floated in diluted solutions of hydrogen fluoride (HF) and a frother. There is no teaching of a process in which silica is separated from silicon using (collectorless) flotation.

JPS63205164 relates to a process for recovering quartz from an impurity-containing quartz ore, specifically an ore containing feldspar. The process involves crushing the ore to obtain a plurality of ore particles which are then added to a solution comprising HF, a capturing agent, and an alcoholic foaming agent. This suspension is then subjected to a flotation procedure in which particles containing a high concentration of impurities such as feldspar attach to the floating foam whilst particles containing a high concentration of quartz remain as sediment in the suspension.

There remains a need to devise a complete process for the preparation of high purity silicon and high purity quartz. The present inventors have now devised a process for preparing high purity silicon and highly pure silica.

30 **Summary of Invention**

Viewed from one aspect the invention provides a process for the purification of silicon metal and/or silica from a plurality of particles comprising silica and silicon metal, said process comprising:

(I) fragmenting a population of particles comprising silicon metal and silica to
5 obtain a population of particles with varying proportions of silica and silicon metal;

(II) sorting the particles obtained in step (I) into at least a first and second pre-concentrate based on the proportion of silica and the proportion of silicon metal in each particle;

(III) fragmenting the particles of the first pre-concentrate and/or second pre-concentrate to form a first and/or second fragmented pre-concentrate comprising
10 liberated particles, preferably liberated silicon metal particles and liberated silica particles, such that at least 90 wt% of the particles in the first and/or second fragmented pre-concentrate have a diameter of 10 to 500 μm ;

(IV) contacting the first and/or second fragmented pre-concentrate with an
15 aqueous solution comprising fluoride ions and a frother to create a suspension and introducing gas bubbles to said suspension to form a froth on top of the suspension to which liberated silicon metal particles adhere;

(V) removing the froth.

Alternatively viewed, the invention provides a process for the purification of silicon
20 metal and/or silica from a plurality of particles comprising silica and silicon metal, said process comprising:

(I) fragmenting a population of particles comprising silicon metal and silica to obtain a fragmented flotation feed comprising liberated particles, preferably
liberated silicon metal particles and liberated silica particles such that at least 90
25 wt% of the particles have a diameter of 10 to 500 μm ;

(II) contacting the fragmented flotation feed with an aqueous solution comprising fluoride ions and a frother to create a suspension and introducing gas bubbles to said suspension to form a froth on top of the suspension to which liberated silicon metal particles adhere; and

(III) removing the froth.

In particular, the invention provides a process for the purification of silicon metal and/or silica from a plurality of particles comprising silica and silicon metal, said process comprising:

5 (I) fragmenting a population of particles comprising silicon metal and silica to obtain a population of particles with varying proportions of silica and silicon metal;

(II) fragmenting the particles of step (I) to form a fragmented flotation feed comprising liberated particles, preferably liberated silicon metal particles and liberated silica particles, such that at least 90 wt% of the particles in the
10 fragmented flotation feed have a diameter of 10 to 500 μm ;

(III) contacting the fragmented flotation feed with an aqueous solution comprising fluoride ions and a frother to create a suspension and introducing gas bubbles to said suspension to form a froth on top of the suspension to which liberated silicon metal particles adhere; and

15 (IV) removing the froth.

In another aspect the invention provides a process for the purification of silicon metal and/or silica from a plurality of particles comprising silica and silicon metal, said process comprising:

(I) fragmenting a population of particles comprising silicon metal and silica to
20 obtain a population of particles with varying proportions of silica and silicon metal;

(II) sorting the particles obtained in step (I) into at least a first and second pre-concentrate, a first pre-concentrate comprising predominantly silica and a second pre-concentrate comprising predominantly silicon metal;

(III) fragmenting the particles of the first and/or second pre-concentrate to form
25 a first and/or second fragmented pre-concentrate comprising liberated particles, preferably liberated silicon metal particles and liberated silica particles such that at least 90 wt% of the particles have a diameter of 10 to 500 μm ;

(IV) contacting the first and/or second fragmented pre-concentrate with an aqueous solution comprising fluoride ions and a frother to create a suspension and introducing gas bubbles to said suspension to form a froth on top of the suspension to which liberated silicon metal particles adhere; and

5 (V) removing the froth.

Viewed from another aspect the invention provides a process for the purification of silicon and/or silica from a plurality of particles comprising silica and silicon, said process comprising:

(I) fragmenting a population of particles comprising silicon metal and silica to
10 obtain a population of particles with varying proportions of silica and silicon metal;

(II) sorting the particles obtained in step (I) into at least a first and second pre-concentrate based on the proportion of silica and the proportion of silicon metal in each particle;

(III) fragmenting the particles of the first pre-concentrate and/or second pre-concentrate to form first and/or second fragmented pre-concentrate comprising
15 liberated particles, preferably liberated silicon metal particles and liberated silica particles, such that at least 90 wt% of the particles in the first and/or second fragmented pre-concentrate have a diameter of 10 to 500 μm ;

(IV) conditioning the first and/or second fragmented pre-concentrate in the
20 presence of an aqueous solution comprising fluoride ions and a frother to create a suspension;

(V) introducing gas bubbles into the suspension of step (IV) in order to form a froth on top of the suspension to which liberated silicon metal particles adhere whilst liberated silica particles remain in the suspension;

25 (VI) removing the froth and/or the silica from the suspension.

Alternatively viewed, the invention provides a process for the purification of silicon metal and/or silica from a plurality of particles comprising silica and silicon metal, said process comprising:

- (I) fragmenting a population of particles comprising silicon metal and silica to obtain a fragmented flotation feed comprising liberated particles, preferably liberated silicon metal particles and liberated silica particles such that at least 90 wt% of the particles have a diameter of 10 to 500 μm ;
- 5 (II) conditioning the fragmented pre-concentrate in the presence of an aqueous solution comprising fluoride ions and a frother to create a suspension;
- (III) introducing gas bubbles into the suspension of step (II) in order to form a froth on top of the suspension to which liberated silicon metal particles adhere whilst liberated silica particles remain in the suspension;
- 10 (IV) removing the froth and/or the silica from the suspension.

