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(54) Title: DIMENSIONALLY CONTROLLED 'ENGINEERED POLYMER BUBBLE' FOR FLOTATION SEPARATION

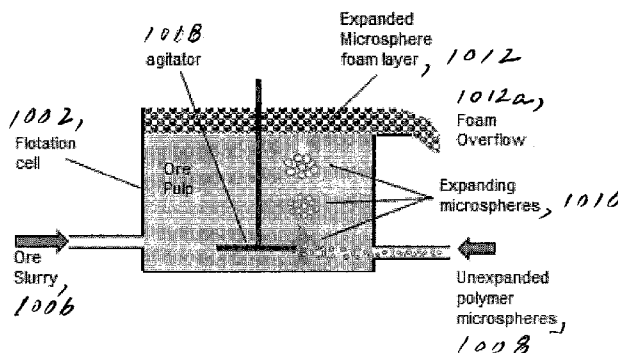


Figure 17a: Flotation cell arrangement utilizing expanding microsphere functionalized polymer 'beads'.

(57) Abstract: Apparatus is provided featuring a first and second cells. The first cell receives an ore slurry having mineral particles of interest, receives unexpanded polymer microspheres comprising a surface having mineral collector chemistry attached thereto with molecules for attaching the mineral particles of interest, causes the unexpanded polymer microspheres to expand substantially in volume into expanded polymer microspheres having a substantially increased sphere surface area, and provides an expanded polymer microsphere foam layer comprising the expanded polymer microspheres with attached mineral particles of interest. The second cell receives the expanded polymer microsphere foam layer, and causes the expanded polymer microspheres to collapse substantially in volume into collapsed polymer microspheres having a substantially reduced sphere surface area that results in a mechanical shearing off of the attached mineral particles of interest. The second cell may also provide a mineral concentrate output having the mineral particles of interest.



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**DIMENSIONALLY CONTROLLED 'ENGINEERED POLYMER BUBBLE'  
FOR FLOTATION SEPARATION**

Cross-Reference to Related Patent Applications

5           The present application claims the benefit of U.S. Provisional Patent Application No. 61/618,046 (CCS-0083//712-2.379), filed 30 March 2012, as well as U.S. Provisional Patent Application No. 61/650,185 (CCS-0085//712-2.388), filed 22 May 2012, which are both hereby incorporated by reference herein in their entirety.

          The present application is also a continuation-in-part (CIP) of, and claims  
10 benefit to, Patent Cooperation Treaty (PCT) application serial no. PCT/US12/39591 (712-2.383), filed 25 May 2012, entitled "Method and system for releasing mineral from synthetic bubbles and beads," which is also incorporated by reference herein in its entirety.

          The present application is also related to eight (8) PCT applications, which  
15 were all concurrently filed on 25 May 2012, and which are all incorporated by reference in their entirety, as follows:

          PCT application no. PCT/US12/39528 (Docket no. WFVA 712-002.356-1//CCS-0052), entitled "Flotation separation using lightweight synthetic bubbles and beads;"

20           PCT application no. PCT/US12/39534 (Docket no. 712-002.359-1//CCS-0087), entitled "Mineral separation using functionalized polymer membranes;"

          PCT application no. PCT/US12/39540 (Docket no. 712-002.359-2//CCS-0088), entitled "Mineral separation using sized, weighted and  
25 magnetized beads;"

PCT application no. PCT/US12/39576 (Docket no. 712-002.382//CCS-0089), entitled "Synthetic bubbles/beads functionalized with molecules for attracting or attaching to mineral particles of interest;"

5 PCT application no. PCT/US12/39596 (Docket no. 712-002.384//CCS-0091), entitled "Synthetic bubbles and beads having hydrophobic surface;"

PCT application no. PCT/US12/39631 (Docket no. 712-002.385//CCS-0092), entitled "Mineral separation using functionalized filters and members;"

PCT application no. PCT/US12/39655 (Docket no. 712-002.386//CCS-0093), entitled "Mineral recovery in tailings using functionalized polymers;"

10 and

PCT application no. PCT/US12/39658 (Docket no. 712-002.387//CCS-0094), entitled "Techniques for transporting synthetic beads or bubbles In a flotation cell or column."

Moreover, the present application is also related to PCT application no.

15 PCT/US12/69402 (Docket no. 712-002.374-1// CCS-0078), filed 13 December 2012, entitled "Mineral separation using functionalized polymer-coated filters and membranes," which is hereby incorporated by reference in its entirety.

The present application is also related to provisional application no.

20 61/604,088, (Docket no. 712-002.377//CCS-0081), filed 28 February 2012, entitled "Mineral separation using functionalized polymer-coated filters and membranes," which is hereby incorporated by reference in its entirety.

The present application is also related to provisional application no.

25 61/604,088, (Docket no. 712-002.389//CCS-0086), filed 22 May 2012, entitled "Charged engineered polymers for flotation separation," which is hereby incorporated by reference in its entirety.



rate. Controlling the air bubble surface area flux has traditionally been very difficult. This is a multivariable control problem and there are no dependable real time feedback mechanisms to use for control.

Flotation processing techniques for the separation of materials are a widely  
5 utilized technology, particularly in the fields of minerals recovery, industrial waste water treatment, and paper recycling for example.

By way of example, in the case of minerals separation the mineral bearing ore may be crushed and ground to a size, typically around 100 microns, such that a high degree of liberation occurs between the ore minerals and the gangue (waste)  
10 material. In the case of copper mineral extraction as an example, the ground ore is then wet, suspended in a slurry, or 'pulp', and mixed with reagents such as xanthates or other reagents, which render the copper sulfide particles hydrophobic.

Froth flotation is a process widely used for separating the valuable minerals from gangue. Flotation works by taking advantage of differences in the  
15 hydrophobicity of the mineral-bearing ore particles and the waste gangue. In this process, the pulp slurry of hydrophobic particles and hydrophilic particles is introduced to a water filled tank containing surfactant/frother which is aerated, creating bubbles. The hydrophobic particles attach to the air bubbles, which rise to the surface, forming a froth. The froth is removed and the concentrate is further  
20 refined.

In standard flotation separation, air is constantly forced through the pulp slurry to create a certain 'flux' of air passing through the pulp. This process, while now used widely, and refined over many decades of use, has limitations:

- Due to the natural dynamics of the bubbles, a mineral-bearing particle may not typically be carried to the surface on one bubble, but may have to attach to several bubbles to reach the froth layer.
  - Larger particles containing minerals may not be lifted due to the limited
- 5        buoyancy of a bubble, and the attractive forces between the bubble and the ore particle (created by the collector / hydrophobic chemical additives)

In general, 10% to 15% of the mineral bearing ore in the pulp is not recovered using air-based flotation processes, and consequently, new separation technologies are being explored and developed.

10        The assignee of the present patent application has previously disclosed the use of polymer shells (aka "engineered bubbles") and polymer plates as a mineral separation method, consistent with that set forth in the patent applications above. In these approaches, a polymer material is modified with an appropriate mineral collector chemistry to make the surface of the polymer attractive to the mineral of

15        interest. In the process, minerals attach to the polymer – in the case of the shells, separation is achieved via flotation, whereas in the case of plates, it is envisioned that the bound mineral can be washed off (with the release being chemically triggered – e.g., pH for example), or mechanically released (e.g., vibration / ultrasonically for example).

20        Expandable polymer shells are widely used in a range of commercial products such as adhesives and sealants for example. One such example is the Dualite brand from a company named, Henkel Corp. In this case, polymer shells made of a thermoset polymer can be expanded at a particular temperature trigger point. The expansion forces come from a 'blowing agent' – a low boiling point liquid.

25        At the point of the liquid – vapor transition temperature, the pressure inside the

microsphere increases and the sphere is 'blown up'. Spheres can increase their size by 50 fold in volume. Their use in sealants and adhesives provides a very low density filler / foam-type expansion material.

There is a need in the industry to provide a better way to separate valuable  
5 material from unwanted material, e.g., including in such a flotation cell, so as to eliminate problems associated with using air bubbles in such a separation process.

For example, a new approach to help solve this problem may be through the use of the expandable polymer shell technology. This expandable polymer shell technology may be adapted for other uses, such as for flotation separation  
10 consistent with that set forth herein.

#### Summary of the Invention

The present application discloses additional improvements/alternatives to the concept for minerals separation set forth in the aforementioned PCT application.

15 The aforementioned type of polymer microsphere expansion may be of interest in the field of mineral separation, as the dimensional changes in the microspheres can be used for attachment and de-attachment of the recovered minerals.

Consistent with the concepts set forth herein for the optimization of flotation  
20 using engineered bubbles or beads, including engineered polymers such as polymer "bubbles" or "beads," this overall approach has several distinct advantages, one of which is that by floating the polymer bubbles up through a solution (such as an ore slurry) having the mineral particles of interest, e.g., chalcopyrite (or copper particles), the probability of an impact and attachment can be very high. The following sets

forth new techniques for collection and release of mineral particles in relation to such a solution:

Consistent with that disclosed herein, two approaches to using polymer based bubbles to capture the mineral particles of interest, such as chalcopyrite, may include imbedding the polymer bubbles with a collector material which attracts, e.g., copper, or second, may include having the polymer bubbles embedded with a hydrophobic material that would attract the standard collectors that are currently available and used today. (For example, assuming that the standard collectors are based on the process of, e.g., a copper collector which is attracted to copper but also with a hydrophobic tail.)

One important aspect of the process that must be optimized regardless of the method used, is that the polymer bubbles must attract and attach to the mineral particles of interest, such as chalcopyrite, during the collection phase of the process and release the mineral particles of interest once that phase is complete. This can be a very difficult task since essentially the bubbles must exhibit a strong attraction to hold, e.g., the chalcopyrite. but not too strong to allow release of the material after the collection. The additional improvements/alternatives to the concept for minerals separation provides further solutions that address the needs of this difficult task.

#### 20 Pressurized Release For Collapsing Polymer Bubbles (CCS-0083)

According to some embodiments, the present invention may take the form of apparatus featuring a first cell and a second cell.

The first cell may be configured to receive an ore slurry having mineral particles of interest, to receive unexpanded polymer microspheres comprising a surface having mineral collector chemistry attached thereto with molecules for

attaching the mineral particles of interest, to cause the unexpanded polymer microspheres to expand substantially in volume into expanded polymer microspheres having a substantially increased sphere surface area, and to provide an expanded polymer microsphere foam layer comprising the expanded polymer  
5 microspheres with attached mineral particles of interest.

The second cell may be configured to receive the expanded polymer microsphere foam layer, and to cause the expanded polymer microspheres to collapse substantially in volume into collapsed polymer microspheres having a substantially reduced sphere surface area that results in a mechanical shearing off  
10 of the attached mineral particles of interest.

The second cell may also be configured to provide a mineral concentrate output having the mineral particles of interest.

In operation, and by way of example, the expandable polymer microspheres which have been modified with mineral collector chemistries may be injected into a  
15 flotation cell along with a mineral ore pulp. Agitation may be induced (as is used in the known air-based flotation system) to mix the mineral ore pulp and the expandable polymer microspheres. A trigger temperature of a blowing agent encapsulated in the expandable polymer microsphere may be set at below the temperature of the pulp/water mixture in the flotation vessel. (This may require cool  
20 or chilled storage of the unexpanded polymer microspheres prior to their induction to the flotation cell.) The polymer microsphere expand, become buoyant, and create an increased bubble flux in the mineral ore pulp, presenting surface area for mineral bearing particles to attach to and be lifted to the surface.

An agglomerated mass of expanded polymer microspheres on the surface is  
25 functionally equivalent to the froth layer on the surface of a conventional flotation

cell, and is skimmed and moved to a release stage. Here, the expanded polymer microspheres are passed to a release tank in a batch process: the tank may be filled with the mineral rich foam, and the tank, e.g., either pressurized to a nominally elevated level, or chilled, such that the blowing agent reverses through a transition  
5 phase (returning to a liquid phase or a low pressure phase). This transition causes the expanded polymer microspheres to collapse, and the dramatic or substantial reduction in sphere surface area will result in a mechanical shearing off of the attached minerals. The mineral particles may separate from the collapsed polymer microspheres due to gravitation separation – e.g., the mineral particles of interest  
10 sink in the tank, whereas the unexpanded polymer microspheres remains nominally buoyant and float.

Alternatively, according to some embodiments of the present invention, the flotation cell may be configured so that the expanded polymer microsphere foam layer on the surface may be allowed to spill over and be received by a spillover  
15 container, then provided for further processing, including being provided to release apparatus.

As this type of process to release the minerals could be done quickly in a batch-step process, the throughput of the cell is not typically compromised.

According to some embodiments, the present invention may also take the  
20 form of a method including the steps of:

In a first cell, receiving an ore slurry having mineral particles of interest, receiving unexpanded polymer microspheres comprising a surface having mineral collector chemistry attached thereto with molecules for attaching the mineral particles of interest, causing the unexpanded polymer microspheres to expand  
25 substantially in volume into expanded microspheres having a substantially increased

sphere surface area, and providing an expanded polymer microsphere foam layer comprising the expanded polymer microspheres with attached mineral particles of interest.

In a second cell, receiving the expanded polymer microsphere foam layer,  
5 and causing the expanded polymer microspheres to collapse substantially in volume into collapsed polymer microspheres having a substantially reduced sphere surface area that results in a mechanical shearing off of the attached mineral particles of interest. The method may also include providing from the second cell a mineral concentrate output having the attached mineral particles of interest.

10 The scope of the invention is also intended to include, or take the form of, apparatus comprising means for receiving an ore slurry having mineral particles of interest, receiving unexpanded polymer microspheres comprising a surface having mineral collector chemistry attached thereto with molecules for attaching the mineral particles of interest, causing the unexpanded polymer microspheres to expand  
15 substantially in volume into expanded microspheres having a substantially increased sphere surface area, and providing an expanded polymer microsphere foam layer comprising the expanded polymer microspheres with attached mineral particles of interest; in combination with means for receiving the expanded polymer microsphere foam layer, and causing the expanded polymer microspheres to collapse  
20 substantially in volume into collapsed polymer microspheres having a substantially reduced sphere surface area that results in a mechanical shearing off of the attached mineral particles of interest. The means for receiving the expanded polymer microsphere foam layer may also include means for providing a mineral concentrate output having the attached mineral particles of interest.

25

### Condensation Release For Collapsing Polymer Bubbles (CCS-0085)

Alternatively, according to some embodiments of the present invention, the releasing apparatus may be configured as a condensing tank for lowering the temperature of the expanded polymer microspheres to collapse substantially in  
5 volume into collapsed polymer microspheres having a substantially reduced sphere surface area that results in a mechanical shearing off of the attached mineral particles of interest.

### The Method

10 According to some embodiments, the present invention may take the form of a method featuring steps for

receiving in a processor a plurality of synthetic beads in the form of polymer microspheres carrying mineral particles, each of the polymer microspheres comprising a surface and a plurality of molecules attached to the surface, the  
15 molecules comprising a functional group having a chemical bond for attracting or attaching one or more of the mineral particles to the molecules, causing the mineral particles to attach to the polymer microspheres; and

interrupting the chemical bond of the functional group so as to remove the mineral particles from the polymer microspheres.

20 The polymer microsphere may include, or take the form of, the expandable polymer microspheres set forth herein. The interruption of the chemical bond of the functional group so as to remove the mineral particles from the expandable polymer microspheres may include, or take the form of, pressurizing or cooling the expandable polymer microspheres to collapse the same.

The present invention may be used alone, or in conjunction with that set forth in the aforementioned PCT application serial no. PCT/US12/39591 (712-2.383) consistent with that summarized below:

According to some embodiments of the present invention, the synthetic beads  
5 carrying the mineral particles may be received in a mixture having a first temperature, and the step of interrupting may include causing the synthetic beads carrying the mineral particles to contact with a medium having a second temperature higher than the first temperature.

According to some embodiments of the present invention, the synthetic beads  
10 carrying the mineral particles may be caused to contact with a liquid, and the step of interrupting may include applying a sonic agitation to the liquid for causing the mineral particles to separate from the synthetic beads, or the step of interrupting may include applying microwaves to the liquid for causing the mineral particles to separate from the synthetic beads. The step for interrupting may include providing  
15 an ultrasonic source to apply the sonic agitation to the liquid, and/or arranging the ultrasonic source to produce ultrasound signals for sonic agitation, for example ultrasound signals in the range of 20KHz to 300KHz for the sonic agitation. The step of interrupting may include providing an ultrasonic signal selected at the resonant frequency of the beads for causing the mineral particles to separate from  
20 the synthetic beads.

According to some embodiments of the present invention, the synthetic beads carrying the mineral particles may be received along with a mixture having a first pH value, and the step for interrupting may include causing the synthetic beads carrying the mineral particles to contact with a medium having a second pH value lower than  
25 the first pH value, including where the second pH value ranges from 0 to 7.

According to some embodiments of the present invention, the step of interrupting may include mechanically causing the synthetic beads to move against each other, including arranging a rotational means or device to stir the synthetic beads.

5           According to some embodiments of the present invention, the synthetic beads may be made of a polymer having a glass transition temperature, and the second temperature may be substantially equal to or higher than the glass transition temperature.

10           According to some embodiments of the present invention, part of the synthetic beads carrying the mineral particles may be made of a magnetic material, and the step of interrupting may include arranging a magnetic stirrer to stir the synthetic beads.

15           According to some embodiments of the present invention, the synthetic beads carrying the mineral particles may be received along with a mixture, wherein said interrupting comprises selecting two or more of the following interrupting techniques: 1) lowering pH value of the mixture, 2) applying an ultrasound to the mixture; 3) increasing temperature of the mixture and 4) mechanically stirring the mixture. The selected interrupting techniques may be used on the mixture concurrently or sequentially.

20

### Apparatus

25           According to some embodiments, the present invention may take the form of an apparatus featuring a processor configured to receive a plurality of synthetic beads in the form of polymer microspheres carrying mineral particles, each of the polymer microspheres comprising a surface and a plurality of molecules attached to

the surface, the molecules comprising a functional group having a chemical bond for attracting or attaching one or more of the mineral particles to the molecules, causing the mineral particles to attach to polymer microspheres; and releasing apparatus configured to interrupt the chemical bond of the functional group so as to remove the  
5 mineral particles from the polymer microspheres.

According to some embodiments, the present invention, the release apparatus may be configured to implement one or more of the features set forth herein.