Viewed from another aspect the invention provides a process for the purification of silicon metal and/or silica from a plurality of particles comprising silica and silicon metal, said process comprising:

- (I) fragmenting a first population of particles comprising silicon metal and silica
15 wherein at least 50 wt% of the particles have a diameter of 50 mm or more to obtain a second population of particles with varying proportions of silica and silicon metal in which at least 50 wt% of the particles have a diameter of 1.0 to 50 mm;
- (II) sorting the particles of the second population obtained in step (I) into at least a first and second pre-concentrate based on the proportion of silica and the
20 proportion of silicon metal in each particle;
- (III) fragmenting the particles of the first and/or second pre-concentrate to form the respective first and/or second fragmented pre-concentrate comprising liberated particles, preferably liberated silicon metal particles and liberated silica particles such that at least 90 wt% of the particles have a diameter of 10 to 500 μm ;
- 25 (IV) contacting the first and/or second fragmented pre-concentrate with a aqueous solution comprising fluoride ions and a frother to create a suspension and introducing gas bubbles to said suspension to form a froth on top of the suspension to which liberated silicon metal particles adhere whilst liberated silica particles remains in the suspension;

(V) removing the froth and/or the silica particles from the suspension.

In one embodiment, both first and second pre-concentrates are subject to conditioning, flotation and recovery steps. In one embodiment, the fragmented flotation feed is subject to conditioning, flotation and recovery steps. In any process
5 defined above, the sorting step can be omitted.

In one embodiment, the process of the invention relates to a process for the purification of silicon metal said process comprising:

(I) conditioning a blend comprising liberated silicon metal particles and liberated silica particles wherein at least 90 wt% of the particles have a diameter of 10 to
10 500 μm in the presence of an aqueous solution comprising fluoride ions and a frother to form a suspension;

(II) introducing gas bubbles into the suspension of step (I) in order to form a froth on top of the suspension to which liberated silicon metal particles adhere whilst liberated silica particles remain in the suspension;

15 (III) removing the froth and/or the silica particles from the suspension.

Definitions

The term liberation is used to define the separation of one phase from another (i.e. the process of creating single phase particles). Liberated particles are ones that consist of a single phase, such as a single silicon metal phase or a single silica
20 phase. Whilst some liberated particles may be prepared in the first fragmentation step, liberated particles are primarily generated during the fragmentation of the preconcentrate particles. As the particles of the pre-concentrate are fragmented to the claimed particle size range, liberated particles are formed. More generally, whilst some liberated particles may be prepared during (the) initial fragmentation
25 step(s), liberated particles are primarily generated in the last fragmentation step prior to the flotation process.

The term pre-concentrate is used to define a population of particles that is the product of the sorting step. The term fragmented pre-concentrate defines the product of the second fragmentation step in the case where the sorting step is
30 included in the process, whereas the term fragmented flotation feed defines the

product of fragmentation in a more general case (i.e. irrespective of whether the sorting step is included or omitted).

In a preferred embodiment, the particles that are present in a fragmented preconcentrate or fragmented flotation feed comprise at least 90 wt%, such as at least 95 wt% of a single phase, e.g. at least 95 wt% silicon metal or at least 95 wt% silica.

In a more preferred embodiment, the first or second fragmented preconcentrate or fragmented flotation feed comprises at least 90 wt%, such as at least 95 wt% of liberated particles, i.e. liberated silicon metal particles and liberated silica particles combined. Ideally all particles within a fragmented preconcentrate or fragmented flotation feed are liberated.

The term 'mixed particles' is used herein to define particles containing two phases such as significant proportions of both silicon metal and silica phases, e.g. at least 5 wt% or at least 10 wt% of both silicon metal and silica phases.

Percentages herein are wt% unless otherwise stated.

The term silicon metal implies elemental silicon.

Detailed Description of Invention

The present invention concerns a process in which an impure silicon metal based feedstock can be converted to highly pure silicon metal product. The present invention also concerns a process in which an impure silica based feedstock can be converted to highly pure silica. The process enables the separation of silicon metal from silica in a cost effective manner to thereby produce (optionally simultaneously) separate products containing highly pure silica and silicon metal particles, respectively.

The feedstock for the process of the invention is typically left over solar grade material which comprises a mixture of silicon metal and silica. In a typical production process for solar grade silicon, a polysilicon feedstock is melted within a quartz crucible. A precisely oriented rod-mounted seed crystal is dipped into the molten silicon. The seed crystal's rod is slowly pulled upwards and rotated simultaneously. By precisely controlling the temperature gradients, rate of pulling

and speed of rotation, it is possible to extract a large, single-crystal, cylindrical ingot from the melt. This is the well-known Czochralski process. The scrap from this process is a valuable resource that this invention targets.

Other processes for the preparation of silicon metal, such as processes for the
 5 preparation of polycrystalline silicon, also have scrap. It is the left over silicon from these processes that forms an ideal feedstock for the present invention.

The feedstock will comprise particles comprising a mixture of silicon metal and silica in which the silica and silicon form two distinct solid phases within the particles.

The silicon metal in the feedstock may be polycrystalline or monocrystalline.
 10 Polycrystalline feedstocks derive from a process in which the silicon material has been cast whereas monocrystalline feedstocks often derive from drawing of the solar grade material from the crucible in which it is prepared. It will be appreciated that the feedstock used in this invention contains silicon metal and silica, e.g. from the crucible in which the silicon metal is melted during the Czochralski process.

15 Typically, the starting feedstock comprises 1 to 40 wt% of silicon metal and 99 to 60 wt% of silica, such as 5 to 20 wt% silicon metal and 80 to 95 wt% silica, as well as smaller amounts of other impurities. Impurities may include small amounts of additional phases and elements in solid solution in the silicon and silica phases. However as the starting material we use is generally recovered from a solar grade
 20 manufacturing process, impurity levels (i.e. content of components other than silicon and silica) are generally low, such as less than 2.0 wt%, especially less than 1.0 wt%, e.g. 0.1 to 1.0 wt%. In any feedstock, the silicon metal and silica occur as distinct separate phases within the feedstock particles.

Typically, the starting feedstock particles of the invention have a diameter of up to
 25 250 mm, such as up to 150 mm. The feedstock particles are typically at least 50 mm in diameter. If the feedstock particles are irregular in shape then their diameter is regarded as their longest cross-section. However, the size distribution of the feedstock is of limited importance since the material will undergo a fragmentation process.

30 **First fragmentation step**

The first step in the process of the invention is a fragmentation step in which the starting particles are fragmented into smaller particles with varying proportions of silica and silicon metal. Particles already smaller than target size for the first fragmentation step, could be removed by screening prior to fragmentation.

5 Fragmenting may be performed by any suitable method including high voltage pulse fragmentation or mechanical fragmentation. Screening of the fragmented material should be performed in order to send back oversize material to the start of the process (e.g. > 50 mm particles). The fragmented particles suitable for sorting will preferably have a diameter of 5-50 mm. It is possible to screen off fines (e.g.
10 < 5 mm particles). The target largest particle diameter for the fragmentation step will depend on the feedstock.

In one embodiment, the fragmented particles may have a diameter of 1 to 50 mm, such as 5 to 50 mm in diameter, e.g. 5 to 25 mm.

It will be appreciated that there may be some outlying larger and smaller particles
15 after fragmentation. It is thus preferred if at least 50 wt% of the particles have a diameter of 5 to 50 mm, such as at least 70 wt%, e.g. at least 90 wt%. Ideally all particles have a diameter in the range of 5 to 50 mm. Larger or smaller particles can be removed before the sorting process begins by screening.

Fragmentation can be achieved manually, mechanically (e.g. by crushing), but it is
20 preferably achieved through pulse fragmentation, such as high voltage pulse fragmentation. It is preferred if the particles that form have a narrow particle size distribution. It is preferred if at least 90 wt% of the fragmented particles are retained on a 1.0 mm sieve but have a maximum diameter of 50 mm. It is more preferred if at least 90 wt% of the fragmented particles are retained on a 4.75 mm
25 sieve (US sieve 4) but have a maximum diameter of 50 mm. Preferably at least 95 wt% of the particles meet these requirements, such as 100 wt% of the particles.

The fragmentation process results in a population of smaller particles in which there is a greater variation in the composition of the individual particles, i.e. some particles will contain a higher proportion of silicon metal whereas others will contain
30 a higher proportion of silica. Some liberated particles may also be formed. The main purpose of the first fragmentation step is to obtain smaller particles which contain a higher proportion of single phase substance. Such a fragmentation process thereby increases the purity of the products that can be obtained in the subsequent sorting

process. It is appreciated that the fragmentation process will result in a distribution of particle sizes and particle compositions. Mixed particles (i.e. particles containing significant proportions of both silicon metal and silica phases) will still be present in the fragmentation product. The resulting particle size distribution and degree of
 5 fragmentation can depend on the choice of fragmentation method.

The extent to which particles are fragmented could be obtained from a mineralogical analysis, but it is more convenient to assess the liberation degree by looking at the result from the subsequent sorting process.

Sorting

10 The majority of the particles resulting from the first fragmentation step will be enriched in either silicon metal or silica. Some of these will be liberated particles (i.e. comprising a single phase), but there will also be mixed particles which still contain both silica and silicon metal phases. The main purpose of the sorting step is to divide these particles into at least two separate products (called pre-
 15 concentrates herein) based on their composition. Whilst sorting is not essential, it is preferred if a sorting process is carried out. The sorting of particles obtained in step (I) into at least a first and second pre-concentrate is based on the proportion of silica and the proportion of silicon metal in each particle

The sorting process separates the particles into at least two products, e.g. by
 20 determining their colour (or reflectance/brightness) since the silicon metal is easily distinguishable from the silica. Hence, in one embodiment, the analysis step of the sorting process determines the relative amount (by area) of each colour (i.e. phase) in each particle. From that measurement you can determine the relative quantity of silica and silicon metal in a particle. Each particle is then categorized as
 25 either accept or reject according to a defined separation criterion.

There are several options available for sorting. One could let apparently liberated particles consisting solely of silica report to one product, whereas particles containing any silicon metal will report to the other. One could let apparently liberated particles consisting solely of silicon metal report to one product, whereas
 30 particles containing any silica will report to the other.

Alternatively and preferably, one could let particles report to the respective product based on their predominant phase/predominant chemical make-up or any defined

proportion between the two phases. For example, particles containing a maximum of 10 wt% silica could report to one pre-concentrate whereas particles containing more than 10 wt% silica could report to the other pre-concentrate and so on.

5 As rejection of a particle from the feed stream requires energy (by using pneumatic nozzles or mechanical flaps) the category in the minority is often treated as reject.

Since both products from the sorting process requires further fragmentation and separation (by flotation), the choice of separation criterion for the sorting process is not critical

10 The sorting process therefore yields at least a first and second sorted product, i.e. a first and a second pre-concentrate. Compared to the composition of the feed to the sorting process, it is preferred if the first pre-concentrate contains a higher proportion of silica, whereas the second pre-concentrate contains a higher proportion of silicon metal.