According to some embodiments of the present invention, the processor may  
10 be configured to cause the polymer microspheres to expand substantially in volume into expanded polymer microspheres having a substantially increased sphere surface area. By way of example, the polymer microspheres may be caused to expand by an increase in temperature, including where the temperature of the ore slurry is greater than the temperature of the polymer microspheres. The polymer  
15 microspheres may be caused to expand by using other techniques consistent with that set forth herein.

According to some embodiments of the present invention, the processor may be configured as a higher temperature flotation cell or tank, e.g., to receive unexpanded polymer microspheres and to cause the unexpanded polymer  
20 microspheres to expand substantially in volume into expanded polymer microspheres having a substantially increased sphere surface area.

According to some embodiments of the present invention, the releasing apparatus may be configured to cause the expanded polymer microspheres to collapse substantially in volume into collapsed polymer microspheres that results in  
25 the mechanical shearing off of the attached mineral particles of interest.

According to some embodiments of the present invention, the processor may be configured to maintain the ore slurry at a predetermined temperature, and the unexpanded polymer microspheres may be configured with a blowing agent encapsulated therein that has a trigger temperature set below the predetermined  
5 temperature so as to cause the unexpanded polymer microspheres to expand substantially in volume into the expanded polymer microspheres having the substantially increased sphere surface area when received in the processor.

According to some embodiments of the present invention, the releasing apparatus may be configured as a re-pressurization cell, or a condensing tank, or a  
10 lower temperature separation tank, or a release tank.

According to some embodiments of the present invention, the releasing apparatus may be configured to be filled with an expanded polymer microsphere foam layer or mineral rich foam, and to be pressurized to a nominally elevated level, or chilled to a lower temperature, such that the blowing agent reverses through a  
15 transition phase, including either returning from a gas phase to a liquid phase or returning from a high pressure phase to a low pressure phase.

According to some embodiments, the present invention may take the form of an apparatus featuring a processing compartment for receiving a plurality of synthetic beads carrying mineral particles, each of the synthetic beads comprising a  
20 surface and a plurality of molecules attached to the surface, the molecules comprising a functional group having a chemical bond for attracting or attaching one or more of the mineral particles to the molecules, causing the mineral particles to attach to synthetic beads; the synthetic beads carrying the mineral particles received in a mixture having a pH value; and a controller arranged to release an acidic  
25 material for lowering the pH value of the mixture.

According to some embodiments, the present invention may take the form of an apparatus featuring a processing compartment for receiving a plurality of synthetic beads carrying mineral particles, each of the synthetic beads comprising a surface and a plurality of molecules attached to the surface, the molecules  
5 comprising a functional group having a chemical bond for attracting or attaching one or more of the mineral particles to the molecules, causing the mineral particles to attach to synthetic beads; the synthetic beads carrying the mineral particles received in a mixture having a physical condition; and a sonic source arranged to apply ultrasonic waves to the mixture.

10 In effect, the present invention provides mineral separation techniques using synthetic beads or bubbles, including size-, weight-, density- and magnetic-based polymer bubbles or beads. The term "polymer" in the specification means a large molecule made of many units of the same or similar structure linked together.

The present invention may consist of replacing or assisting the air bubbles in  
15 a flotation cell that are presently used in the prior art with a similar density material that has very controllable size characteristics. By controlling the size and the injection rate a very accurate surface area flux can be achieved. This type of control would enable the bead or bubble size to be tuned or selected to the particle size of interest in order to better separate valuable or desired material from unwanted  
20 material in the mixture. Additionally, the buoyancy of the bubble or bead may be selected to provide a desired rate of rise within a flotation cell to optimize attraction and attachment to mineral particles of interest. By way of example, the material or medium could be a polymer or polymer-based bubble or bead. These polymer or polymer-based bubbles or beads are very inexpensive to manufacture and have a  
25 very low density. They behave very similar to a bubble, but do not pop.

Since this lifting medium size is not dependent on the chemicals in the flotation cell, the chemicals may be tailored to optimize hydrophobicity. There is no need to compromise the performance of the frother in order to generate the desired bubble size. A controlled size distribution of medium may be customized to  
5 maximize recovery of different feed matrixes to flotation as ore quality changes.

There may be a mixture of both air and lightweight beads or bubbles. The lightweight beads or bubbles may be used to lift the valuable material and the air may be used to create the desired froth layer in order to achieve the desired material grade.

10 Bead or bubble chemistry is also developed to maximize the attachment forces of the lightweight beads or bubbles and the valuable material.

A bead recovery process is also developed to enable the reuse of the lightweight beads or bubbles in a closed loop process. This process may consist of a washing station whereby the valuable mineral is mechanically, chemically,  
15 thermally or electromagnetically removed from the lightweight beads or bubbles. In particular, the removal process may be carried out by way of controlling the pH value of the medium in which the enriched polymer beads or bubbles are embedded, controlling the temperature of the medium, applying mechanical or sonic agitation to the medium, illuminating the enriched polymer beads with light of a certain range of  
20 frequencies, or applying electromagnetic waves on the enriched polymer beads in order to weaken or interrupting the bonds between the valuable material and the surface of the polymer beads or bubbles.

The Separation Process or Processor

According to some embodiments of the present invention, and by way of example, the separation process may utilize existing mining industry equipment, including traditional column cells and thickeners. The lightweight synthetic beads or bubbles, including polymer bubbles, may be injected into a first traditional column or cell at an injection air port and rise to the surface. This first traditional column or cell has an environment that is conducive to particle attachment. As the lightweight synthetic beads or bubbles rise they collide with the falling mineral particles. The falling mineral particles stick to the lightweight synthetic beads or bubbles and float or report to the surface. The wash water can be used to clean off the entrained gangue. The recovered bubbles and mineral may be sent to another traditional column or cell and injected into, e.g., the middle of the column. This traditional column or cell has an environment that will promote release of the mineral particles. The mineral particles fall to the bottom and the synthetic bubbles or beads float or go to the surface. The synthetic bubbles or beads may be reclaimed and then sent back through the process taking place in the first traditional column or cell. Thickeners may be used to reclaim the process water at both stages of the process.

#### Flotation Recovery of Coarse Ore Particles in Mining

According to some embodiments, the present invention may be used for flotation recovery of coarse ore particles in mining.

For example, the concept may take the form of the creation of the lightweight synthetic beads or bubbles in a flotation recovery for lifting particles, e.g., greater than 150 micron, to the surface in a flotation cell or column.

The fundamental notion is to create a shell or "semi-porous" structured bead or bubble of a predetermined size and use this as an 'engineered 'air bubble' for improving flotation recovery, e.g., of coarse ore particles in mining.

Flotation recovery may be implemented in multiple stages, e.g., where the  
5 first stage works well at recovering the ground ore at the right size (<150 microns), but ore particles that are too small or too large pass on to later stages and are more difficult to recover.

The present invention includes creating the "bubbles," and engineering them to carry the ore to the surface using, e.g., a polymer shell or structure, appropriately  
10 chemically activated to attract or attach to the ore.

Depending on the method of "engineering" the bubble, at or near the surface the shell could dissolve (time activated), and release an agent that further promotes the frothing.

15 Polymer Blocks having Incorporated Air or Light-weight Material

According to some embodiments, the present invention may take the form of synthetic flotation bubbles, using a concept such as incorporating air bubbles into polymer blocks, which are designed to attract or attach mineral rich ore onto their surface and then float to the top of the flotation tank. It is also possible to  
20 incorporate light-weight material such as Styrofoam into the polymer blocks to aid buoyancy.

The benefits of this approach include the fact that "engineered bubbles" in a polymer may enable a much larger range of ore grains to be lifted to the surface hence improving recover efficiency.

According to some embodiments, optimally sized polymer blocks with a high percentage of air may be produced with appropriate collector chemicals also encapsulated into the polymer.

Once the blocks are in, e.g., a mixture such as a slurry pulp, the collector  
5 chemicals may be released to initially attract or attach to mineral rich ore particles and then rise to the surface.

### Example of Embodiments

#### Apparatus in the Form of a Cell or Column

10 According to some embodiments, the present invention may take the form of apparatus featuring a cell or column configured to receive a mixture of fluid (e.g. water) and valuable material and unwanted material; receive synthetic bubbles or beads constructed to be buoyant when submerged in the mixture and functionalized to control the chemistry of a process being performed in the cell or column; and  
15 provide enriched synthetic bubbles or beads having the valuable material attached thereto.

According to some embodiments of the present invention, the synthetic bubbles or beads may be made from a polymer or polymer-based material, or silica or silica-based material, or glass or glass-based material.

20 According to some embodiments of the present invention, the cell or column may take the form of a flotation cell or column, and the synthetic bubbles or beads may be functionalized to attach to the valuable material in the mixture that forms part of a flotation separation process being performed in the flotation cell or column.

According to some embodiments of the present invention, the synthetic bubbles or beads may be functionalized to release a chemical to control the chemistry of the flotation separation process.

5 According to some embodiments of the present invention, the synthetic bubbles or beads may be configured with firm outer shells functionalized with a chemical to attach to the valuable material in the mixture. Alternatively, the synthetic bubbles or beads may include a chemical that may be released to attach to the valuable material in the mixture.

10 According to some embodiments of the present invention, the synthetic bubbles or beads may be constructed with firm outer shells configured to contain a gas, including air, so as to increase be buoyant when submerged in the mixture. Alternatively, the synthetic bubbles or beads may be made from a low-density material so as to be buoyant when submerged in the mixture, including the synthetic bubbles being configured as a solid without an internal cavity.

15 According to some embodiments of the present invention, the synthetic bubbles or beads may include a multiplicity of hollow objects, bodies, elements or structures, each configured with a respective cavity, unfilled space, or hole to trap and maintain a bubble inside. The hollow objects, bodies, elements or structures may include hollow cylinders, or spheres, or globules, or capillary tubes, or some  
20 combination thereof. Each hollow object, body, element or structure may be configured with a dimension so as not to absorb liquid, including water, including where the dimension is in a range of about 20-30 microns. The multiplicity of hollow objects, bodies, elements or structures may be configured with chemicals applied to prevent migration of liquid into respective cavities, including where the chemicals are  
25 hydrophobic chemicals. The synthetic bubbles or beads made from the silica or

silica-based material, or glass or glass-based material, may take the form of hollow glass cylinders manufactured using a drawing and dicing process.

The scope of the invention is not intended to be limited to the size or shape of the synthetic beads or bubbles, so as to enhance their rise or fall in the mixture.

5 The scope of the invention is also intended to include other types or kinds of ways to construct and functionalize the synthetic bubbles or beads either now known or later developed in the future in order to perform the aforementioned functionality of being buoyant when submerged in the mixture and to attach to the valuable material in the mixture.

10 According to some embodiments of the present invention, the mixture may take the form of a slurry pulp containing, e.g., water and the valuable material of interest.

#### A Method for Implementing in a Flotation Separation Device

15 The present invention may also take the form of a method, e.g., for implementing in a flotation separation device having a flotation cell or column. The method may include steps for receiving in the flotation cell or column a mixture of fluid and valuable material; receiving in the flotation cell or column synthetic bubbles or beads constructed to be buoyant when submerged in the mixture and  
20 functionalized to attach to the valuable material in the mixture and; and providing from the flotation cell or column enriched synthetic bubbles or beads having the valuable material attached thereto.

According to some embodiments of the present invention, the method may include being implemented consistent with one or more of the features set forth  
25 herein.

### Apparatus in the Form of a Flotation Separation Device

According to some embodiments, the present invention may take the form of apparatus such as a flotation separation device, including a flotation cell or column  
5 configured to receive a mixture of water, valuable material and unwanted material; receive polymer or polymer-based materials, including polymer or polymer bubbles or beads, configured to attach to the valuable material in the mixture; and provide enriched polymer or polymer-based materials, including enriched polymer or polymer-based bubbles or beads, having the valuable material attached thereon.

10 According to some embodiments, the polymer or polymer-based material may be configured with a surface area flux by controlling some combination of the size of the polymer or polymer-based material and/or the injection rate that the mixture is received in the flotation cell or column; or the polymer or polymer-based material may be configured with a low density so as to behave like air bubbles; or the  
15 polymer or polymer-based material may be configured with a controlled size distribution of medium that may be customized to maximize recovery of different feed matrixes to flotation as valuable material quality changes, including as ore quality changes; or some combination thereof.

The present invention may take the form of apparatus for use in, or forming  
20 part of, a separation process to be implemented in separation processor technology, the apparatus featuring synthetic bubbles or beads configured with a polymer or polymer-based material functionalized to attach to a valuable material in a mixture so as to form an enriched synthetic bubbles or beads having the valuable material attached thereto, and also configured to be separated from the mixture based at

least partly on a difference in a physical property between the enriched synthetic bubbles or beads having the valuable material attached thereto and the mixture.

The separation process may be implemented in separation processor technology which combines the synthetic bubbles or beads and the mixture, and  
5 which provides the enriched synthetic bubbles or beads having the valuable material attached thereto that are separated from the mixture based at least partly on the difference in the physical property between the enriched synthetic bubbles or beads having the valuable material attached thereto and the mixture.

#### 10 Size-based Separation

The separation process may be implemented using sized-based separation, where the synthetic bubbles or beads may be configured to be separated from the mixture based at least partly on the difference between the size of the enriched synthetic bubbles or beads having the valuable material attached thereto in relation  
15 to the size of unwanted material in the mixture.

According to some embodiments of the present invention, the synthetic bubbles or beads may be configured either so that the size of the synthetic bubbles or beads is greater than a maximum ground ore particle size in the mixture, or so that the size of the synthetic bubbles or beads is less than a minimum ground ore  
20 particle size in the mixture.

According to some embodiments of the present invention, the synthetic bubbles or beads may be configured as solid polymer bubbles or beads.

According to some embodiments of the present invention, the synthetic bubbles or beads may be configured with a core material of sand, silica or other  
25 suitable material and also configured with a polymer encapsulation.

### Weight-based Separation

The separation process may be implemented using weight-based separation, where the synthetic bubbles or beads are configured to be separated from the  
5 mixture based at least partly on the difference between the weight of the enriched synthetic bubbles or beads having the valuable material attached thereto in relation to the weight of unwanted material in the mixture.

According to some embodiments of the present invention, the synthetic bubbles or beads may be configured so that the weight of the synthetic bubbles or  
10 beads is greater than a maximum ground ore particle weight in the mixture, or so that the weight of the synthetic bubbles or beads is less than a minimum ground ore particle weight in the mixture.

According to some embodiments of the present invention, the synthetic bubbles or beads may be configured as solid polymer bubbles or beads.

15 According to some embodiments of the present invention, the synthetic bubbles or beads may be configured with a core material of magnetite, air or other suitable material and also configured with a polymer encapsulation.

### Magnetic-based Separation

20 The separation process may be implemented using magnetic-based separation, where the synthetic bubbles or beads may be configured to be separated from the mixture based at least partly on the difference between the para-, ferri-, ferro-magnetism of the enriched synthetic bubbles or beads having the valuable material attached thereto in relation to the para-, ferri-, ferro-magnetism of  
25 unwanted material in the mixture.



Figure 1 is a diagram of a flotation system, process or apparatus according to some embodiments of the present invention.

Figure 2 is a diagram of a flotation cell or column that may be used in place of the flotation cell or column that forms part of the flotation system, process or  
5 apparatus shown in Figure 1 according to some embodiments of the present invention.

Figure 3a shows a generalized synthetic bead which can be a size-based bead or bubble, weight-based polymer bead and bubble, and magnetic-based bead and bubble, according to some embodiments of the present invention.

10 Figure 3b illustrates an enlarged portion of the synthetic bead showing a molecule or molecular segment for attaching a function group to the surface of the synthetic bead, according to some embodiments of the present invention.

Figure 4a illustrates a synthetic bead having a body made of a synthetic material, according to some embodiments of the present invention.

15 Figure 4b illustrates a synthetic bead with a synthetic shell, according to some embodiments of the present invention.

Figure 4c illustrates a synthetic bead with a synthetic coating, according to some embodiments of the present invention.

20 Figure 4d illustrates a synthetic bead taking the form of a porous block, a sponge or a foam, according to some embodiments of the present invention.

Figure 5a illustrates the surface of a synthetic bead with grooves and/or rods, according to some embodiments of the present invention.

Figure 5b illustrates the surface of a synthetic bead with dents and/or holes, according to some embodiments of the present invention.

Figure 5c illustrates the surface of a synthetic bead with stacked beads, according to some embodiments of the present invention.

Figure 5d illustrates the surface of a synthetic bead with hair-like physical structures, according to some embodiments of the present invention.

5 Figure 6 is a diagram of a bead recovery processor in which the valuable material is thermally removed from the polymer bubbles or beads, according to some embodiments of the present invention.

Figure 7 is a diagram of a bead recovery processor in which the valuable material is sonically removed from the polymer bubbles or beads, according to some  
10 embodiments of the present invention.

Figure 8 is a diagram of a bead recovery processor in which the valuable material is chemically removed from the polymer bubbles or beads, according to some embodiments of the present invention.

Figure 9 is a diagram of a bead recovery processor in which the valuable  
15 material is electromagnetically removed from the polymer bubbles or beads, according to some embodiments of the present invention.

Figure 10 is a diagram of a bead recovery processor in which the valuable material is mechanically removed from the polymer bubbles or beads, according to some embodiments of the present invention.

20 Figure 11 is a diagram of a bead recovery processor in which the valuable material is removed from the polymer bubbles or beads in two or more stages, according to some embodiments of the present invention.

Figure 12 is a diagram of an apparatus using counter-current flow for mineral separation, according to some embodiments of the present invention.

Figure 13a shows a generalized synthetic bead functionalized to be hydrophobic, wherein the bead can be a size-based bead or bubble, weight-based polymer bead and bubble, and magnetic-based bead and bubble, according to some embodiments of the present invention.

5           Figure 13b illustrates an enlarged portion of the hydrophobic synthetic bead showing a wetted mineral particle attaching the hydrophobic surface of the synthetic bead.

          Figure 13c illustrates an enlarged portion of the hydrophobic synthetic bead showing a hydrophobic non-mineral particle attaching the hydrophobic surface of the  
10   synthetic bead.

          Figures 14a illustrates a mineral particle being attached to a number of much smaller synthetic beads at the same time.

          Figures 14b illustrates a mineral particle being attached to a number of slightly larger synthetic beads at the same time.

15           Figures 15a illustrates a wetted mineral particle being attached to a number of much smaller hydrophobic synthetic beads at the same time.

          Figures 15b illustrates a wetted mineral particle being attached to a number of slightly larger hydrophobic synthetic beads at the same time.

          Figures 16a and 16b illustrate some embodiments of the present invention  
20   wherein the synthetic bead or bubble have one portion functionalized to have collector molecules and another portion functionalized to be hydrophobic.

          Figure 17a illustrates apparatus according to some embodiments of the present invention, in the form of an arrangement of a flotation cell for a minerals recovery process.

Figure 17b illustrates apparatus according to some embodiments of the present invention, in the form of a combined flotation cell and re-pressurization cell for mineral release from an expanded polymer foam.

Figure 17c illustrates a re-pressurization release concept, which may form  
5 part of some embodiments of the present invention.

Figure 18a illustrates an expanded polymer bubble having chalcopyrite attached thereto, according to, or forming part of, some embodiments of the present invention.

Figure 18b illustrates a collapsed expanded polymer bubble having the  
10 chalcopyrite detached, according to, or forming part of, some embodiments of the present invention.

Figure 18c illustrates apparatus according to some embodiments of the present invention, including where the expanded polymer bubble in Figure 18a having chalcopyrite attached thereto overflow a flotation cell or tank and are  
15 provided to a condensation cell or tank to be collapsed into the collapsed expanded polymer bubble in Figure 18b.

### Detailed Description of the Invention

#### Figures 17a to 17c (CCS-0083)

20 By way of example, and according to some embodiments of the present invention, Figures 17a to 17c show apparatus generally indicated as 1000 featuring a first cell 1002 (e.g., a flotation cell or tank) in combination with a second cell 1004 (e.g., a release, re-pressurization or condensing cell).

The first cell 1002 may be configured to receive an ore slurry 1006 having  
25 mineral particles of interest, to receive unexpanded polymer microspheres 1008

comprising a surface having mineral collector chemistry attached thereto with molecules for attaching the mineral particles of interest, to cause the unexpanded polymer microspheres 1008 to expand substantially in volume into expanded polymer microspheres 1010 having a substantially increased sphere surface area, and to provide an expanded polymer microsphere foam layer 1012 comprising the expanded polymer microspheres 1010 with attached mineral particles of interest.

The second cell 1004 may be configured to receive the expanded polymer microsphere foam layer 1012, to cause the expanded polymer microspheres 1010 to collapse substantially in volume into collapsed polymer microspheres 1014 having a substantially reduced sphere surface area that results in a mechanical shearing off of the attached mineral particles 1016 of interest, and to provide a mineral concentrate output 1018 having the mineral particles 1016 of interest.

The first cell 1002 may be, or take the form of, a flotation cell or tank, e.g., that is known in the art, including those that form part of known mineral separation processes. However, the scope of the invention is not intended to be limited to any particular type or kind of first cell or tank, and may include first cells or tanks that are now known or later developed in the future.

By way of example, the first cell 1002 may include an agitator 1018 configured to cause or induce agitation to mix the ore slurry 1006 and polymer microspheres like elements 1008 and/or 1010. Agitators are known in the art, and the scope of the invention is not intended to be limited to any particular type or kind thereof either now known or later developed in the future.

In the embodiment shown in Figures 17a to 17c, the first cell 1002 is configured to receive unexpanded polymer microspheres 1008 that are expanded by a change in temperature, e.g., caused by a higher temperature of the ore slurry

1006. However, the scope of the invention is intended to include the first cell 1002 receiving previously expanded polymer microspheres that have a lower density than the ore slurry, are buoyant and rise and float upwardly in the first cell 1002. In this embodiment, the expanded polymer microspheres in the expanded microsphere  
5 foam layer 1012 are similarly collapsed to cause the mechanical shearing off of the attached mineral particles 1016 of interest. The scope of the invention is not intended to be limited to the degree of expansion (e.g., no expansion, partially expanded, or fully expanded) of the polymer microspheres received in the flotation cell 1002.

10 The unexpanded polymer microspheres 1008 may be configured with a blowing agent encapsulated therein that has a trigger temperature set below the predetermined temperature so as to cause the unexpanded polymer microspheres 1008 to expand substantially in volume into the expanded polymer microspheres 1010 having the substantially increased sphere surface area when received in the  
15 first cell 1002. The blowing agent may be encapsulated, e.g., in an interior part (see Figure 4b, element 86 below). By way of example, the blowing agent may include either a liquid that responds to a change in temperature and transforms into a gas, or a gas that responds to a change in temperature and transforms from a low pressure phase into a high pressure phase. The scope of the invention is not  
20 intended to be limited to the type or kind of gas or liquid used as the blowing agent, and is intended to include gases and liquids both now known and later developed in the future. Embodiments are also envisioned, and the scope of the invention is intended to include, the blowing agent taking the form of an expandable solid or semi-solid (e.g. gel) either now known and later developed in the future, e.g., that  
25 once expanded, cause the polymer microspheres 1010 to have a lower density than

the ore slurry, be buoyant and rise and float upwardly in the first cell 1002. In particular, the first cell 1002 may be configured to maintain the ore slurry 1006 at a predetermined temperature, and the unexpanded polymer microspheres 1008 may be configured with the blowing agent encapsulated therein that has a trigger

5 temperature set below the predetermined temperature so as to cause the unexpanded polymer microspheres 1008 to expand substantially in volume into the expanded polymer microspheres having the substantially increased sphere surface area when received in the first cell 1002. According to some embodiments of the present invention, the unexpanded polymer microspheres 1008 may be cooled or

10 chilled to a temperature below the predetermined temperature prior to induction to the first cell 1002.

The expanded polymer microspheres 1010 may be configured to become buoyant and create an increased bubble flux in the ore slurry 1006, presenting surface area for mineral bearing particles to attach to and be lifted to the surface

15 and form the expanded polymer microsphere foam layer 1012. In particular, the expanded polymer microsphere foam layer 1012 may take the form of an agglomerated mass of expanded spheres on the surface to be skimmed and moved to the second cell 104, including a release stage, or provided as foam overflow 1012a as shown in Figure 17b. Alternatively, the expanded polymer microsphere

20 foam layer 1012 may spill over the first cell or tank 1002, collected in a spillover tank 1013 (Figure 18c) and provided to the second tank 1004, consistent with that disclosed in relation to Figures 18a to 18c.

The second cell 1004 may include a re-pressurization cell or tank, or a condensing tank or cell, or a release tank. Cell or tanks for pressurizing or

25 condensing its contents are known in the art, and the scope of the invention is not

intended to be limited to any particular type or kind thereof either now known or later developed in the future. Moreover, a person skilled in the art would be able to configured the second cell or tank 1004 to cause, e.g., the expanded polymer microspheres 1010 to collapse substantially in volume into the collapsed polymer microspheres 1014 having the substantially reduced sphere surface area that results in the mechanical shearing off of the attached mineral particles 1016 of interest without undue experimentation based at least partly on that disclosed herein. By way of example, the second cell 1004 may be configured to be filled with the expanded polymer microsphere foam layer 1012 or mineral rich foam, and to be pressurized to a nominally elevated level, or chilled to a lower temperature (e.g. to cause condensing), such that the blowing agent reverses through a transition phase, including either returning from a gas phase to a liquid phase or returning from a high pressure phase to a low pressure phase.

By way of example, and according to some embodiments of the present invention, the mineral particles 1016 of interest may separate from the collapsed polymer microspheres 1014 due to gravitation separation, including where minerals sink in the second cell 1004 and where the unexpanded or collapsed polymer microspheres generally indicated by arrow labeled 1008' (e.g., with or without some attached mineral of interest) tend to remain nominally buoyant and may float to the top surface, e.g., as shown in Figure 18c.

By way of example, and according to some embodiments of the present invention, the second cell 1004 may also be configured to provide the mineral concentrate output 1018 having the mineral particles 1016 of interest, e.g., for further processing, including by processing either now known or later developed in the future. The scope of the invention is not intended to be limited to either how the

second cell 1004 may be configured to provide the mineral concentrate output 1018, or how the mineral concentrate output 1018 is further processed once provided from the second cell 1004.

By way of example, and according to some embodiments of the present invention, the second cell 1004 may also be configured to provide a discarded foam output 1020 having the collapsed polymer microspheres, e.g., for further processing, including discarding, cleaning and recirculation, or for or by some other processing either now known or later developed in the future. The scope of the invention is not intended to be limited to either how the second cell 1004 may be configured to provide the discarded foam output 1020, or how the discarded foam output 1020 is further processed once discarded from the second cell 1004.

By way of example, and according to some embodiments of the present invention, and consistent with that set forth herein, the molecules may include a functional group having a chemical bond for attaching the mineral particles of interest, e.g., consistent with that disclosed herein. The scope of the invention is not intended to be limited to any particular type or kind of molecule, functional group, or chemical bond for attaching the mineral particles of interest to the polymer microspheres that may be used to implement the present invention, and is intended to include molecules, functional groups, or chemical bonds that are now known and later developed in the future.

By way of example, and according to some embodiments of the present invention, the volume of the expanded polymer microspheres 1010 may be about 50 times the volume of the unexpanded polymer microspheres 1008. However, scope of the invention is not intended to be limited to any particular volumetric expansion or contraction between the unexpanded polymer microspheres 1008 and the expanded

polymer microspheres 1010, and is intended to include volumetric expansions or contractions less than or greater than 50.

The second cell or tank 1004 may be configured with flow/pressure valves 1022 configured for controlling the flow of the foam overflow 1012a from the first cell 1002 to the second cell 1004, the mineral concentrate output 1018 from the second cell 1004, and the discard foam output 1020 from the second cell 1004. Such flow/pressure valves 1022 are known in the art, and the scope of the invention is not intended to be limited to any particular type or kind thereof.

Figures 18a to 18c (CCS-0085)

Figures 18a to 18c show an alternative approach that builds on the basic idea that the bubbles may be expanded during the collection phase where the larger surface area would be able to collect the mineral of interest, e.g., chalcopyrite, and fill the outer surface. After collection, the mineral of interest, e.g., chalcopyrite, may be removed from the polymer bubble. For example, the bubble may be collapsed or shrunk and the chalcopyrite particles of interest would be forced or mechanically sheared off. Figures 18a and 18b shows the two states of the polymer bubble, including an expanded stated in Figure 18a and a collapsed state in Figure 18b.

Consistent with that set forth herein a variety of conditions could be used to cause the polymer bubble to expand. Temperature is a typical parameter used to control the two-state bubble as demonstrated with Henkel's polymer microsphere offering, consistent with that shown in Figure 18c where a higher temperature flotation tank 1002 is shown with expanded polymer bubbles 1010. Other options may include or be pH, illumination with optical wavelengths or microwave. The scope of the invention is not intended to be limited to any particular way to expand

the polymer bubbles, and is intended to include techniques now and later developed in the future.

Figure 18c shows a technique where temperature may be used to collapse the polymer bubbles and release the chalcopyrite attached thereto. As shown, the polymer bubbles would be activated by the higher temperature bath of chalcopyrite  
5 polymer bubbles would be activated by the higher temperature bath of chalcopyrite which would cause the bubble to expand and attach to the material or mineral particle of interest. The bubbles would float the material to the top of the floatation tank 1002 where it would, e.g., spill over as an expanded microsphere foam layer 1012, be collected in the spillover container 1013 and sent to a second tank, e.g., a  
10 lower temperature condensing tank 1004'. Here, the bubbles and chalcopyrite may be cooled so that the bubbles would collapse and shed the chalcopyrite particles 1016 of interest. The chalcopyrite could then be collected from the bottom of the second tank 1004'.

Condensing tanks like element 1004' and spillover tanks like element 1013  
15 are known in the art, and the scope of the invention is not intended to be limited to any particular type or kind thereof either now known or later developed in the future.

Embodiments are also envisioned, and the scope of the invention is intended to include, the pressure release technique disclosed in relation to Figures 17a-17c being used in combination with the cooling release technique disclosed in relation to  
20 Figures 18a-18c, for collapsing the polymer bubbles and releasing chalcopyrite particles.

Figures 1 to 16c of PCT application serial no. PCT/US12/39591

Moreover, embodiments are envisioned in which the present invention shown  
25 and described in relation to Figures 17a to 17c and 18a to 18c may be used alone,

or in conjunction with that set forth in the aforementioned PCT application serial no. PCT/US12/39591 consistent with that disclosed in relation to Figures 1 to 16b below:

Figure 1

5           By way of example, Figure 1 shows the present invention is the form of apparatus 10, having a flotation cell or column 12 configured to receive a mixture of fluid (e.g. water), valuable material and unwanted material, e.g., a pulp slurry 14; receive synthetic bubbles or beads 70 (Fig. 3a to Fig. 5d) that are constructed to be buoyant when submerged in the pulp slurry or mixture 14 and functionalized to control the chemistry of a process being performed in the flotation cell or column, including to attach to the valuable material in the pulp slurry or mixture 14; and provide enriched synthetic bubble or beads 18 having the valuable material attached thereon. The terms “synthetic bubbles or beads” and “polymer bubbles or beads” are used interchangeably in this disclosure. The terms “valuable material”, “valuable mineral” and “mineral particle” are also used interchangeably. By way of example, the synthetic bubbles or beads 70 may be made from polymer or polymer-based materials, or silica or silica-based materials, or glass or glass-based materials, although the scope of the invention is intended to include other types or kinds of material either now known or later developed in the future. For the purpose of describing one example of the present invention, in Figure 1 the synthetic bubbles or beads 70 and the enriched synthetic bubble or beads 18 are shown as enriched polymer or polymer-based bubbles labeled 18. The flotation cell or column 12 is configured with a top portion or piping 20 to provide the enriched polymer or polymer-based bubbles 18 from the flotation cell or column 12 for further processing consistent with that set forth herein.

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The flotation cell or column 12 may be configured with a top part or piping 22, e.g., having a valve 22a, to receive the pulp slurry or mixture 14 and also with a bottom part or piping 24 to receive the synthetic bubbles or beads 70. In operation, the buoyancy of the synthetic bubbles or beads 70 causes them to float upwardly

5 from the bottom to the top of the flotation cell or column 12 through the pulp slurry or mixture 14 in the flotation cell or column 12 so as to collide with the water, valuable material and unwanted material in the pulp slurry or mixture 14. The functionalization of the synthetic bubbles or beads 70 causes them to attach to the valuable material in the pulp slurry or mixture 14. As used herein, the term

10 “functionalization” means that the properties of the material making up the synthetic bubbles or beads 70 are either selected (based upon material selection) or modified during manufacture and fabrication, to be “attracted” to the valuable material, so that a bond is formed between the synthetic bubbles or beads 70 and the valuable material, so that the valuable material is lifted through the cell or column 12 due to

15 the buoyancy of the synthetic bubbles or beads 70. For example, the surface of synthetic bubbles or beads has functional groups for collecting the valuable material. Alternatively, the synthetic bubbles or beads are functionalized to be hydrophobic for attracting wetted mineral particles – those mineral particles having collector molecules attached thereto. As a result of the collision between the synthetic

20 bubbles or beads 70 and the water, valuable material and unwanted material in the pulp slurry or mixture 14, and the attachment of the synthetic bubbles or beads 70 and the valuable material in the pulp slurry or mixture 14, the enriched polymer or polymer-based bubbles 18 having the valuable material attached thereto will float to the top of the flotation cell 12 and form part of the froth formed at the top of the

25 flotation cell 12. The flotation cell 12 may include a top part or piping 20 configured

to provide the enriched polymer or polymer-based bubbles 18 having the valuable material attached thereto, which may be further processed consistent with that set forth herein. In effect, the enriched polymer or polymer-based bubbles 18 may be taken off the top of the flotation cell 12 or may be drained off by the top part or  
5 piping 20.

The flotation cell or column 12 may be configured to contain an attachment rich environment, including where the attachment rich environment has a high pH, so as to encourage the flotation recovery process therein. The flotation recovery process may include the recovery of ore particles in mining, including copper. The  
10 scope of the invention is not intended to be limited to any particular type or kind of flotation recovery process either now known or later developed in the future. The scope of the invention is also not intended to be limited to any particular type or kind of mineral of interest that may form part of the flotation recovery process either now known or later developed in the future.

15 According to some embodiments of the present invention, the synthetic bubbles or beads 70 may be configured with a surface area flux by controlling some combination of the size of the polymer or polymer-based bubbles and/or the injection rate that the pulp slurry or mixture 14 is received in the flotation cell or column 12. The synthetic bubbles or beads 70 may also be configured with a low density so as  
20 to behave like air bubbles. The synthetic bubbles or beads 70 may also be configured with a controlled size distribution of medium that may be customized to maximize recovery of different feed matrixes to flotation as valuable material quality changes, including as ore quality changes.

According to some embodiments of the present invention, the flotation cell or  
25 column 12 may be configured to receive the synthetic bubbles or beads 70 together

with air, where the air is used to create a desired froth layer in the mixture in the flotation cell or column 12 in order to achieve a desired grade of valuable material. The synthetic bubbles or beads 70 may be configured to lift the valuable material to the surface of the mixture in the flotation cell or column.

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#### The Thickener 28

The apparatus 10 may also include piping 26 having a valve 26a for providing tailings to a thickener 28 configured to receive the tailings from the flotation cell or column 12. The thickener 28 includes piping 30 having a valve 30a to provide  
10 thickened tailings. The thickener 28 also includes suitable piping 32 for providing reclaimed water back to the flotation cell or column 12 for reuse in the process. Thickeners like element 28 are known in the art, and the scope of the invention is not intended to be limited to any particular type or kind either now known or later developed in the future.

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#### The Bead Recovery Process or Processor 50

According to some embodiments of the present invention, the apparatus 10 may further comprises a bead recovery process or processor generally indicated as  
50 configured to receive the enriched polymer or polymer-based bubbles 18 and  
20 provide reclaimed polymer or polymer-based bubbles 52 without the valuable material attached thereon so as to enable the reuse of the polymer or polymer-based bubbles 52 in a closed loop process. By way of example, the bead recovery

process or processor 50 may take the form of a washing station whereby the valuable mineral is mechanically, chemically, or electro-statically removed from the polymer or polymer-based bubbles 18.

The bead recovery process or processor 50 may include a releasing  
5 apparatus in the form of a second flotation cell or column 54 having piping 56 with a valve 56a configured to receive the enriched polymer bubbles or beads 18; and substantially release the valuable material from the polymer bubbles or beads 18, and also having a top part or piping 57 configured to provide the reclaimed polymer bubbles or beads 52, substantially without the valuable material attached thereon  
10 The second flotation cell or column 54 may be configured to contain a release rich environment, including where the release rich environment has a low pH, or including where the release rich environment results from ultrasonic waves pulsed into the second flotation cell or column 54.