15 Given sufficient liberation in the fragmentation step, the purity of either of the two sorted pre-concentrates may be above 90%, i.e. the pre-concentrate enriched in silicon metal comprises at least 90 wt% silicon metal or the pre-concentrate enriched in silica comprises at least 90 wt% silica.

20 The sorting is preferably achieved using a sensor based sorting machine although manual sorting could also be used. In practice, most sorters will produce only two products. More products can be achieved by multiple sorting steps.

Irrespective of whether the sorting is performed manually or automatically, the silicon phase is easily distinguished from the white/greyish silica phase due to its silvery colour and metallic reflectance.

25 So the sorting process yields two separate pre-concentrates, a first pre-concentrate enriched in silica and a second pre-concentrate enriched in silicon metal. In addition to liberated particles consisting of a single phase, the fragmentation process will also produce mixed particles containing appreciable proportions of both silicon and silica. Depending on the choice of the sorting criterion, these particles can be allowed to report to one or either of the aforementioned sorting products or
30 removed as a third sorting product to be treated separately from sorting product 1 and 2.

In one embodiment, the sorting process is not used and the invention simply requires a fragmentation, such as a multistep fragmentation process that effectively leads to a fragmented flotation feed as defined herein. So in one embodiment, the sorting process is not used and the product from the first fragmentation step simply reports to the second fragmentation step.

Second fragmentation step

The pre-concentrate particles can then be fragmented further in a fine fragmentation step. Alternatively, when the sorting process is not employed, the product of the first fragmentation step can be subject to this second fragmentation to form a fragmented flotation feed.

In this fine fragmentation step, particles might be ground in a tumbling mill or high pressure grinding rolls (HPGR) could be used. Crushing or milling may be performed by any suitable method including mechanical crushing, tumble milling, roll milling, jet milling, stirred milling, pulse fragmentation etc.

The process is designed to prepare particles (called a fragmented preconcentrate or fragmented flotation feed) having a diameter of less than 500 μm . It is therefore preferred if at least 90 wt%, such as at least 95 wt% of the fine fragmented particles pass through a 500 μm sieve and are retained on a 10 μm sieve. Preferably, at least 90 wt% of the particles, such as at least 95 wt% of the particles, have a diameter in the range of 10 to 250 μm , such as 20 to 200 μm . In one embodiment, all particles have a diameter in the range of 10 to 500 μm , preferably 10 to 250 μm .

Particle size control can be effected with screening or classifying. Removal of particles having a diameter of less than 10 μm may also be performed with classifiers. Particle sizes can be determined using laser diffraction or other methods well known in the art. Both sets of particles (pre-concentrates) can be fragmented in this way although it will be appreciated that the fragmented pre-concentrates are floated separately.

The particles formed in the fine fragmentation step will be called fragmented pre-concentrates or fragmented flotation feed herein.

The fine fragmentation process results in a fragmented pre-concentrate or fragmented flotation feed suitable for use as the 'flotation feed' to the flotation cell. The fine fragmentation process results in a product with an increased proportion of liberated particles and a reduced proportion of mixed particles, e.g. no mixed
5 particles. The purpose of the second fragmentation process is to achieve as high as possible liberation whilst still retaining particles within the size range suitable for flotation.

Without wishing to be limited by theory, the fragmentation to particle size of 10 to 500 μm results in the formation of liberated silica and silicon metal particles. During
10 the second fragmentation step, the particles tend to fragment in a way that separates different phases present in larger particles. At the particle size required in the second fragmentation step, inventors have observed that liberation of single phase particles occurs.

The fine fragmentation operation produces particles that have a higher surface area to volume ratio to maximise the chance for liberated silicon metal particles to
15 adhere to the froth in the flotation step.

The silica content within the first fragmented pre-concentrate may be at least 90 wt%, especially 95 wt%. The silicon metal content within the second pre-concentrate may be at least 90 wt%, especially 95 wt%.

20 More importantly, it is preferred if the fragmented preconcentrates or fragmented flotation feed comprise a minimum of 90wt% liberated particles, such as at least 95 wt% liberated particles. It will be appreciated that both first and second pre-concentrates or fragmented flotation feed can contain both liberated silica and liberated silicon metal particles. It is envisaged that the second preconcentrate will
25 contain a higher content of liberated silicon metal particles than the first preconcentrate and the first preconcentrate will contain a higher proportion of liberated silica particles. Ideally, all the particles that are present in either fragmented preconcentrate or fragmented flotation feed are liberated particles. Ideally, both fragmented preconcentrates or fragmented flotation feed contain
30 liberated silica and liberated silicon metal particles.

The fragmented pre-concentrate particles or fragmented flotation feed produced can be washed and cleaned at this stage if desired. For example, particles can be scrubbed at high speed in water followed by a desliming operation, optionally in the

presence of a surfactant solution. This process not only cleans the particles but also removes fines (e.g. particles of less than 10 μm in diameter) from the fragmented pre-concentrates or fragmented flotation feed.

Flotation

5 The first and second fragmented pre-concentrate particulates or fragmented flotation feed preferably contain liberated silicon metal particles and liberated silica particles which have a target particle size diameter. Some mixed particles may also be present although this is not preferred. In order to separate the liberated silica particles from the liberated silicon metal particles, the fragmented pre-concentrates
10 or fragmented flotation feed are subjected to a flotation process. The point of the flotation process is not to remove the last traces of impurities from the essentially liberated particles, but to separate the liberated silicon metal particles from liberated silica particles. The flotation process is performed without the need for a collector chemical. For example the flotation process may be performed in the
15 absence of an amine, e.g. dodecylamine acetate. It will be appreciated that either the fragmented flotation feed, first group of pre-concentrate particles or the second group of pre-concentrate particles may be treated in essentially the same way in order to recover valuable product. The same principles apply to the treatment of the first or second fragmented pre-concentrate or fragmented flotation feed. It may
20 be that different conditioning and frother regimens are required to maximise purification but variation of the themes discussed herein are within the skills of the artisan.