The bead recovery process or processor 50 may also include piping 58  
15 having a valve 56a for providing concentrated minerals to a thickener 60 configured to receive the concentrated minerals from the flotation cell or column 54. The thickener 60 includes piping 62 having a valve 62a to provide thickened concentrate. The thickener 60 also includes suitable piping 64 for providing reclaimed water back to the second flotation cell or column 54 for reuse in the process. Thickeners like  
20 element 60 are known in the art, and the scope of the invention is not intended to be limited to any particular type or kind either now known or later developed in the future.

Embodiments are also envisioned in which the enriched synthetic beads or bubbles are placed in a chemical solution so the valuable material is dissolved off, or are sent to a smelter where the valuable material is burned off, including where the synthetic beads or bubbles are reused afterwards.

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#### Dosage control

According to some embodiments of the present invention, the synthetic beads or bubbles 70 may be functionalized to control the chemistry of the process being performed in the cell or column, e.g. to release a chemical to control the chemistry of the flotation separation process.

In particular, the flotation cell or column 12 in Figure 1 may be configured to receive polymer-based blocks like synthetic beads containing one or more chemicals used in a flotation separation of the valuable material, including mining ores, that are encapsulated into polymers to provide a slow or targeted release of the chemical once released into the flotation cell or column 12. By way of example, the one or more chemicals may include chemical mixes both now known and later developed in the future, including typical frothers, collectors and other additives used in flotation separation. The scope of the invention is not intended to be limited to the type or kind of chemicals or chemical mixes that may be released into the flotation cell or column 12 using the synthetic bubbles according to the present invention.

The scope of the invention is intended to include other types or kinds of functionalization of the synthetic beads or bubbles in order to provide other types or kinds of control of the chemistry of the process being performed in the cell or column, including either functionalizations and controls both now known and later developed in the future. For example, the synthetic beads or bubbles may be

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functionalized to control the pH of the mixture that forms part of the flotation separation process being performed in the flotation cell or column.

#### Figure 2: The Collision Technique

5           Figure 2 shows alternative apparatus generally indicated as 200 in the form of an alternative flotation cell 201 that is based at least partly on a collision technique between the mixture and the synthetic bubbles or beads, according to some embodiments of the present invention. The mixture 202, e.g. the pulp slurry, may be received in a top part or piping 204, and the synthetic bubbles or beads 206 may be  
10 received in a bottom part or piping 208. The flotation cell 201 may be configured to include a first device 210 for receiving the mixture 202, and also may be configured to include a second device 212 for receiving the polymer-based materials. The first device 210 and the second device 212 are configured to face towards one another so as to provide the mixture 202 and the synthetic bubbles or beads 206, e.g.,  
15 polymer or polymer-based materials, using the collision technique. In Figure 2, the arrows 210a represent the mixture being sprayed, and the arrows 212a represent the synthetic bubbles or beads 206 being sprayed towards one another in the flotation cell 201.

In operation, the collision technique causes vortices and collisions using  
20 enough energy to increase the probability of touching of the polymer or polymer-based materials 206 and the valuable material in the mixture 202, but not too much energy to destroy bonds that form between the polymer or polymer-based materials 206 and the valuable material in the mixture 202. Pumps, not shown, may be used to provide the mixture 202 and the synthetic bubbles or beads 206 are the  
25 appropriate pressure in order to implement the collision technique.

By way of example, the first device 210 and the second device 212 may take the form of shower-head like devices having a perforated nozzle with a multiplicity of holes for spraying the mixture and the synthetic bubbles or beads towards one another. Shower-head like devices are known in the art, and the scope of the invention is not intended to be limited to any particular type or kind thereof either now known or later developed in the future. Moreover, based on that disclosed in the instant patent application, a person skilled in the art without undue experimentation would be able to determine the number and size of the holes for spraying the mixture 202 and the synthetic bubbles or beads 206 towards one another, as well as the appropriate pumping pressure in order to provide enough energy to increase the probability of touching of the polymer or polymer-based materials 206 and the valuable material in the mixture 202, but not too much energy to destroy bonds that form between the polymer or polymer-based materials 206 and the valuable material in the mixture 202.

As a result of the collision between the synthetic bubbles or beads 206 and the mixture, enriched synthetic bubbles or beads having the valuable material attached thereto will float to the top and form part of the froth in the flotation cell 201. The flotation cell 201 may include a top part or piping 214 configured to provide enriched synthetic bubbles or beads 216, e.g., enriched polymer bubbles as shown, having the valuable material attached thereto, which may be further processed consistent with that set forth herein.

The alternative apparatus 200 may be used in place of the flotation columns or cells, and inserted into the apparatus or system shown in Figure 1, and may prove to be more efficient than using the flotation columns or cells.

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## Figures 3a-5d: The Synthetic Bubbles or Beads

The bubbles or beads used in mineral separation are referred herein as synthetic bubbles or beads. At least the surface of the synthetic bubbles or beads has a layer of polymer functionalized to attract or attach to the value material or mineral particles in the mixture. The term "polymer bubbles or beads", and the term "synthetic bubbles or beads" are used interchangeably. The term "polymer" in this specification means a large molecule made of many units of the same or similar structure linked together. The unit can be a monomer or an oligomer which forms the basis of, for example, polyamides (nylon), polyesters, polyurethanes, phenol-formaldehyde, urea-formaldehyde, melamine-formaldehyde, polyacetal, polyethylene, polyisobutylene, polyacrylonitrile, poly(vinyl chloride), polystyrene, poly(methyl methacrylates), poly(vinyl acetate), poly(vinylidene chloride), polyisoprene, polybutadiene, polyacrylates, poly(carbonate), phenolic resin, polydimethylsiloxane and other organic or inorganic polymers. The list is not necessarily exhaustive. Thus, the synthetic material can be hard or rigid like plastic or soft and flexible like an elastomer. While the physical properties of the synthetic beads can vary, the surface of the synthetic beads is chemically functionalized to provide a plurality of functional groups to attract or attach to mineral particles. (By way of example, the term "functional group" may be understood to be a group of

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atoms responsible for the characteristic reactions of a particular compound, including those define the structure of a family of compounds and determine its properties.)

For aiding a person of ordinary skill in the art in understanding various  
5 embodiments of the present invention, Figure 3a shows a generalized synthetic bead and Figure 3b shows an enlarged portion of the surface. The synthetic bead can be a size-based bead or bubble, weight-based polymer bead and bubble, and/or magnetic-based bead and bubble. As shown in Figures 3a and 3b, the synthetic bead 70 has a bead body to provide a bead surface 74. At least the outside part of  
10 the bead body is made of a synthetic material, such as polymer, so as to provide a plurality of molecules or molecular segments 76 on the surface 74. The molecule 76 is used to attach a chemical functional group 78 to the surface 74. In general, the molecule 76 can be a hydrocarbon chain, for example, and the functional group 78 can have an anionic bond for attracting or attaching a mineral, such as copper to the  
15 surface 74. A xanthate, for example, has both the functional group 78 and the molecular segment 76 to be incorporated into the polymer that is used to make the synthetic bead 70. A functional group 78 is also known as a collector that is either ionic or non-ionic. The ion can be anionic or cationic. An anion includes oxyhydril, such as carboxylic, sulfates and sulfonates, and sulfhydryl, such as xanthates and  
20 dithiophosphates. Other molecules or compounds that can be used to provide the function group 78 include, but are not limited to, thionocarboamates, thioureas, xanthogens, monothiophosphates, hydroquinones and polyamines. Similarly, a chelating agent can be incorporated into or onto the polymer as a collector site for attracting a mineral, such as copper. As shown in Figure 3b, a mineral particle 72 is  
25 attached to the functional group 78 on a molecule 76. In general, the mineral

particle 72 is much smaller than the synthetic bead 70. Many mineral particles 72 can be attracted to or attached to the surface 74 of a synthetic bead 70.

In some embodiments of the present invention, a synthetic bead has a solid-phase body made of a synthetic material, such as polymer. The polymer can be  
5 rigid or elastomeric. An elastomeric polymer can be polyisoprene or polybutadiene, for example. The synthetic bead 70 has a bead body 80 having a surface comprising a plurality of molecules with one or more functional groups for attracting mineral particles to the surface. A polymer having a functional group to collect  
10 entire interior part 82 of the synthetic bead 80 is made of the same functionalized material, as shown in Figure 4a. In another embodiment, the bead body 80 comprises a shell 84. The shell 84 can be formed by way of expansion, such as thermal expansion or pressure reduction. The shell 84 can be a micro-bubble or a balloon. In Figure 4b, the shell 84, which is made of functionalized material, has an  
15 interior part 86. The interior part 86 can be filled with air or gas to aid buoyancy, for example. The interior part 86 can be used to contain a liquid to be released during the mineral separation process. The encapsulated liquid can be a polar liquid or a non-polar liquid, for example. The encapsulated liquid can contain a depressant composition for the enhanced separation of copper, nickel, zinc, lead in sulfide ores  
20 in the flotation stage, for example. The shell 84 can be used to encapsulate a powder which can have a magnetic property so as to cause the synthetic bead to be magnetic, for example. The encapsulated liquid or powder may contain monomers, oligomers or short polymer segments for wetting the surface of mineral particles when released from the beads. For example, each of the monomers or oligomers  
25 may contain one functional group for attaching to a mineral particle and an ion for

attaching the wetted mineral particle to the synthetic bead. The shell 84 can be used to encapsulate a solid core, such as Styrofoam to aid buoyancy, for example. In yet another embodiment, only the coating of the bead body is made of functionalized polymer. As shown in Figure 4c, the synthetic bead has a core 90 made of ceramic, glass or metal and only the surface of core 90 has a coating 88 made of functionalized polymer. The core 90 can be a hollow core or a filled core depending on the application. The core 90 can be a micro-bubble, a sphere or balloon. For example, a filled core made of metal makes the density of the synthetic bead to be higher than the density of the pulp slurry, for example. The core 90 can be made of a magnetic material so that the para-, ferri-, ferro-magnetism of the synthetic bead is greater than the para-, ferri-, ferro-magnetism of the unwanted ground ore particle in the mixture. In a different embodiment, the synthetic bead can be configured with a ferro-magnetic or ferri-magnetic core that attract to paramagnetic surfaces. A core 90 made of glass or ceramic can be used to make the density of the synthetic bead substantially equal to the density of the pulp slurry so that when the synthetic beads are mixed into the pulp slurry for mineral collection, the beads can be in a suspension state.

According to a different embodiment of the present invention, the synthetic bead 70 can be a porous block or take the form of a sponge or foam with multiple segregated gas filled chambers. The combination of air and the synthetic beads or bubbles 70 can be added to traditional naturally aspirated flotation cell.

It should be understood that the term "bead" does not limit the shape of the synthetic bead of the present invention to be spherical, as shown in Figure 3. In some embodiments of the present invention, the synthetic bead 70 can have an

elliptical shape, a cylindrical shape, a shape of a block. Furthermore, the synthetic bead can have an irregular shape.

It should also be understood that the surface of a synthetic bead, according to the present invention, is not limited to an overall smooth surface as shown in Figure 3a. In some embodiments of the present invention, the surface can be irregular and rough. For example, the surface 74 can have some physical structures 92 like grooves or rods as shown in Figure 5a. The surface 74 can have some physical structures 94 like holes or dents as shown in Figure 5b. The surface 74 can have some physical structures 96 formed from stacked beads as shown in Figure 5c. The surface 74 can have some hair-like physical structures 98 as shown in Figure 5d. In addition to the functional groups on the synthetic beads that attract mineral particles to the bead surface, the physical structures can help trapping the mineral particles on the bead surface. The surface 74 can be configured to be a honeycomb surface or sponge-like surface for trapping the mineral particles and/or increasing the contacting surface.

It should also be noted that the synthetic beads of the present invention can be realized by a different way to achieve the same goal. Namely, it is possible to use a different means to attract the mineral particles to the surface of the synthetic beads. For example, the surface of the polymer beads, shells can be functionalized with a hydrophobic chemical molecule or compound. Alternatively, the surface of beads made of glass, ceramic and metal can be coated with hydrophobic chemical molecules or compounds. Using the coating of glass beads as an example, polysiloxanates can be used to functionalize the glass beads in order to make the synthetic beads. In the pulp slurry, xanthate and hydroxamate collectors can also be added therein for collecting the mineral particles and making the mineral particles

hydrophobic. When the synthetic beads are used to collect the mineral particles in the pulp slurry having a pH value around 8-9, it is possible to release the mineral particles on the enriched synthetic beads from the surface of the synthetic beads in an acidic solution, such as a sulfuric acid solution. It is also possible to release the mineral particles carrying with the enriched synthetic beads by sonic agitation, such as ultrasonic waves.

The multiplicity of hollow objects, bodies, elements or structures may include hollow cylinders or spheres, as well as capillary tubes, or some combination thereof. The scope of the invention is not intended to be limited to the type, kind or geometric shape of the hollow object, body, element or structure or the uniformity of the mixture of the same. Each hollow object, body, element or structure may be configured with a dimension so as not to absorb liquid, including water, including where the dimension is in a range of about 20-30 microns. Each hollow object, body, element or structure may be made of glass or a glass-like material, as well as some other suitable material either now known or later developed in the future.

By way of example, the multiplicity of hollow objects, bodies, elements or structures that are received in the mixture may include a number in a range of multiple thousands of bubbles or beads per cubic foot of mixture, although the scope of the invention is not intended to be limited per se to the specific number of bubbles. For instance, a mixture of about three thousand cubic feet may include multiple millions of bubbles or beads, e.g., having a size of about 1 millimeter, in three thousand cubic feet of the mixture.

The multiplicity of hollow objects, bodies, elements or structures may be configured with chemicals applied to prevent migration of liquid into respective



and a stirrer 188 (Figure 10) configured to stir the enriched synthetic beads or bubbles for the removal of the valuable minerals from the enriched synthetic beads or bubbles; and multiple release or recovery processors (Figure 11) configured to use multiple release or recovery techniques for the removal of the valuable minerals  
5 from the enriched synthetic beads or bubbles. According to some embodiments of the present invention, the aforementioned releasing apparatus may be responsive to signalling, e.g., from a controller or control processor. In view of the aforementioned, and by way of example, the releasing techniques are set forth in detail below:

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#### Thermally Releasing Valuable Material

The synthetic beads or bubbles 70, as shown in Figure 3a to 5c, can be made of a polymer which is softened when subjected to elevated temperature. It is known that a polymer may become rubbery above a certain temperature. This is due to the  
15 polymer-glass transition at a glass transition temperature,  $T_g$ . In general, the physical properties of a polymer are dependent on the size or length of the polymer chain. In polymers above a certain molecular weight, increasing chain length tends to increase the glass transition temperature  $T_g$ . This is a result of the increase in chain interactions such as Van der Waals attractions and entanglements that may  
20 come with increased chain length. A polymer such as polyvinyl chloride (PVC), has a glass transition temperature around 83 degrees Celsius. If the polymer bubbles or beads 70 have a hair-like surface structures 98 (see Figure 5d) in order to trap the mineral particles 72 (see Figure 3b), the hair-like surface structures 98 could become soft. Thus, in a certain polymer at the rubbery state, the hair-like surface  
25 structures 98 could lose the ability of holding the mineral particles. Since the

separation process as shown in Figures 1 and 2 is likely to take place in room temperature or around 23 degrees Celsius. Any temperature, say, higher than 50 degrees Celsius, could soften the hair-like surface structures 98 (see Figure 5d). For synthetic bubbles or beads 70 made of PVC, a temperature around or higher than 83 degrees Celsius can be used to dislodge the mineral particles from the surface structure of the synthetic bubbles or beads. According to one embodiment of the present invention, the bead recovery process or processor 50 as shown in Figure 1 can be adapted for removing the mineral particles in the enriched polymer bubbles 18. For example, as the reclaimed water is moved out of the thickener 60 through piping 64, a heater 150 can be used to heat the reclaimed water as shown in Figure 6. As such, the heated reclaimed water 152 can be arranged to wash the enriched polymer bubbles 18 inside the flotation column 54, thereby releasing at least some of the valuable material or mineral particles attached on the enriched polymer bubbles 18 to piping 58. It is possible to heat the reclaimed water to or beyond the glass transition temperature of the polymer that is used to make the polymer bubbles. The elevated temperature of the heated reclaimed water 152 could also weaken the bonds between the collectors 78 and the mineral particles 72 (see Figure 3b). It is possible to use a heater to boil the water into steam and to apply the steam to the enriched polymer bubbles. It is also possible to generate superheated steam under a pressure and to apply the superheated steam to the enriched polymer bubbles.

#### Sonically Releasing Valuable Material

When ultrasonic waves are applied in a solution or mixture containing the enriched polymer bubbles or beads, at least two possible effects could take place in

interrupting the attachment of the valuable material to the surface of the polymer bubbles or beads. The sound waves could cause the attached mineral particles to move rapidly against the surface of the polymer bubbles or beads, thereby shaking the mineral particles loose from the surface. The sound waves could also cause a

5 shape change to the synthetic bubbles, affecting the physical structures on the surface of the synthetic bubbles. It is known that ultrasound is a cyclic sound pressure with a frequency greater than the upper limit of human hearing. Thus, in general, ultrasound goes from just above 20 kilohertz (KHz) all the way up to about 300KHz. In ultrasonic cleaners, low frequency ultrasonic cleaners have a tendency

10 to remove larger particle sizes more effectively than higher operational frequencies. However, higher operational frequencies tend to produce a more penetrating scrubbing action and to remove particles of a smaller size more effectively. In mineral releasing applications involving mineral particles finer than 100 $\mu$ m to 1mm or larger, according to some embodiments of the present invention, the ultrasonic wave

15 frequencies range from 10Hz to 10MHz. By way of example, the bead recovery process or processor 50 as shown in Figure 1 can be adapted for removing the mineral particles in the enriched polymer bubbles 18 by applying ultrasound to the solution in the flotation column 54. For example, as the reclaimed water from piping

20 64 is used to wash the enriched polymer bubbles 18 inside the flotation column 54, it is possible to use an ultrasonic wave producer 164 to apply the ultrasound 166 in order to release the valuable material (mineral particles 72, Figure 3b) from the enriched polymer bubbles 18. A diagram illustrating the ultrasonic application is shown in Figure 7. According to some embodiments of the present application, an ultrasonic frequency that is the resonant frequency of the synthetic beads or bubbles

25 is selected for mineral releasing applications.

### Chemically Releasing Valuable Material

In physisorption, the valuable minerals are reversibly associated with the synthetic bubbles or beads, attaching due to electrostatic attraction or van der Waals bonding. The physisorbed mineral particles can be desorbed or released from the surface of the synthetic bubbles or beads if the pH value of the solution changes. Furthermore, the surface chemistry of the most minerals is affected by the pH. Some minerals develop a positive surface charge under acidic conditions and a negative charge under alkaline conditions. The effect of pH changes is generally dependent on the collector and the mineral collected. For example, chalcopyrite becomes desorbed at a higher pH value than galena, and galena becomes desorbed at a higher pH value than pyrite. If the valuable mineral is collected at a pH of 8 to 11, it is possible to weaken the bonding between the valuable mineral and the surface of the polymer bubbles or beads by lower the pH to 7 and lower. However, an acidic solution having a pH value of 5 or lower would be more effective in releasing the valuable mineral from the enriched polymer bubbles or beads. According to one embodiment of the present invention, the bead recovery process or processor 50 as shown in Figure 1 can be adapted for removing the mineral particles in the enriched polymer bubbles 18 by changing the pH of the solution in the flotation column 54. For example, as the reclaimed water from piping 64 is used to wash the enriched polymer bubbles 18 inside the flotation column 54, it is possible to use a container 168 to release an acid or acidic solution 170 into the reclaimed water as shown in Figure 8. There are a number of acids easily available for changing the pH. For example, sulfuric acid (HCl), hydrochloric acid (H<sub>2</sub>SO<sub>4</sub>), nitric acid (HNO<sub>3</sub>), perchloric acid (HClO<sub>4</sub>), hydrobromic acid (HBr) and hydroiodic

acid (HI) are among the strong acids that completely dissociate in water. However, sulfuric acid and hydrochloric acid can give the greater pH change at the lowest cost. The pH value used for mineral releasing ranges from 7 to 0. Using a very low pH may cause the polymer beads to degrade. It should be noted that, however, 5 when the valuable material is copper, for example, it is possible to provide a lower pH environment for the attachment of mineral particles and to provide a higher pH environment for the releasing of the mineral particles from the synthetic beads or bubbles.

In general, the pH value is chosen to facilitate the strongest attachment, and a 10 different pH value is chosen to facilitate release. Thus, according to some embodiments of the present invention, one pH value is chosen for mineral attachment, and a different pH value is chosen for mineral releasing. The different pH could be higher or lower, depending on the specific mineral and collector.

#### 15 Electromagnetically Releasing Valuable Material

More than one way can be used to interrupt the bonding between the mineral particles and the synthetic bubbles or beads electromagnetically. For example, it is possible to use microwaves to heat up the enriched synthetic bubbles or beads and the water in the flotation column. It is also possible use a laser beam to weaken the 20 bonds between the functional groups and the polymer surface itself. Thus, it is possible to provide a microwave source or a laser light source where the enriched synthetic bubbles or beads are processed. By way of example, the bead recovery process or processor 50 as shown in Figure 1 can be adapted for removing the mineral particles in the enriched polymer bubbles 18 by using an electromagnetic 25 source to provide electromagnetic waves to the solution or mixture in the flotation

column 54. For example, as the reclaimed water from piping 64 is used to wash the enriched polymer bubbles 18 inside the flotation column 54, it is possible to use a microwave source 172 to apply the microwave beam 174 in order to release the valuable material (mineral particles 72, Figure 3b) from the enriched polymer bubbles 18. A diagram illustrating the ultrasonic application is shown in Figure 9.

#### Mechanically Releasing Valuable Material

When the enriched synthetic bubbles or beads are densely packed such that they are in a close proximity to each other, the rubbing action among adjacent synthetic bubbles or beads may cause the mineral particles attached to the enriched synthetic bubbles or beads to be detached. By way of example, the bead recovery process or processor 50 as shown in Figure 1 can be adapted for removing the mineral particles in the enriched polymer bubbles 18 mechanically. For example, a motor 186 and a stirrer 188 are used to move the enriched polymer bubbles around, causing the enriched polymer bubbles or beads 18 inside the flotation column 54 to rub against each other. If the synthetic bubbles or beads are magnetic, the stirrer 188 can be a magnetic stirrer. A diagram illustrating a mechanical release of valuable material is shown in Figure 10.

#### Other Types or Kinds of Release Techniques

A heater like element 150 (Figure 6), an ultrasonic wave producer like element 164 (Figure 7), a container like element 168 (Figure 8), a microwave source like element 172 (Figure 9), a motor and stirrer like elements 186 188 (Figure 10) are known in the art, and the scope of the invention is not intended to be limited to any particular type or kind thereof either now known or later developed in the future.



Figure 12: Horizontal Pipeline

According to some embodiments of the present invention, the separation process can be carried out in a horizontal pipeline as shown in Figure 12. As shown in Figure 12, the synthetic bubbles or beads 308 may be used in, or form part of, a size-based separation process using countercurrent flows with mixing implemented in apparatus such as a horizontal pipeline generally indicated as 300. In Figure 12, the horizontal pipeline 310 is configured with a screen 311 to separate the enriched synthetic bubbles or beads 302 having the valuable material attached thereto from the mixture based at least partly on the difference in size. The horizontal pipeline 10 310 may be configured to separate the enriched synthetic bubbles or beads 302 having the valuable material attached thereto from the mixture using countercurrent flows with mixing, so as to receive in the horizontal pipeline 310 slurry 304 flowing in a first direction A, receive in the horizontal pipeline 300 synthetic bubbles or beads 308 flowing in a second direction B opposite to the first direction A, provide from the 15 horizontal pipeline 308 the enriched synthetic bubbles or beads 302 having the valuable material attached thereto and flowing in the second direction B, and provide from the horizontal pipeline 310 waste or tailings 306 that is separated from the mixture using the screen 311 and flowing in the second direction B. In a horizontal pipeline 310, it is not necessary that the synthetic beads or bubbles 308 be lighter 20 than the slurry 304. The density of the synthetic beads or bubbles 308 can be substantially equal to the density of the slurry 304 so that the synthetic beads or bubbles can be in a suspension state while they are mixed with slurry 304 in the horizontal pipeline 310.

It should be understood that the sized-based bead or bubble, weight-based 25 bead or bubble, magnetic-based bead or bubble as described in conjunction with

Figures 3a-5d can be functionalized to be hydrophobic so as to attract mineral particles. Figure 13a shows a generalized hydrophobic synthetic bead, Figure 13b shows an enlarged portion of the bead surface and a mineral particle, and Figure 13c shows an enlarged portion of the bead surface and a non-mineral particle. As shown in Figure 13a the hydrophobic synthetic bead 170 has a polymer surface 174 and a plurality of particles 172, 172' attached to the polymer surface 174. Figure 13b shows an enlarged portion of the polymer surface 174 on which a plurality of molecules 179 rendering the polymer surface 174 hydrophobic.

A mineral particle 171 in the slurry, after combined with one or more collector molecules 73, becomes a wetted mineral particle 172. The collector molecule 73 has a functional group 78 attached to the mineral particle 171 and a hydrophobic end or molecular segment 76. The hydrophobic end or molecular segment 76 is attracted to the hydrophobic molecules 179 on the polymer surface 174. Figure 13c shows an enlarged portion of the polymer surface 174 with a plurality of hydrophobic molecules 179 for attracting a non-mineral particle 172'. The non-mineral particle 172' has a particle body 171' with one or more hydrophobic molecular segments 76 attached thereto. The hydrophobic end or molecular segment 76 is attracted to the hydrophobic molecules 179 on the polymer surface 174. The term "polymer" in this specification means a large molecule made of many units of the same or similar structure linked together. Furthermore, the polymer associated with Figures 13a-13c can be naturally hydrophobic or functionalized to be hydrophobic. Some polymers having a long hydrocarbon chain or silicon-oxygen backbone, for example, tend to be hydrophobic. Hydrophobic polymers include polystyrene, poly(d,l-lactide), poly(dimethylsiloxane), polypropylene, polyacrylic, polyethylene, etc. The bubbles or beads, such as synthetic bead 170 can be made of glass to be coated with

hydrophobic silicone polymer including polysiloxanates so that the bubbles or beads become hydrophobic. The bubbles or beads can be made of metal to be coated with silicone alkyd copolymer, for example, so as to render the bubbles or beads hydrophobic. The bubbles or beads can be made of ceramic to be coated with  
5 fluoroalkylsilane, for example, so as to render the bubbles and beads hydrophobic. The bubbles or beads can be made of hydrophobic polymers, such as polystyrene and polypropylene to provide a hydrophobic surface. The wetted mineral particles attached to the hydrophobic synthetic bubble or beads can be released thermally, ultrasonically, electromagnetically, mechanically or in a low pH environment.

10 Figure 14a illustrates a scenario where a mineral particle 72 is attached to a number of synthetic beads 74 at the same time. Thus, although the synthetic beads 74 are much smaller in size than the mineral particle 72, a number of synthetic beads 74 may be able to lift the mineral particle 72 upward in a flotation cell. Likewise, a smaller mineral particle 72 can also be lifted upward by a number of  
15 synthetic beads 74 as shown in Figure 14b. In order to increase the likelihood for this "cooperative" lifting to occur, a large number of synthetic beads 74 can be mixed into the slurry. Unlike air bubbles, the density of the synthetic beads can be chosen such that the synthetic beads may stay along in the slurry before they rise to surface in a flotation cell.

20 Figures 15a and 15b illustrate a similar scenario. As shown, a wetted mineral particle 172 is attached to a number of hydrophobic synthetic beads 174 at the same time.

According to some embodiments of the present invention, only a portion of the surface of the synthetic bead is functionalized to be hydrophobic. This has the  
25 benefits as follows:

1. Keeps too many beads from clumping together – or limits the clumping of beads,

2. Once a mineral is attached, the weight of the mineral is likely to force the bead to rotate, allowing the bead to be located under the bead as it rises through the flotation cell;

a. Better cleaning as it may let the gangue to pass through

b. Protects the attached mineral particle or particles from being knocked off, and

c. Provides clearer rise to the top collection zone in the flotation cell.

10

According to some embodiments of the present invention, only a portion of the surface of the synthetic bead is functionalized with collectors. This also has the benefits of

1. Once a mineral is attached, the weight of the mineral is likely to force the bead to rotate, allowing the bead to be located under the bead as it rises through the flotation cell;

a. Better cleaning as it may let the gangue to pass through

b. Protects the attached mineral particle or particles from being knocked off, and

c. Provides clearer rise to the top collection zone in the flotation cell.

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According to some embodiments of the present invention, one part of the synthetic bead is functionalized with collectors while another part of same synthetic bead is functionalized to be hydrophobic as shown in Figures 16a and 16b. As shown in Figure 16a, a synthetic bead 74 has a surface portion where polymer is

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functionalized to have collector molecules 73 with functional group 78 and molecular segment 76 attached to the surface of the bead 74. The synthetic bead 74 also has a different surface portion where polymer is functionalized to have hydrophobic molecules 179. In the embodiment as shown in Figure 16b, the entire surface of the synthetic bead 74 can be functionalized to have collector molecules 73, but a portion of the surface is functionalized to have hydrophobic molecules 179 render it hydrophobic.

This "hybrid" synthetic bead can collect mineral particles that are wet and not wet.

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### Applications

The scope of the invention is described in relation to mineral separation, including the separation of copper from ore. It should be understood that the synthetic beads according to the present invention, whether functionalized to have a collector or functionalized to be hydrophobic, are also configured for use in oilsands separation – to separate bitumen from sand and water in the recovery of bitumen in an oilsands mining operation. Likewise, the functionalized filters and membranes, according to some embodiments of the present invention, are also configured for oilsands separation.

According to some embodiments of the present invention, the surface of a synthetic bead can be functionalized to have a collector molecule. The collector has a functional group with an ion capable of forming a chemical bond with a mineral particle. A mineral particle associated with one or more collector molecules is referred to as a wetted mineral particle. According to some embodiments of the

present invention, the synthetic bead can be functionalized to be hydrophobic in order to collect one or more wetted mineral particles.

The scope of the invention is intended to include other types or kinds of applications either now known or later developed in the future, e.g., including a  
5 flotation circuit, leaching, smelting, a gravity circuit, a magnetic circuit, or water pollution control.

#### The Scope of the Invention

It should be further appreciated that any of the features, characteristics,  
10 alternatives or modifications described regarding a particular embodiment herein may also be applied, used, or incorporated with any other embodiment described herein. In addition, it is contemplated that, while the embodiments described herein are useful for homogeneous flows, the embodiments described herein can also be used for dispersive flows having dispersive properties (e.g., stratified flow). Although  
15 the invention has been described and illustrated with respect to exemplary embodiments thereof, the foregoing and various other additions and omissions may be made therein and thereto without departing from the spirit and scope of the present invention.

What is claimed is:

1. Apparatus comprising:

a first cell configured to receive an ore slurry having mineral particles of interest, to receive unexpanded polymer microspheres comprising a surface having mineral collector chemistry attached thereto with molecules for attaching the mineral particles of interest, to cause the unexpanded polymer microspheres to expand substantially in volume into expanded polymer microspheres having a substantially increased sphere surface area, and to provide an expanded polymer microsphere foam layer comprising the expanded polymer microspheres with attached mineral particles of interest; and

a second cell configured to receive the expanded polymer microsphere foam layer, and to cause the expanded polymer microspheres to collapse substantially in volume into collapsed polymer microspheres having a substantially reduced sphere surface area that results in a mechanical shearing off of the attached mineral particles of interest.

2. Apparatus according to claim 1, wherein the first cell comprises a flotation cell.

3. Apparatus according to claim 1, wherein the first cell comprises an agitator configured to cause or induce agitation to mix the ore slurry and polymer microspheres.

4. Apparatus according to claim 1, wherein the unexpanded polymer microspheres are configured with a blowing agent encapsulated therein that has a

trigger temperature set below the predetermined temperature so as to cause the unexpanded polymer microspheres to expand substantially in volume into the expanded polymer microspheres having the substantially increased sphere surface area when received in the first cell.

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5. Apparatus according to claim 4, wherein the blowing agent comprises a liquid that responds to a change in temperature and transforms into a gas.

6. Apparatus according to claim 4, wherein the blowing agent comprises a  
10 gas that responds to a change in temperature and transforms from a low pressure phase into a high pressure phase.

7. Apparatus according to claim 1, wherein the first cell is configured to maintain the ore slurry at a predetermined temperature, and the unexpanded  
15 polymer microspheres are configured with a blowing agent encapsulated therein that has a trigger temperature set below the predetermined temperature so as to cause the unexpanded polymer microspheres to expand substantially in volume into the expanded polymer microspheres having the substantially increased sphere surface area when received in the first cell.

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8. Apparatus according to claim 7, wherein the unexpanded polymer microspheres are cooled or chilled to a temperature below the predetermined temperature prior to induction to the first cell.

9. Apparatus according to claim 1, wherein the expanded polymer microspheres are configured to become buoyant and create an increased bubble flux in the ore slurry, presenting surface area for mineral bearing particles to attach to and be lifted to the surface and form the expanded polymer microsphere foam  
5 layer.

10. Apparatus according to claim 1, wherein the expanded polymer microsphere foam layer takes the form of an agglomerated mass of expanded spheres on the surface to be skimmed and moved to, or spilled over into a spillover  
10 container and moved to, the second cell, including a release stage.

11. Apparatus according to claim 1, wherein the second cell comprises a release tank in the form of a re-pressurization cell tank or a condensation cell or tank configured to collapse the expanded polymer microspheres substantially in volume  
15 into the collapsed polymer microspheres that results in the mechanical shearing off of the attached mineral particles of interest.

12. Apparatus according to claim 4, wherein the second cell is configured to be filled with the expanded polymer microsphere foam layer or mineral rich foam,  
20 and to be pressurized to a nominally elevated level, or chilled to a lower temperature, such that the blowing agent reverses through a transition phase, including either returning from a gas phase to a liquid phase or returning from a high pressure phase to a low pressure phase.

13. Apparatus according to claim 1, wherein the mineral particles of interest separate from the collapsed polymer microspheres due to gravitation separation, including where minerals sink in the second cell and where the unexpanded polymer microspheres tend to remain nominally buoyant and float.

5

14. Apparatus according to claim 1, wherein the second cell is also configured to provide either a mineral concentrate output having the mineral particles of interest, or a discarded foam output having the collapsed polymer microspheres, or both.

10

15. Apparatus according to claim 1, wherein the molecules comprise a functional group having a chemical bond for attaching the mineral particles of interest.

15

16. Apparatus according to claim 1, wherein the volume of the expanded polymer microspheres is about 50 times the volume of the unexpanded polymer microspheres.

17. A method comprising:

in a first cell, receiving an ore slurry having mineral particles of interest,  
receiving unexpanded polymer microspheres comprising a surface having mineral  
collector chemistry attached thereto with molecules for attaching the mineral  
5 particles of interest, causing the unexpanded polymer microspheres to expand  
substantially in volume into expanded microspheres having a substantially increased  
sphere surface area, and providing an expanded polymer microsphere foam layer  
comprising the expanded polymer microspheres with attached mineral particles of  
interest; and

10 in a second cell, receiving the expanded polymer microsphere foam layer,  
and causing the expanded polymer microspheres to collapse substantially in volume  
into collapsed polymer microspheres having a substantially reduced sphere surface  
area that results in a mechanical shearing off of the attached mineral particles of  
interest.

15

18. A method according to claim 17, wherein the method comprises  
configuring the first cell a flotation cell.

19. A method according to claim 17, wherein the method comprises  
20 configuring the first cell with an agitator to cause or induce agitation to mix the ore  
slurry and polymer microspheres.

20. A method according to claim 17, wherein the method comprises  
configuring the unexpanded polymer microspheres with a blowing agent  
25 encapsulated therein that has a trigger temperature set below the predetermined

temperature so as to cause the unexpanded polymer microspheres to expand substantially in volume into the expanded polymer microspheres having the substantially increased sphere surface area when received in the first cell.

5           21. A method according to claim 20, wherein the method comprises configuring the blowing agent with a liquid that responds to a change in temperature and transforms into a gas.

          22. A method according to claim 20, wherein the method comprises  
10 configuring the blowing agent with a gas that responds to a change in temperature and transforms from a low pressure phase into a high pressure phase.

          23. A method according to claim 17, wherein the method comprises configuring the first cell to maintain the ore slurry at a predetermined temperature,  
15 and the unexpanded polymer microspheres are configured with a blowing agent encapsulated therein that has a trigger temperature set below the predetermined temperature so as to cause the unexpanded polymer microspheres to expand substantially in volume into the expanded polymer microspheres having the substantially increased sphere surface area when received in the first cell.

20

          24. A method according to claim 23, wherein the method comprises cooling or chilling the unexpanded polymer microspheres to a temperature below the predetermined temperature prior to induction to the first cell.