The fragmented pre-concentrate particles or fragmented flotation feed particles are first treated with aqueous solution of fluoride ions in a conditioning step. These ions
25 may derive from HF or a fluoride salt. In either embodiment, it is possible to combine the fluoride ion source with an inorganic acid.

Ideally, the fragmented pre-concentrate particles or fragmented flotation feed particles are first treated with aqueous hydrofluoric acid (HF), or a combination of another inorganic acid (e.g. H_2SO_4 , HCl, HNO_3) and HF, or a combination of an
30 inorganic acid and a fluoride salt (e.g. NaF) in a conditioning step. This makes the silicon metal phase in the particles hydrophobic. The amount of inorganic acid and/or fluorine compound used is important as the concentration of the inorganic acid and/or fluorine compound in the conditioning step can be too high. If the concentration is too high then the silica present can also float in the subsequent

flotation step thus preventing the separation of the silicon and silica. It is an important aspect of the present invention that liberated silica particles do not float and hence they remain in the aqueous suspension, e.g. sink in the flotation cell, whilst liberated silicon metal particles float. Liberated silicon metal particles adhere
 5 to the gas bubbles during the flotation process whereas liberated silica particles do not.

When the source of fluoride ions is HF and no other acid is used, it is preferred that the HF concentration (as kg of HF per tonne of solids in the flotation feed) is less than 50 kg/1000 kg solids in the flotation feed in the conditioning step. A preferred
 10 concentration of HF is 2 to 20 kg HF per 1000 kg, such as 5 to 15 kg HF per 1000 kg. Higher concentrations of HF than 50 kg/1000 kg appear to cause the quartz to float in the flotation process.

It is possible to combine HF with a further inorganic acid or use HF on its own. However, if the source of fluoride ions is a fluoride salt, it is preferred if an
 15 inorganic acid is present in order to obtain an acidic solution. Preferred inorganic acids are H₂SO₄, HCl, and HNO₃.

Preferred sources of fluoride ions include alkali and alkaline earth metal fluoride salts such as NaF.

If an inorganic acid is used, such as H₂SO₄, the acid concentration (as kg of acid
 20 per tonne of solids in the flotation feed) is preferably less than 100 kg/1000 kg solids in the flotation feed in the conditioning step. A preferred concentration of acid is 0 to 75 kg acid per 1000 kg, such as 0 to 50 kg acid per 1000 kg.

Preferably the fluoride salt concentration (as kg of salt per tonne of solids in the flotation feed) is less than 50 kg/1000 kg solids in the flotation feed in the
 25 conditioning step. A preferred concentration of salt is 0.1 to 40 kg salt per 1000 kg, such as 0.2 to 30 kg salt per 1000 kg.

Higher concentrations of acid than 100 kg/1000 kg in addition to higher concentrations of salt than 50 kg/1000 kg appear to cause the quartz to float in the flotation process.

30 Considering the amount of H and F ions, the preferable H ion concentration is less than 10 kg/1000 kg solids. The preferable F ion concentration is less than 10

kg/1000 kg solids, in the flotation feed. A preferred concentration of H ions is 0.5 to 7.5 kg H ions per 1000 kg, such as 0.5 to 5 kg H ions per 1000 kg. A preferred concentration of F ions is 0.5 to 7.5 kg F ions per 1000 kg, such as 0.5 to 5 kg F ions per 1000 kg.

- 5 The amount of particles present may be measured in solids content. Typically, the conditioning process uses a solids content of 5 to 70 wt%, i.e. there are around 5 to 70 wt% of particles in the conditioning process and 95 to 30 wt% of water, fluoride ions, optional acid and frother.

The conditioning step may last for up to 120 mins, such as 5 to 60 mins, especially
10 10 to 30 minutes. A longer conditioning step might be required if the concentration of fluoride ions is lower whereas higher concentrations of fluoride ions might allow a shorter conditioning step. The condition step is designed to introduce hydrophobic character to the silicon phase present in the pre-concentrate particles.

The invention also requires the use of a frother. The frother is a compound that
15 enables the formation of bubbles within the flotation process to which silicon can adhere. Frothers can therefore be considered surfactant like compounds. In a preferred embodiment, the frother is an oligomeric or polymeric alcohol or ether such as an oligomeric or polymeric polyol or polyether. Preferred frothers are based on polyoxyalkylene compounds such as polyoxyethylene ethers or oligomeric or
20 polymeric glycols such as polypropylene glycol ether.

These compounds are available commercially from various suppliers. The molar mass of the frother is preferably in the range of 100 to 2000 g/mol, such as 200 to 1500 g/mol. The frother is preferably soluble in the fluoride ion solution at room temperature, i.e. it should have a solubility of at least 20 g/L. A preferred frother is
25 a polyoxyalkylene cetyl ether.

It is preferred to condition the particles with the frother after conditioning with the fluoride ion solution. After therefore a conditioning step in the presence of the fluoride ions, a frother solution can be added to the fluoride ion solution containing the fragmented preconcentrate particles or fragmented flotation feed of interest.
30 Conditioning with the frother may take up to 10 minutes such as up to 5 minutes. Conditioning steps can be effected at room temperature.

The frother is typically added at levels of 10 to 2000 g/1000 kg of solids, such as 20 to 1000 g/1000 kg.

The conditioning step or steps can take place in a separate conditioning vessel or may take place in the flotation cell. As the process is preferably run continuously, it is preferred if the conditioning step takes place in a separate vessel.

After any frother conditioning step, the suspension comprising the conditioned particles, fluoride ion solution and frother are transferred to a flotation cell. Alternatively, these components may already be present in the flotation cell if conditioning was effected in such cell. The flotation cell is typically a rotor stator which contains impellers. The pH at the start of the process is typically in the range of 2.0 to 4.0. The solids content in the flotation process is typically in the range of 5 to 50 wt%, such as 20 to 30 wt%.

A gas such as air is then supplied to the cell to generate bubbles in the suspension and a froth forms on top of the suspension. This is typically achieved by blowing or sucking gas into the suspension although bubbles could be introduced by boiling the suspension. A gas could also be introduced via a chemical reaction. In a preferred embodiment the gas, e.g. air is introduced via a duct in the impeller mechanism. The frother reinforces the gas bubbles and increase the mechanical stability of the resulting froth.

Due to the hydrophobic nature of the fluoride ion treated silicon phase within the particles, this has a tendency to adhere to the gas bubbles that are generated. The liberated silicon particles therefore adhere to the bubbles which float to the top of the flotation cell and can be removed by any convenient method such as by allowing the froth to overflow the top of the cell or, more conveniently, using a scraper. In a preferred embodiment, the froth is continuously removed from the top of the cell thus providing a froth that is high in very pure silicon metal particles.

As froth is removed, it is possible to add more water, acid, fluoride ions and/or frother to maintain the concentration of components in the flotation cell.

The silicon particles in the froth can then be recovered from the froth by simple work up procedures, e.g. dewatered and dried. The silicon recovered from the froth is in the form of particles. Such particles preferably have a diameter of 10 to 250 μm , preferably 20 to 200 μm .

At the fluoride ion concentrations employed in the invention, the liberated silica particles do not adhere to the bubbles. The silica particles do not float and remain in the cell, e.g. in suspension or they may sink to the base of the cell where they can be removed.

5 The particles which adhere to the froth require a high silicon metal content in order to be sufficiently hydrophobic to adhere to the bubbles. In a preferred embodiment, the only silicon particles that float are liberated silicon particles that contain a single silicon metal phase. It is also possible however that mixed particles comprising, for example, at least 90wt% silicon, such as at least 95 wt% silicon metal also float.

10 It will be appreciated that silica present in mixed particles could float if the particle contains a sufficient proportion of the silicon phase. This can be prevented by one or more of the following: better liberation, refloating and stepwise addition of small amounts of fluoride ions.

Simultaneously therefore, the invention provides a highly pure silicon metal product
15 in the froth and a highly pure silica product remaining in the aqueous suspension. The silica particles that remain in the aqueous suspension can be recovered, dewatered and dried either continuously or as a batch process.

When the particles in the feed to the flotation process are predominantly silica, the process is essentially the same but more silica is recovered in the base product and
20 less silicon metal recovered via the froth. In both cases however, a much purer product is obtained and silica and silicon are separated.

There is generally a correlation between fluoride ion concentration and frother concentration. Higher fluoride ion concentration allows reduced frother concentration and vice versa. Longer conditioning improves the recovery of silicon
25 and might allow a less strong fluoride ion solution to be employed. The person skilled in the art can tailor the process to suit his needs by adjusting the concentration of the fluoride ion solution, the amount and nature of the frother, the conditioning times and so on.

It will be appreciated that the flotation step of the invention might be repeated in
30 order to maximise purity. It may also be possible to regrind the products and repeat the conditioning and floating process to maximise purity.

The product silicon and silica particles may be subjected to washing and scrubbing steps. Acid leaching may also be used to remove any lingering impurity.

Silica obtained by the process of the invention may have a purity of at least 99.5 % such as at least 99.8%, more preferably at least 99.95 %, especially 99.99% or
5 more.

The silicon recovered in the process of the invention may be monocrystalline or polycrystalline. Silicon obtained by the process of the invention may have a purity of at least 99.5 % such as at least 99.8%, more preferably at least 99.95 %, especially 99.99% or more.

10 Recovery of silicon or silica in this process can be high. For example 95 wt% or more of the silicon or silica in the feed stock can be recovered in the process.

The invention will now be further defined with reference to the following non limiting figure and examples.

Description of the Figures

15 **Figure 1** is a flow diagram explaining the steps of a typical, non-limiting process of the invention.

Figure 2 shows principles of the flotation separation step. In step A, during conditioning, hydrofluoric acid (HF) reacts with the silicon metal surface and renders it hydrophobic. Quartz remains hydrophilic. A frother (e.g. an alcohol),
20 shown as light dots, is also added to stabilise the air bubbles that will be introduced to the cell.

In step B, air bubbles are introduced to the mixing zone of the flotation cell. Upon collision, the hydrophobic silicon particles attach to the air bubbles whereas the hydrophilic quartz particles remain immersed in the water phase. The frother
25 adsorbs to the surface of the air bubbles and prevents them from bursting when they rise to the top of the cell.

In step C, the reinforced air bubbles carrying the silicon particles form a froth on top of the cell. The particle laden froth is skimmed off and dewatered. Some quartz particles could still be trapped in the froth (false flotation) and rinsing steps may be

required. The vast bulk of the quartz particles towards the bottom of the cell where they are removed as a slurry. This may also require further rinsing.

Example 1

5 A crucible waste material containing high purity silica and high purity silicon was treated by coarse crushing, manual sorting, milling and flotation.

After coarse crushing (first fragmentation) in a yaw crusher, the large silica and silicon particles were sorted manually in order to produce silica and silicon metal pre-concentrates. Each of the two products was then subject to fine crushing, milling and screening (second fragmentation). The particle size distribution of the
10 two milled (fragmented) pre-concentrates was approximately in the range of 30-100 µm after screening. These products were used as feeds for the flotation separation.

The silica pre-concentrate was conditioned in 10 kg/t HF for 20 min, followed by the addition of 100 g/t polyoxyethylene cetyl ether used as frother for another 1 min,
15 prior to the introduction of air. Flotation occurs until a barren froth is achieved (after approximately 2-3 min). Less than 5 wt% of the particles of the fragmented silica preconcentrate were floated. The floating particles mainly contained silicon metal. The remainder particles in the flotation cell were purified silica (purified from silicon metal).