25. A method according to claim 17, wherein the method comprises configuring the expanded polymer microspheres to become buoyant and create an increased bubble flux in the ore slurry, presenting surface area for mineral bearing particles to attach to and be lifted to the surface and form the expanded polymer  
5 microsphere foam layer.

26. A method according to claim 17, wherein the expanded polymer microsphere foam layer takes the form of an agglomerated mass of expanded spheres on the surface to be skimmed and moved to, or spilled over into a spillover  
10 container and moved to, the second cell, including a release stage.

27. A method according to claim 17, wherein the method comprises configuring the second cell as a release tank in the form of a re-pressurization cell tank or a condensation cell or tank configured to collapse the expanded polymer  
15 microspheres substantially in volume into the collapsed polymer microspheres that results in the mechanical shearing off of the attached mineral particles of interest.

28. A method according to claim 20, wherein the method comprises filling the second cell with the expanded polymer microsphere foam layer or mineral rich foam,  
20 and pressurizing to a nominally elevated level, or chilled to a lower temperature, such that the blowing agent reverses through a transition phase, including either returning from a gas phase to a liquid phase or returning from a high pressure phase to a low pressure phase.

29. A method to claim 17, wherein the method comprises separating the mineral particles of interest from the collapsed polymer microspheres based at least partly on or due to gravitation separation, including where minerals sink in the second cell and where the unexpanded polymer microspheres tend to remain  
5 nominally buoyant and float.

30. A method according to claim 17, wherein the method comprises configuring the second cell to provide either a mineral concentrate output having the mineral particles of interest, or a discarded foam output having the collapsed  
10 polymer microspheres, or both.

31. A method according to claim 17, wherein the method comprises configuring the molecules with a functional group having a chemical bond for attaching the mineral particles of interest.  
15

32. A method according to claim 17, wherein the method comprises using polymer microspheres so that the volume of the expanded polymer microspheres is about 50 times the volume of the unexpanded polymer microspheres.

20 33. Apparatus comprising:  
means for receiving an ore slurry having mineral particles of interest,  
receiving unexpanded polymer microspheres comprising a surface having mineral collector chemistry attached thereto with molecules for attaching the mineral particles of interest, causing the unexpanded polymer microspheres to expand  
25 substantially in volume into expanded microspheres having a substantially increased

sphere surface area, and providing an expanded polymer microsphere foam layer comprising the expanded polymer microspheres with attached mineral particles of interest; and

means for receiving the expanded polymer microsphere foam layer, causing  
5 the expanded polymer microspheres to collapse substantially in volume into collapsed polymer microspheres having a substantially reduced sphere surface area that results in a mechanical shearing off of the attached mineral particles of interest, and providing a mineral concentrate output having the mineral particles of interest.

10 34. Apparatus comprising:

a first cell configured to receive an ore slurry having mineral particles of interest, to receive polymer microspheres comprising a surface having mineral collector chemistry attached thereto with molecules for attaching the mineral particles of interest, and to provide a polymer microsphere foam layer comprising the  
15 polymer microspheres with attached mineral particles of interest; and

a second cell configured to receive the polymer microsphere foam layer and to cause the polymer microspheres to collapse substantially in volume into collapsed polymer microspheres having a substantially reduced sphere surface area that results in a mechanical shearing off of the attached mineral particles of interest.

20

35. Apparatus according to claim 34, wherein the first cell is also configured to cause the polymer microspheres to expand substantially in volume into expanded polymer microspheres having a substantially increased sphere surface area.

36. Apparatus according to claim 34, wherein the first cell is configured to receive unexpanded polymer microspheres and to cause the unexpanded polymer microspheres to expand substantially in volume into expanded polymer microspheres having a substantially increased sphere surface area.

5

37. Apparatus according to claim 36, wherein the second cell configured to cause the expanded polymer microspheres to collapse substantially in volume into collapsed polymer microspheres that results in the mechanical shearing off of the attached mineral particles of interest.

10

38. Apparatus according to claim 36, wherein the first cell is configured to maintain the ore slurry at a predetermined temperature, and the unexpanded polymer microspheres are configured with a blowing agent encapsulated therein that has a trigger temperature set below the predetermined temperature so as to cause the unexpanded polymer microspheres to expand substantially in volume into the expanded polymer microspheres having the substantially increased sphere surface area when received in the first cell.

15

39. Apparatus according to claim 34, wherein the second cell is also configured to provide a mineral concentrate output having the attached mineral particles of interest.

20

40. An apparatus comprising:

a processor configured to receive a plurality of synthetic beads, including in the form of polymer microspheres, carrying mineral particles, each of the polymer microspheres comprising a surface and a plurality of molecules attached to the surface, the molecules comprising a functional group having a chemical bond for  
5 attracting one or more of the mineral particles to the molecules, causing the mineral particles to attach to polymer microspheres; and

releasing apparatus configured to interrupt the chemical bond of the functional group so as to remove the mineral particles from the polymer microspheres, including  
10 by causing the polymer microspheres to collapse substantially in volume into collapsed polymer microspheres having a substantially reduced sphere surface area that results in a mechanical shearing off of the attached mineral particles of interest.

41. Apparatus according to claim 40, wherein the processor is also configured  
15 to cause the polymer microspheres to expand substantially in volume into expanded polymer microspheres having a substantially increased sphere surface area.

42. Apparatus according to claim 40, wherein the processor is configured to receive unexpanded polymer microspheres and to cause the unexpanded polymer  
20 microspheres to expand substantially in volume into expanded polymer microspheres having a substantially increased sphere surface area.

43. Apparatus according to claim 42, wherein the releasing apparatus is configured to cause the expanded polymer microspheres to collapse substantially in volume into collapsed polymer microspheres that results in the mechanical shearing off of the attached mineral particles of interest.

5

44. Apparatus according to claim 42, wherein the processor is configured to maintain the ore slurry at a predetermined temperature, and the unexpanded polymer microspheres are configured with a blowing agent encapsulated therein that has a trigger temperature set below the predetermined temperature so as to cause  
10 the unexpanded polymer microspheres to expand substantially in volume into the expanded polymer microspheres having the substantially increased sphere surface area when received in the processor.

45. Apparatus according to claim 40, wherein the releasing apparatus is  
15 configured to provide a mineral concentrate output having the mineral particles of interest.

46. Apparatus according to claim 40, wherein the releasing apparatus comprises a re-pressurization cell tank or a condensation cell or tank configured to  
20 collapse the polymer microspheres substantially in volume into the collapsed polymer microspheres that results in the mechanical shearing off of the attached mineral particles of interest.

47. Apparatus according to claim 44, wherein the releasing apparatus is configured to be filled with an expanded polymer microsphere foam layer or mineral rich foam, and to be pressurized to a nominally elevated level, or chilled to a lower temperature, such that the blowing agent reverses through a transition phase,  
5 including either returning from a gas phase to a liquid phase or returning from a high pressure phase to a low pressure phase.

48. Apparatus according to claim 1, wherein the mineral particles of interest are chalcopyrite.

10

49. A method according to claim 18, wherein the mineral particles of interest are chalcopyrite.

50. Apparatus according to claim 40, wherein the mineral particles of interest  
15 are chalcopyrite.

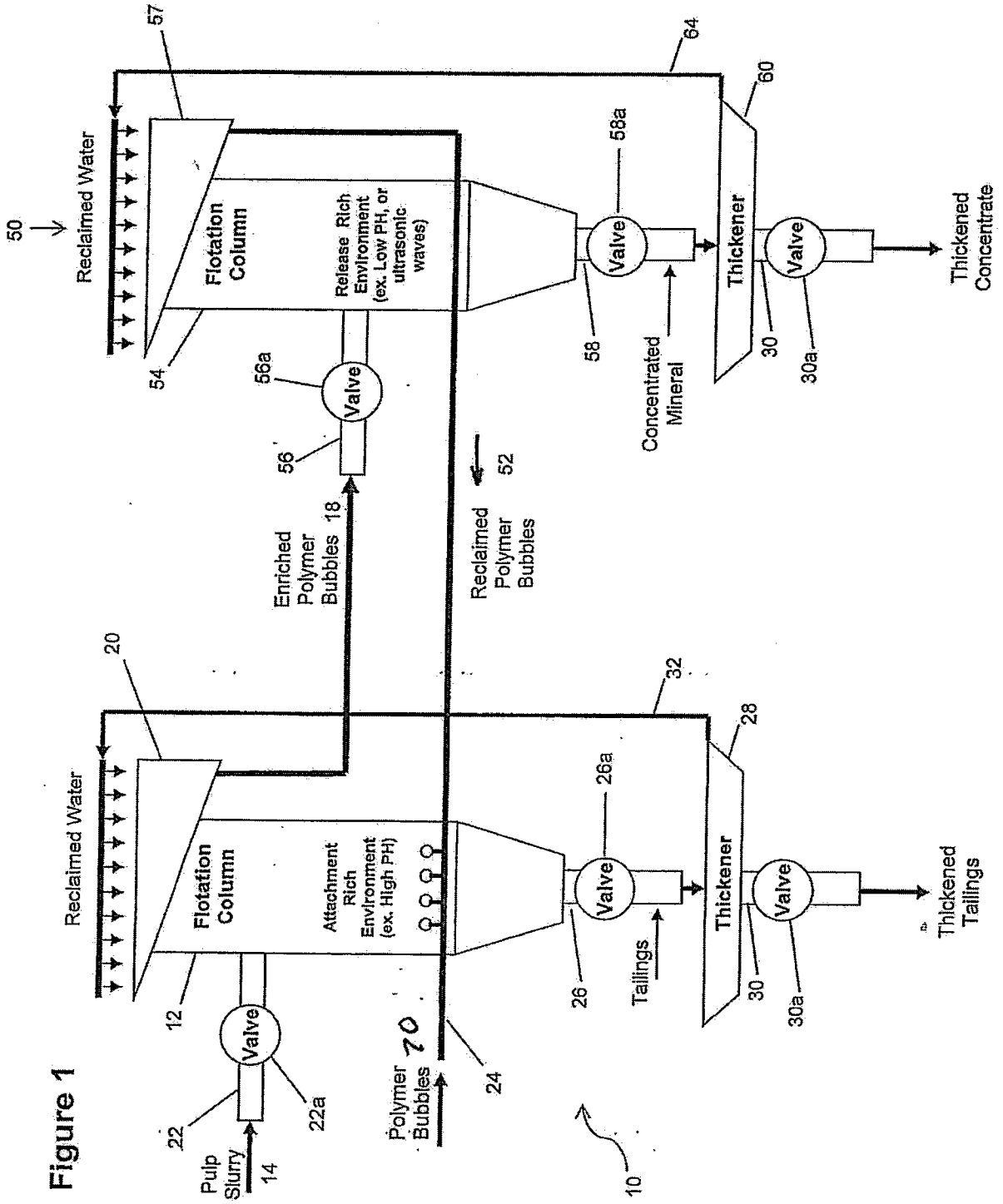
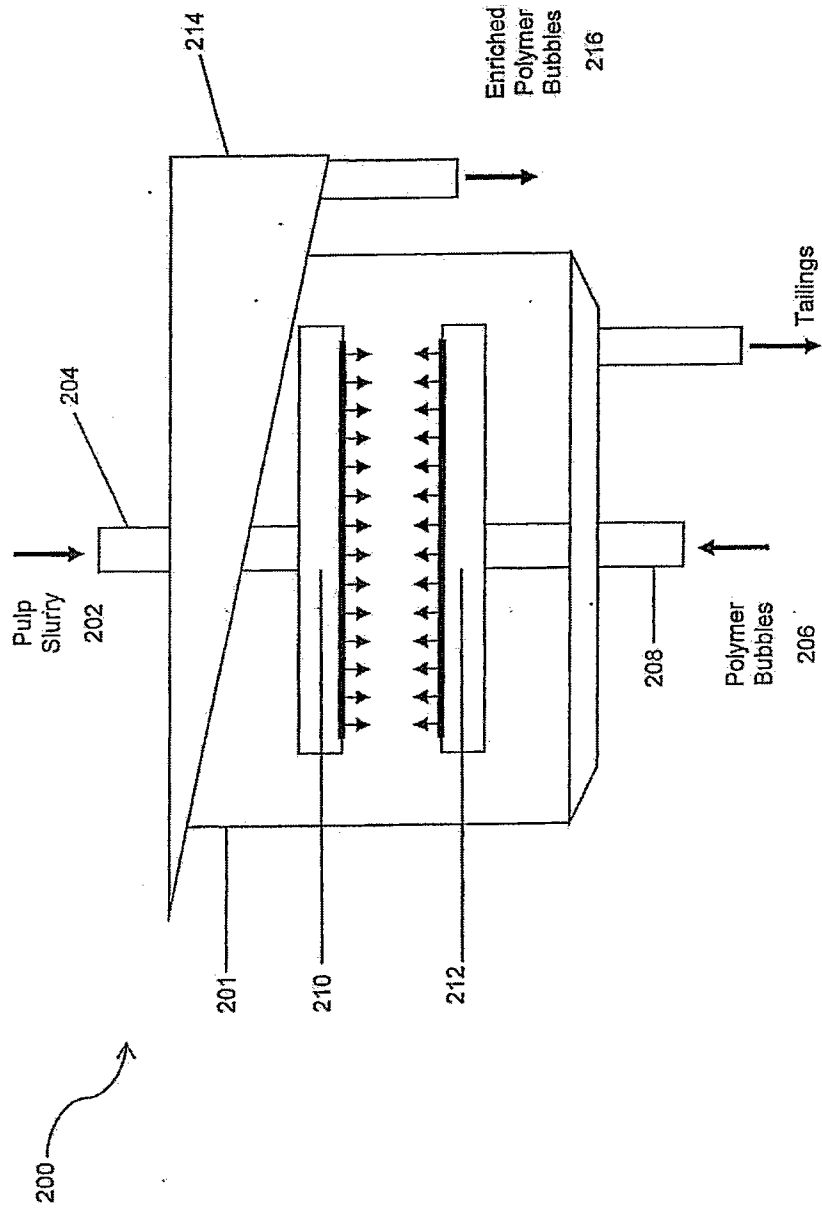


Figure 1

Figure 2 - Alternative Flotation Cell or Column



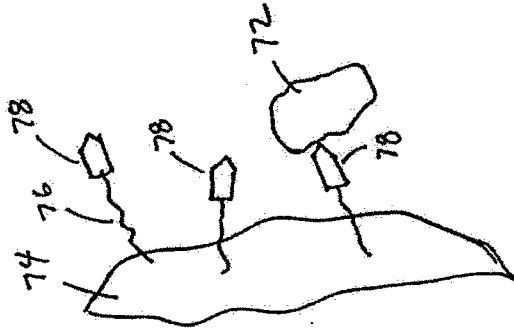


Fig. 3b

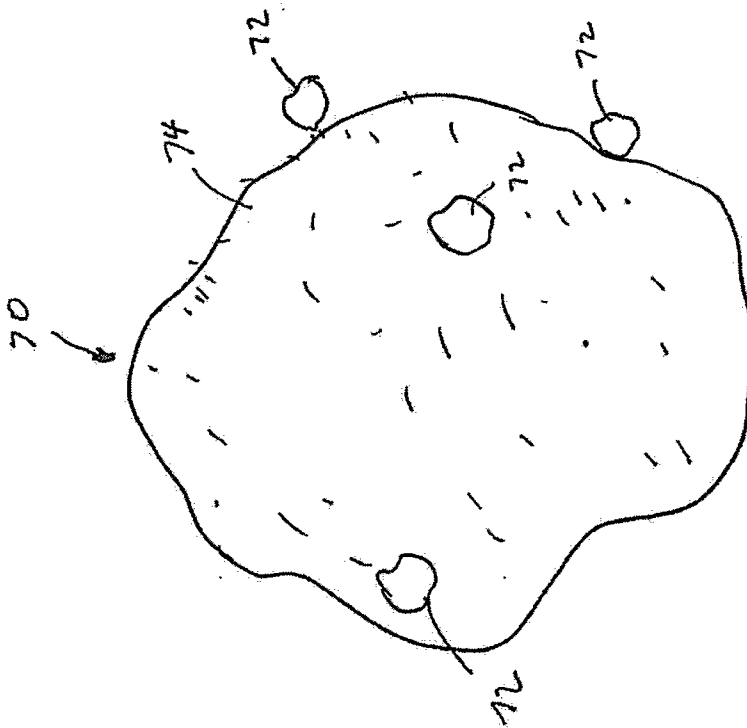


Fig. 3a

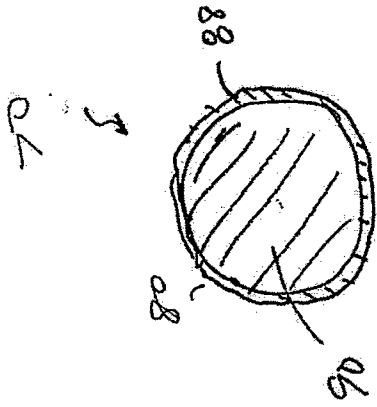


Fig. 4c

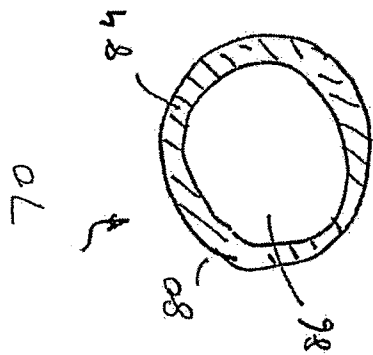


Fig. 4b

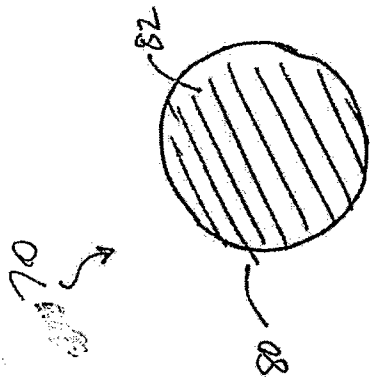


Fig. 4a

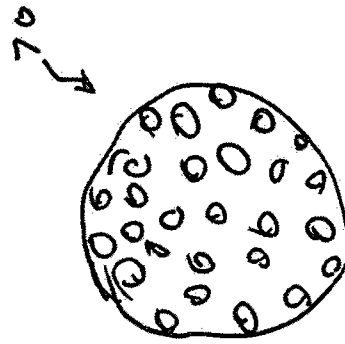


Fig. 4d

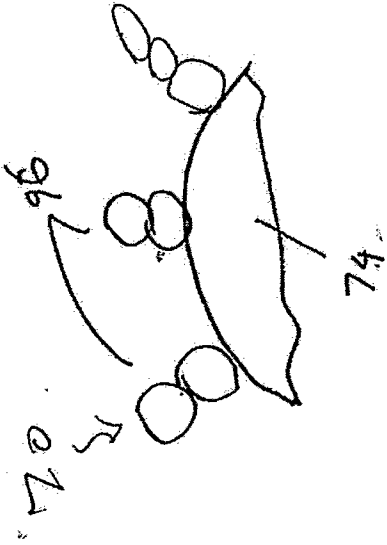


Fig 5c



Fig 5b

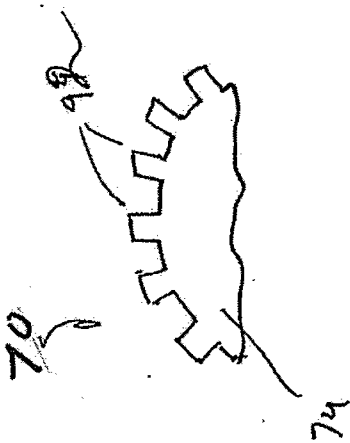
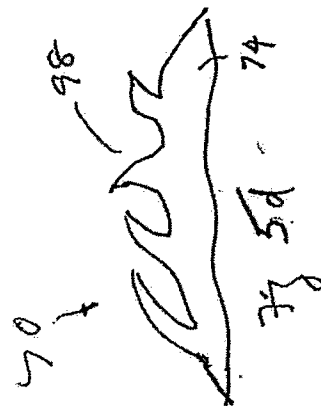