20 The fragmented silicon metal pre-concentrate was conditioned in 10 kg/t HF for 20 min, followed by the addition of 100 g/t polyoxyethylene cetyl ether used as frother for another 1 min, prior to the introduction of air and flotation until a barren froth was achieved (after approximately 3-4 min). More than 90 wt% of the particles floated. The remainder particles in the flotation cell were mainly silica.

25 Example 2

A crucible waste material containing high purity silica and high purity silicon was treated by coarse crushing, manual sorting, milling and flotation. After coarse crushing in a yaw crusher (first fragmentation), the large silica and silicon metal particles were sorted manually in order to produce silica and silicon pre-
30 concentrates. The silicon metal preconcentrate was then subject to fine crushing,

milling and screening (second fragmentation). Two fragmented silicon metal pre-concentrates are prepared.

The particle size distributions of the fragmented silicon metal pre-concentrates were approximately in the range of 30-100 μm and 100-200 μm after screening.

- 5 The 30-100 μm silicon metal pre-concentrate was conditioned in 36 kg/t H_2SO_4 and 21 kg/t NaF for 14 min, followed by the addition of 100 g/t polyoxyethylene cetyl ether used as frother for another 1 min, prior to the introduction of air and flotation until a barren froth was achieved (after approximately 1-2 min).

- 10 After the first flotation, the addition of 100 g/t frother and subsequent flotation was repeated three times.

99.8 wt% of the particles were floated. The remainder particles in the flotation cell were mainly silica.

- 15 The 100-200 μm fragmented silicon metal pre-concentrate was conditioned in 36 kg/t H_2SO_4 and 21 kg/t NaF for 20 min, followed by the addition of 100 g/t polyoxyethylene cetyl ether used as frother for another 1 min, prior to the introduction of air and flotation until a barren froth was achieved (after approximately 1-2 min). After the first flotation, the addition of 100 g/t frother and subsequent flotation was repeated three times. 99.9 wt% were floated. The remainder particles in the flotation cell was mainly silica.

Claims

1. A process for the purification of silicon metal and/or silica from a plurality of particles comprising silica and silicon metal, said process comprising:
 - (I) fragmenting a population of particles comprising silicon metal and silica to obtain a fragmented flotation feed comprising liberated particles, preferably liberated silicon metal particles and liberated silica particles such that at least 90 wt% of the particles have a diameter of 10 to 500 μm ;
 - (II) contacting the fragmented flotation feed with an aqueous solution comprising fluoride ions and a frother to create a suspension and introducing gas bubbles to said suspension to form a froth on top of the suspension to which liberated silicon metal particle adhere; and
 - (III) removing the froth.
2. A process for the purification of silicon metal and/or silica from a plurality of particles comprising silica and silicon metal, said process comprising:
 - (I) fragmenting a population of particles comprising silicon metal and silica to obtain a population of particles with varying proportions of silica and silicon metal;
 - (II) fragmenting the particles of step (I) to form a fragmented flotation feed comprising liberated particles, preferably liberated silicon metal particles and liberated silica particles, such that at least 90 wt% of the particles in the fragmented flotation feed have a diameter of 10 to 500 μm ;
 - (III) contacting the fragmented flotation feed with an aqueous solution comprising fluoride ions and a frother to create a suspension and introducing gas bubbles to said suspension to form a froth on top of the suspension to which liberated silicon metal particles adhere; and
 - (IV) removing the froth.
3. A process for the purification of silicon metal and/or silica from a plurality of particles comprising silica and silicon metal, said process comprising:
 - (I) fragmenting a population of particles comprising silicon metal and silica to obtain a population of particles with varying proportions of silica and silicon metal;

- (II) sorting the particles obtained in step (I) into at least a first and second pre-concentrate based on the proportion of silica and the proportion of silicon metal in each particle;
 - (III) fragmenting the particles of the first pre-concentrate and/or second pre-concentrate to form a first and/or second fragmented pre-concentrate comprising liberated particles, preferably liberated silicon metal particles and liberated silica particles such that at least 90 wt% of the particles in the first and/or second fragmented pre-concentrate have a diameter of 10 to 500 μm ;
 - (IV) contacting the first and/or second fragmented pre-concentrate with an aqueous solution comprising fluoride ions and a frother to create a suspension and introducing gas bubbles to said suspension to form a froth on top of the suspension to which liberated silicon metal particles adhere;
 - (V) removing the froth.
4. A process as claimed in any preceding claim wherein the particles for use in step (I) derive from solar grade scrap.
5. A process as claimed in any preceding claim wherein the fragmented particles of step (I) have a diameter of between 1.0 and 50 mm, such as 5 to 50 mm.
6. A process as claimed in any preceding claim wherein fragmentation in step (I) is effected using a pulse fragmentation.
7. A process as claimed in claim 3 to 6 in which the sorting step is effected using a sensor based sorting device.
8. A process as claimed in claim 3 to 7 wherein the sorting step (II) produces a first pre-concentrate comprising predominantly silica and a second pre-concentrate comprising predominantly silicon metal.
9. A process as claimed in any preceding claim wherein substantially all of the particles in the fragmented preconcentrate or fragmented flotation feed have a diameter of 10 to 500 μm .

10. A process as claimed in any preceding claim wherein the fragmented pre-concentrate or fragmented flotation feed comprises liberated silica particles and liberated silicon metal particles.

5 11. A process as claimed in any preceding claim wherein the fragmented pre-concentrate or fragmented flotation feed comprises 90 wt% or more of liberated particles, such as 95 wt% or more.

12. A process as claimed in any preceding claim wherein the fragmented pre-
10 concentrate or fragmented flotation feed consists of liberated silica particles and liberated silicon metal particles.

13. A process as claimed in any preceding claim in which the fragmented pre-concentrate particles or fragmented flotation feed are washed and deslimed before
15 flotation.

14. A process as claimed in any preceding claim in which the solution of fluoride ions comprises HF.

20 15. A process as claimed in any preceding claim in which the solution of fluoride ions comprises HF and a further inorganic acid.

16. A process as claimed in any preceding claim in which the solution of fluoride ions comprises a fluoride salt and an inorganic acid.

25 17. A process as claimed in any preceding claim in which the solution of fluoride ions comprises sodium fluoride and sulphuric acid, nitric acid or hydrochloric acid.

18. A process as claimed in any preceding claim wherein the fragmented
30 preconcentrate or fragmented flotation feed is conditioned in the presence of an aqueous solution of fluoride ions and a frother to create a suspension.

19. A process as claimed in any preceding claim wherein the frother is an oligomeric or polymeric alcohol or ether.

35 20. A process as claimed in any preceding claim wherein the fluoride ion concentration is less than 50 kg/1000kg as kg of fluoride ion per tonne of solids in the flotation feed.

21. A process as claimed in any preceding claim wherein the frother is present at a level of 10 to 2000 g/1000kg solids.

22. A process as claimed in any preceding claim which is a continuous process.

5

23. A process as claimed in any preceding claim in which the recovered silica or silicon metal particles are subject to acid leaching.

24. A process for the purification of silicon metal said process comprising:

- 10 (I) conditioning a blend comprising liberated silicon metal particles and liberated silica particles wherein at least 90 wt% of the particles have a diameter of 10 to 500 μm in the presence of an aqueous solution of fluoride ions and a frother to form a suspension;
- 15 (II) introducing gas bubbles into the suspension of step (I) in order to form a froth on top of the suspension to which liberated silicon metal particles adhere whilst liberated silica particles remain in the suspension;
- (III) removing the froth and/or the silica particles from the suspension.

Figure 1

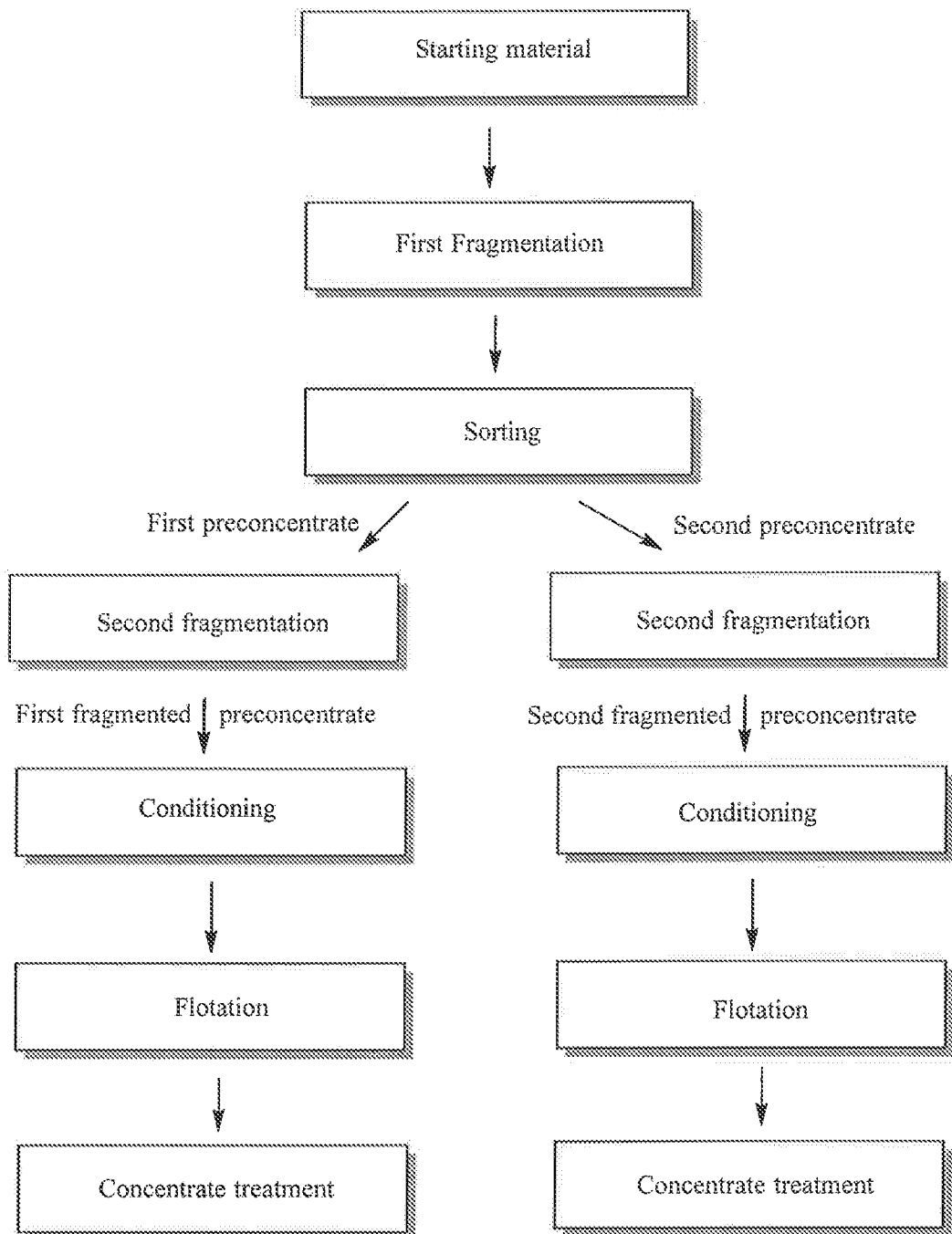


Figure 2