Fig 5a



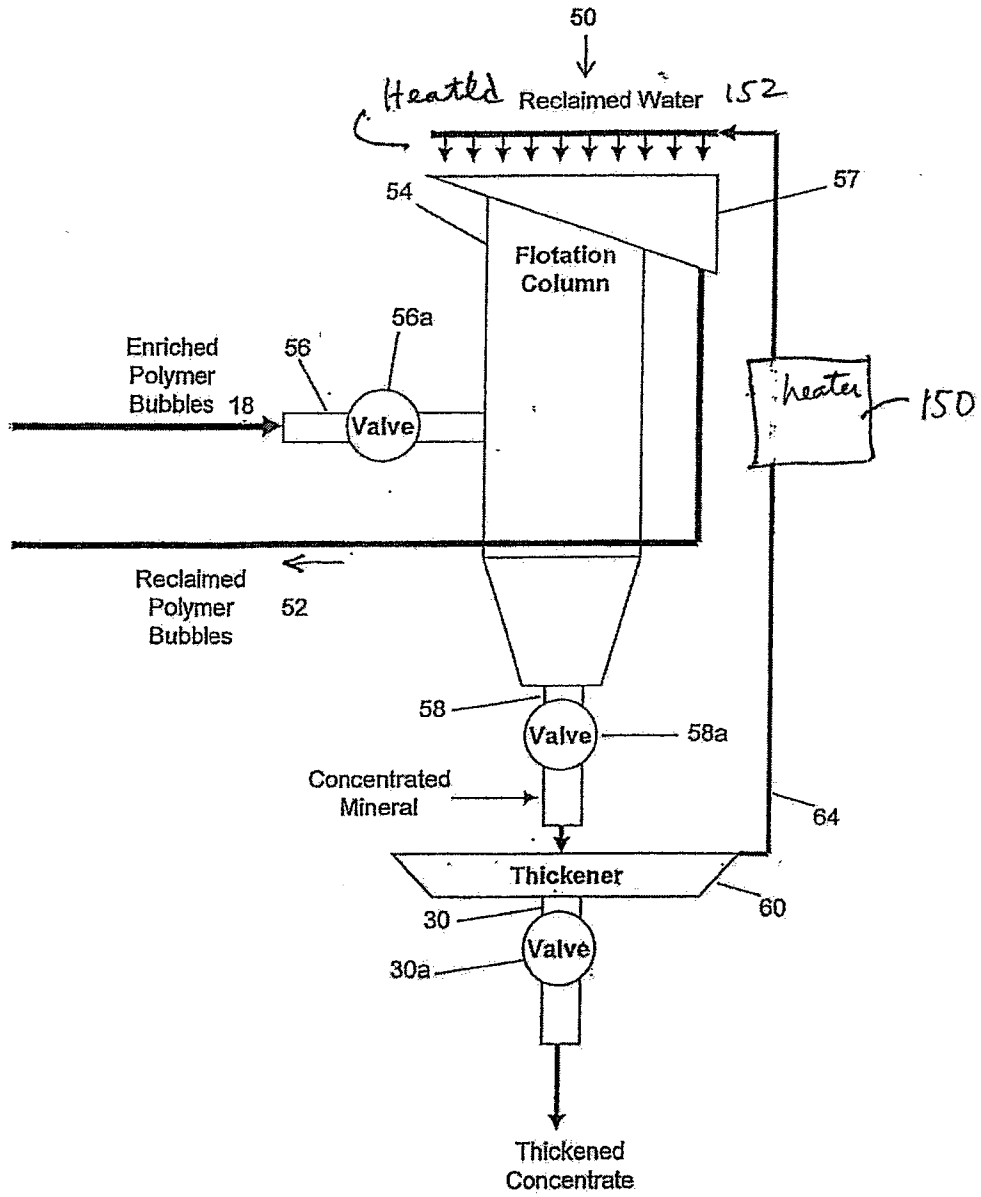


Fig 6

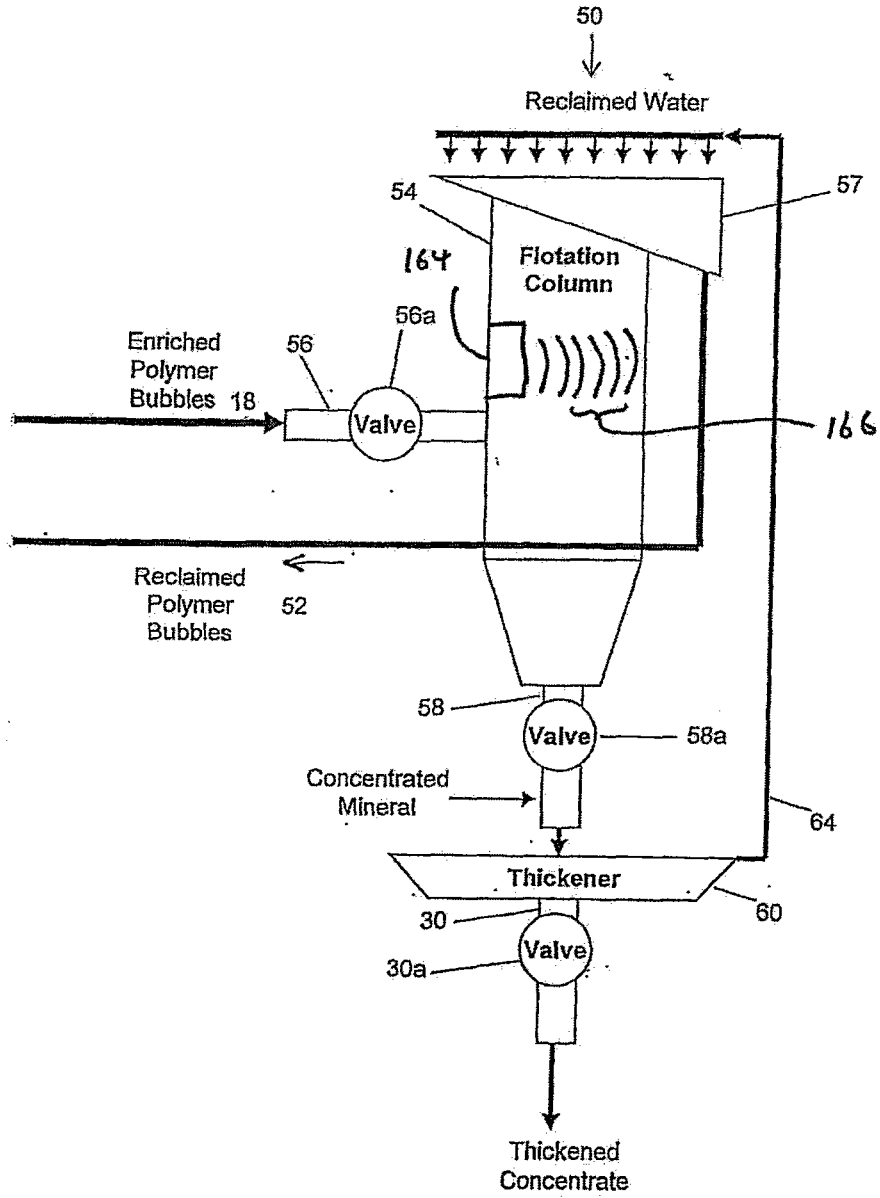


Fig. 7

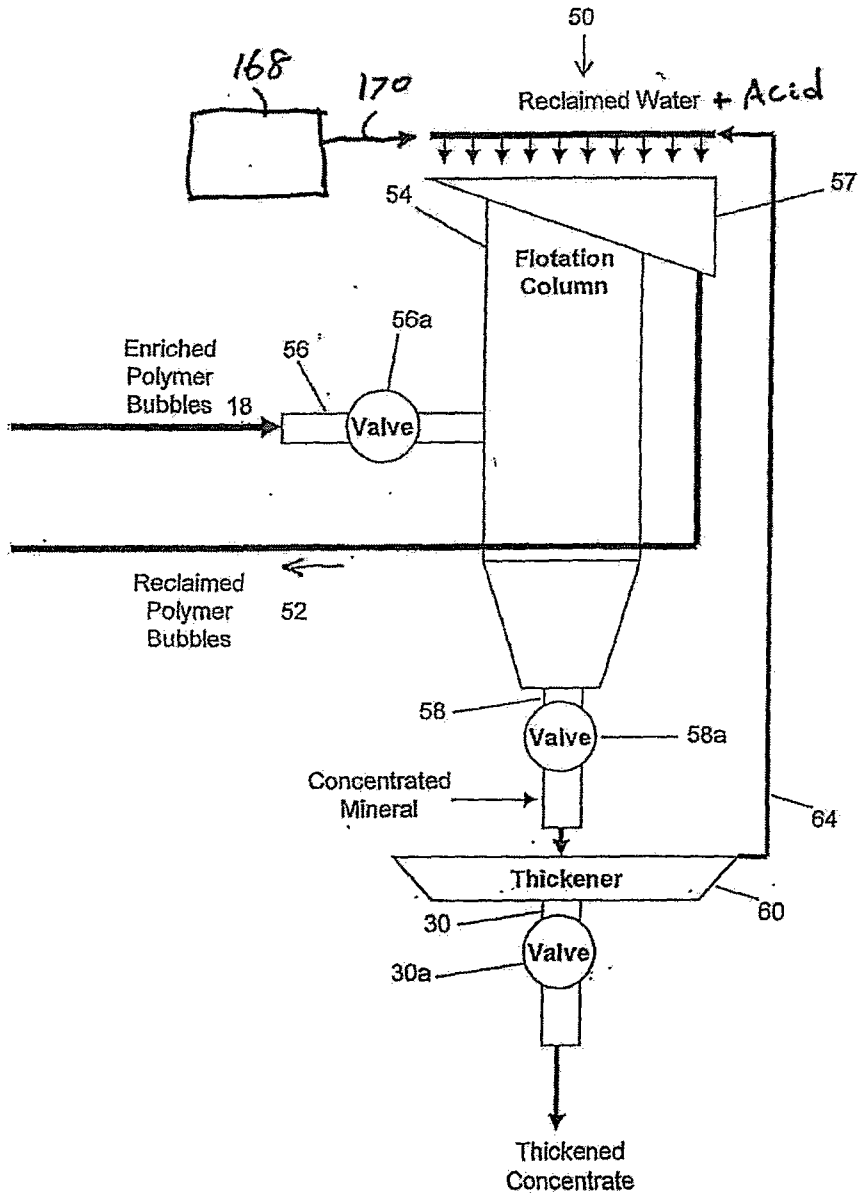


Fig. 8

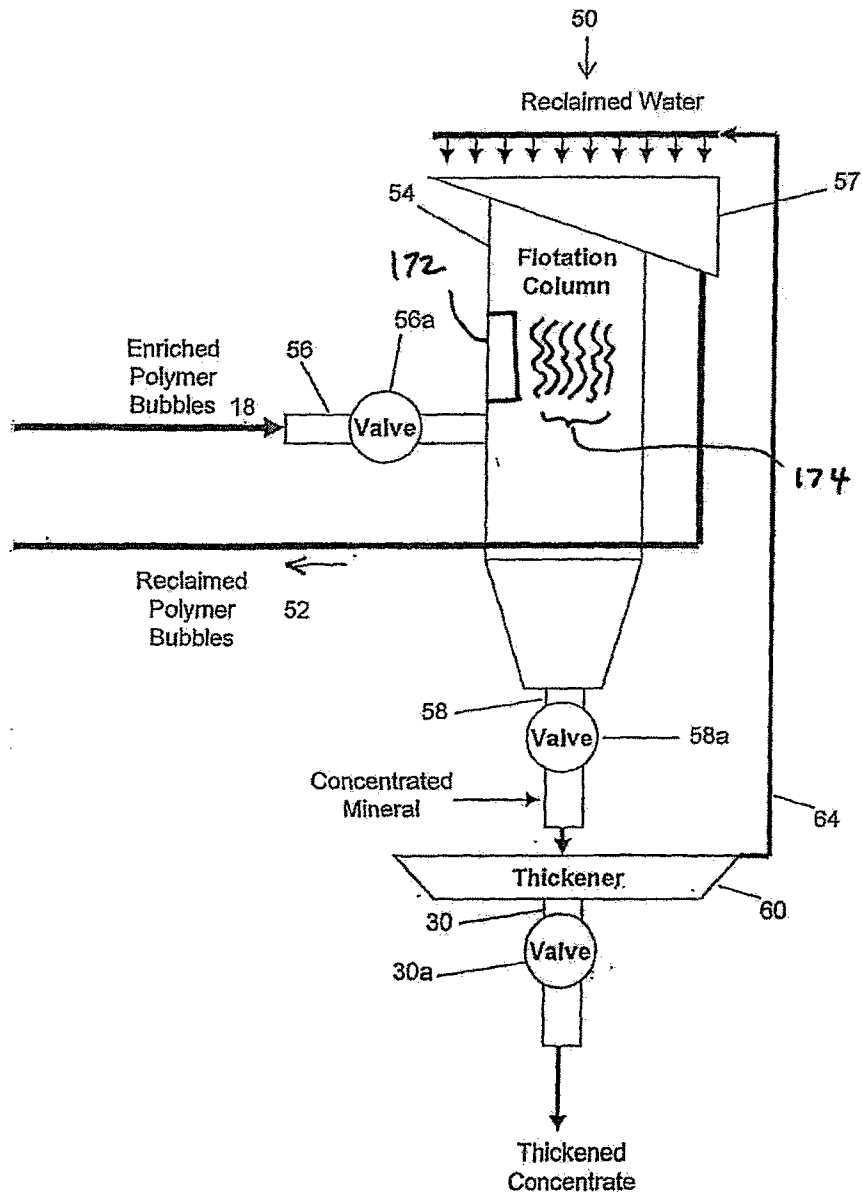


Fig. 9

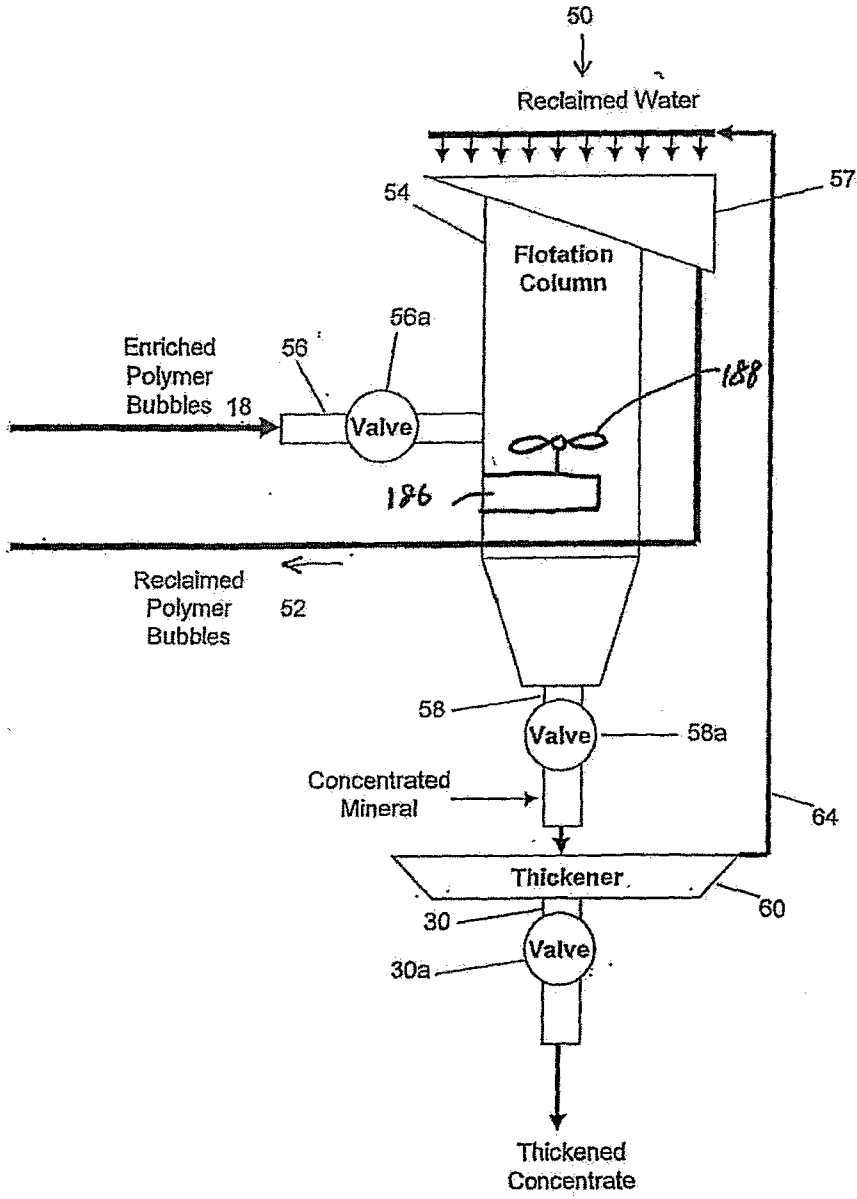


Fig 10

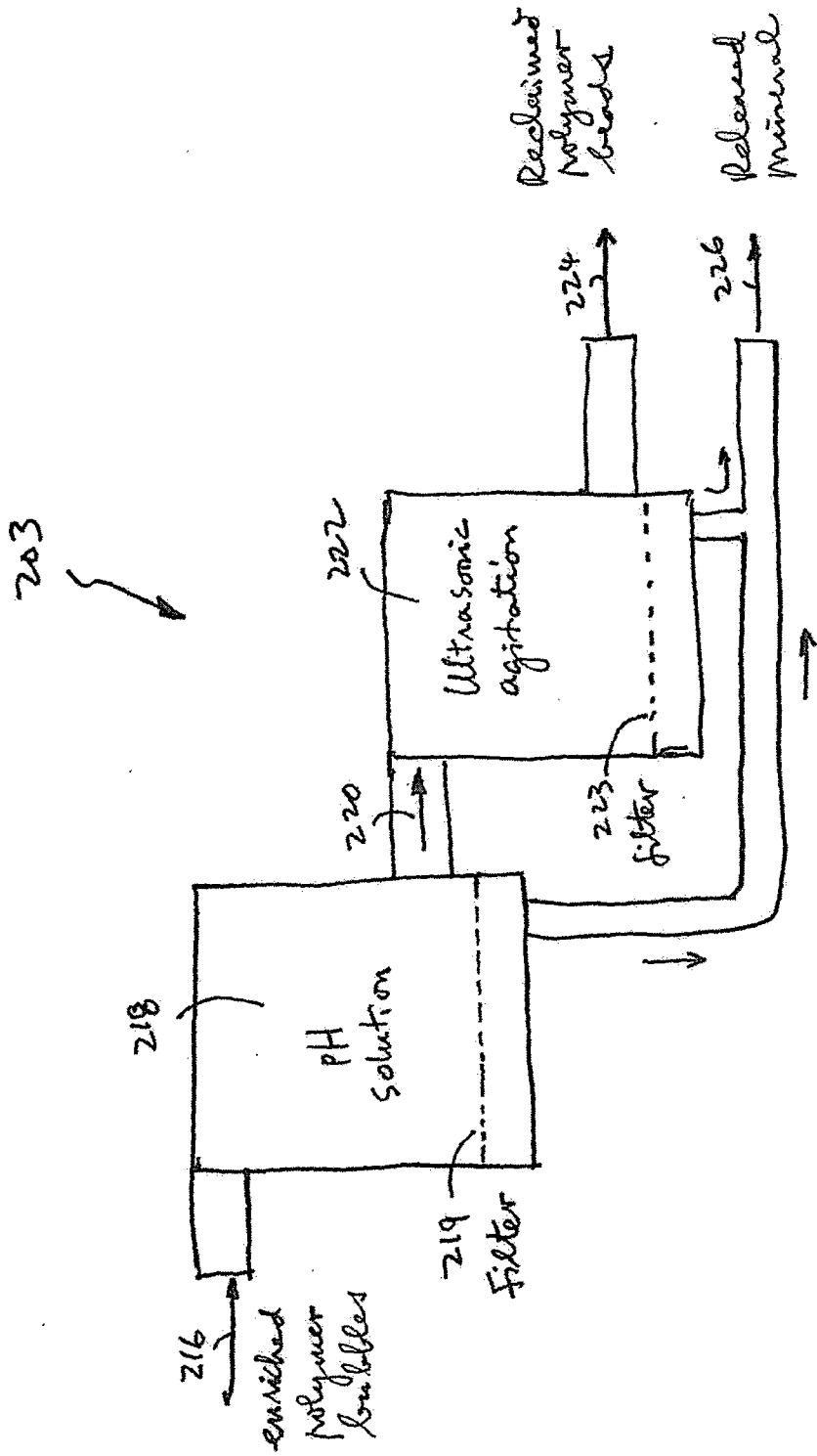


Fig. 11

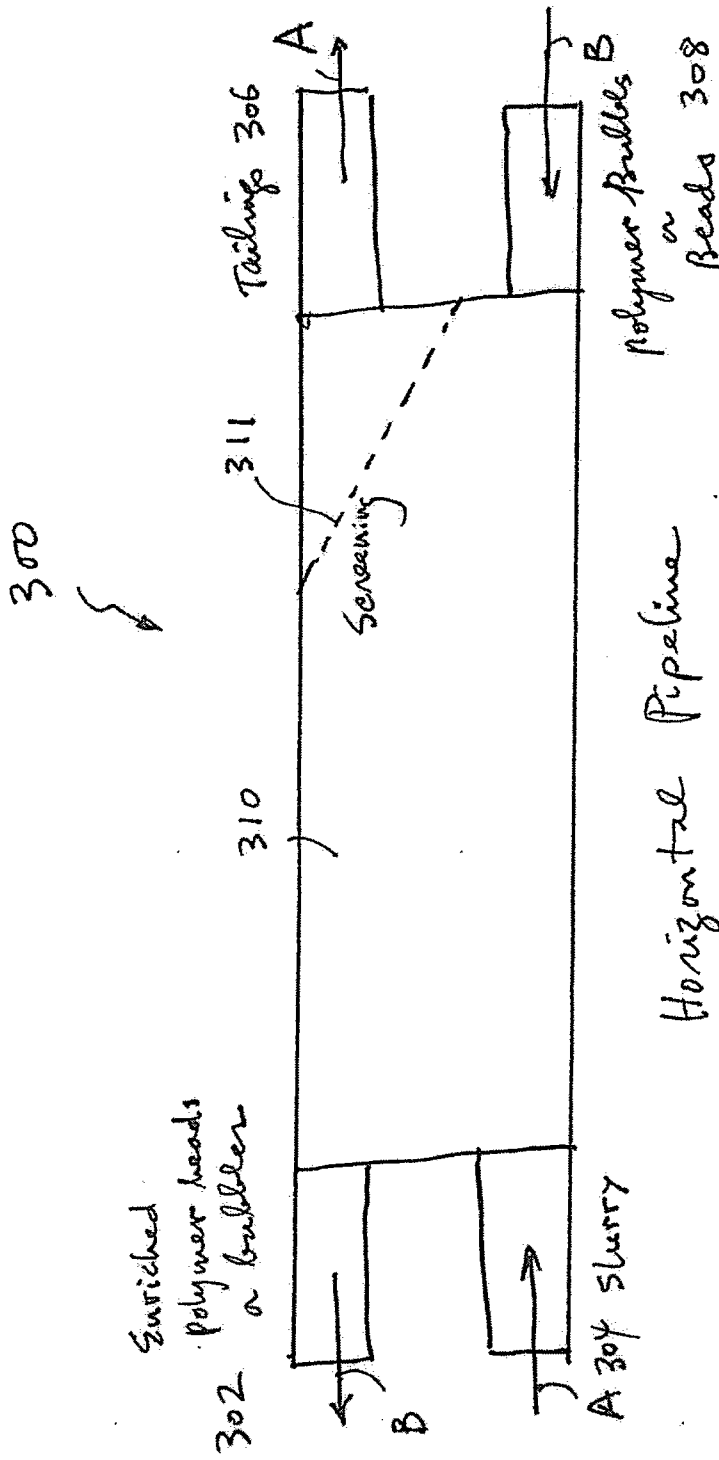


Fig. 12  
Separation of Sized-based bubbles or beads  
Using Countercurrent flows with Mixing

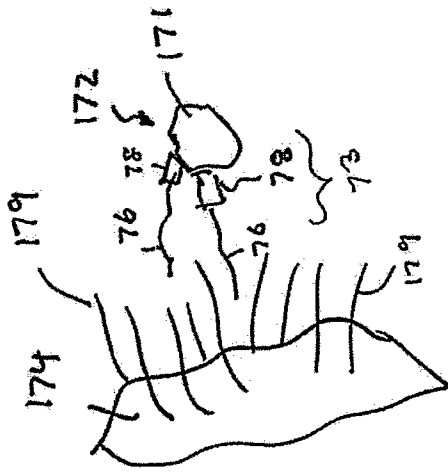


Fig 13b

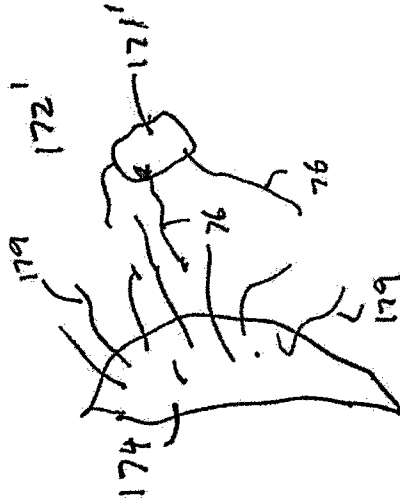


Fig 13c

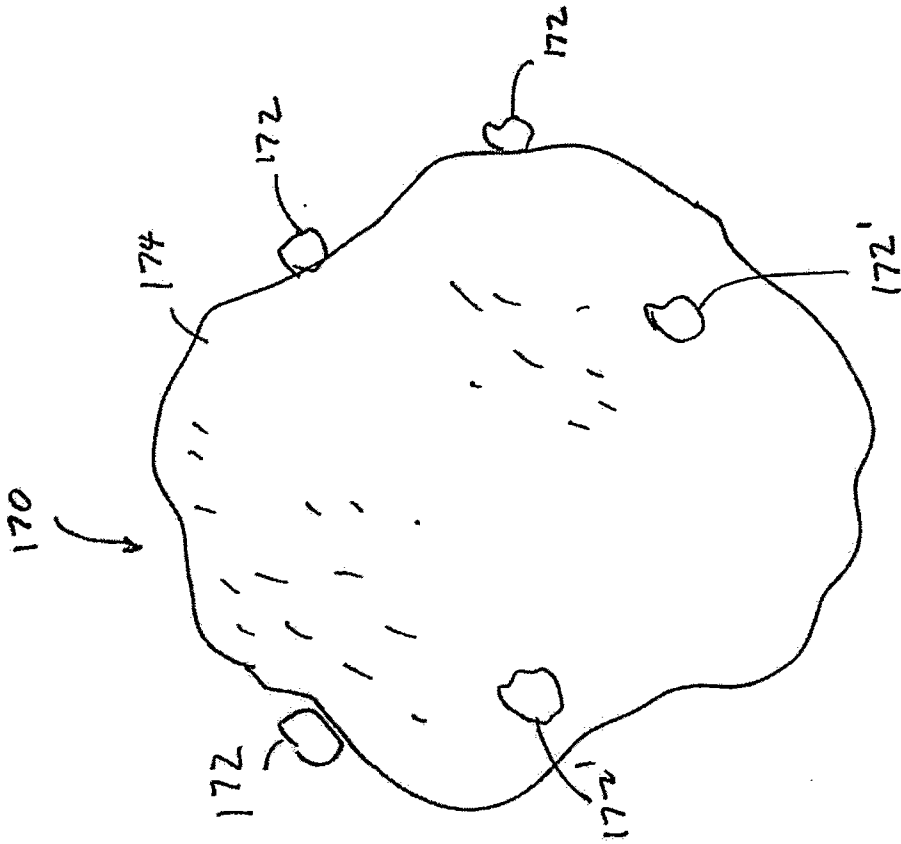


Fig 13a

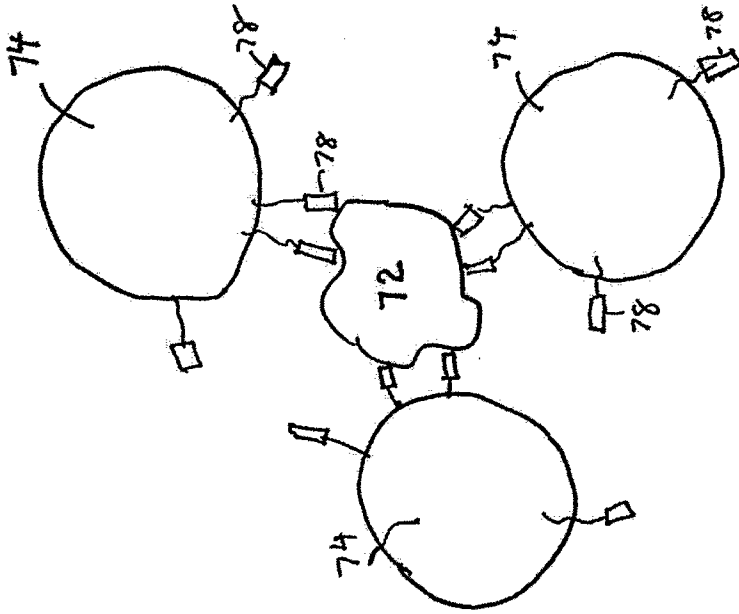


FIG. 14b

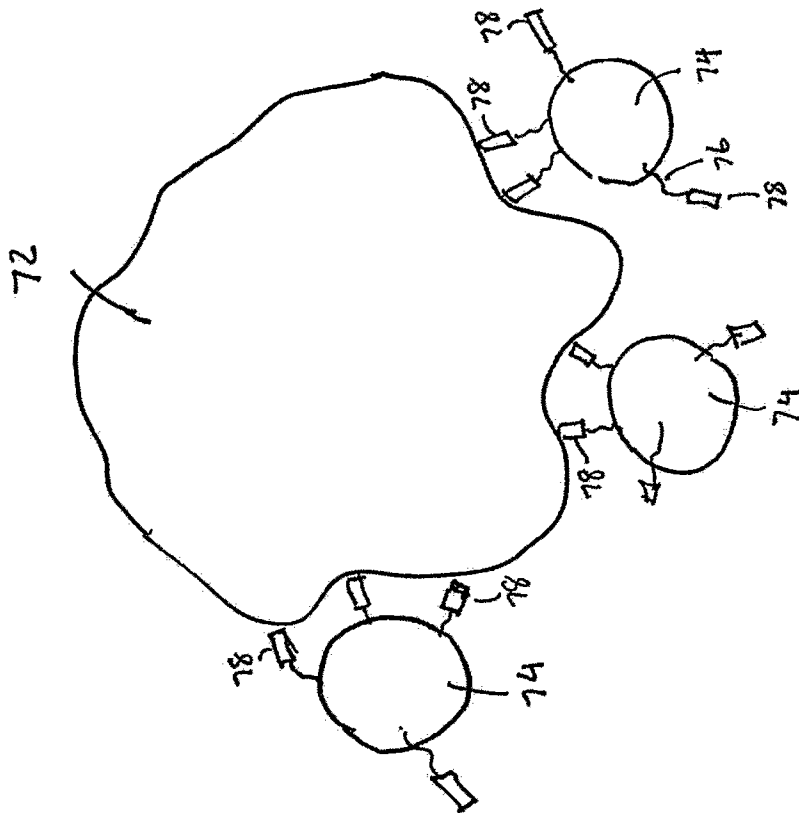


FIG. 14a

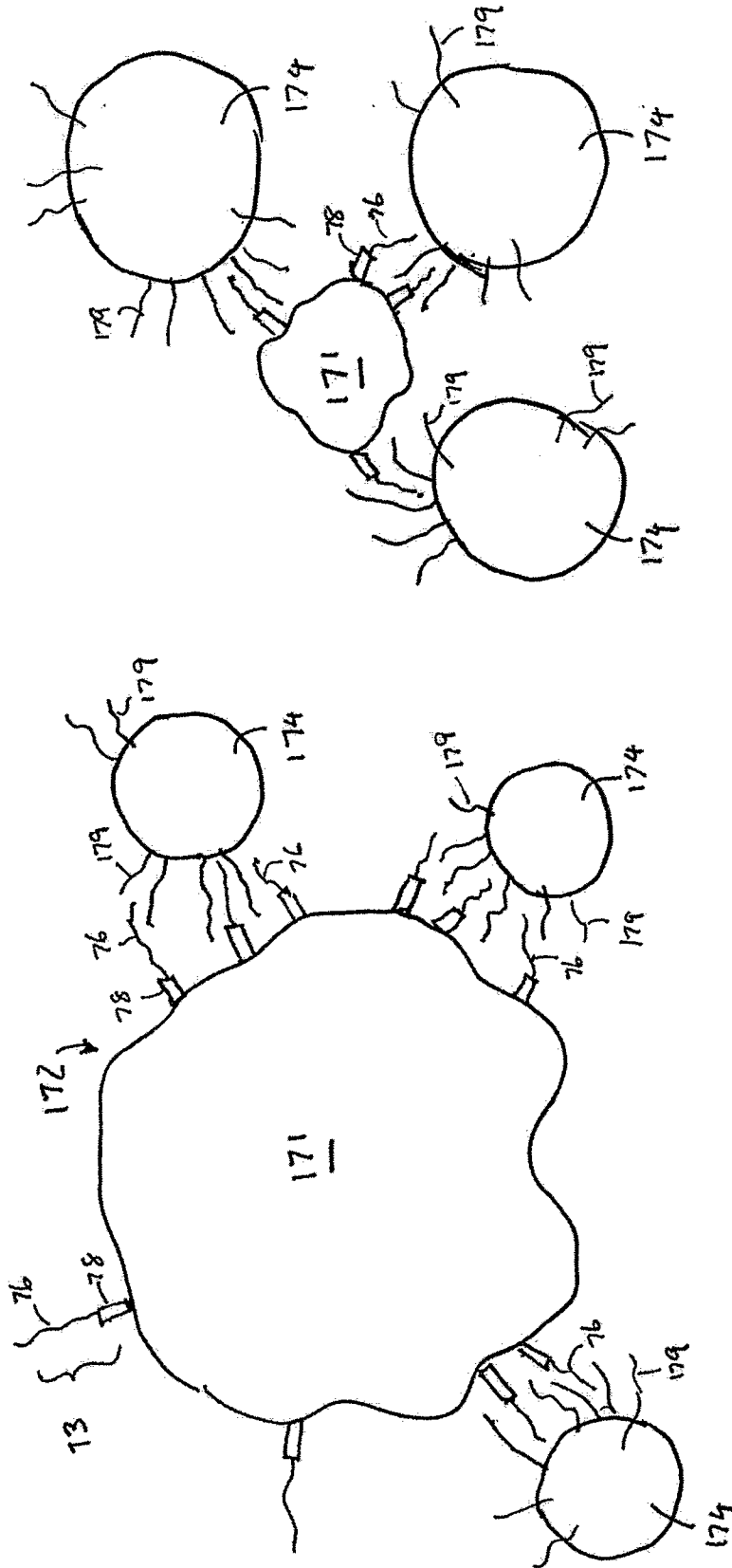
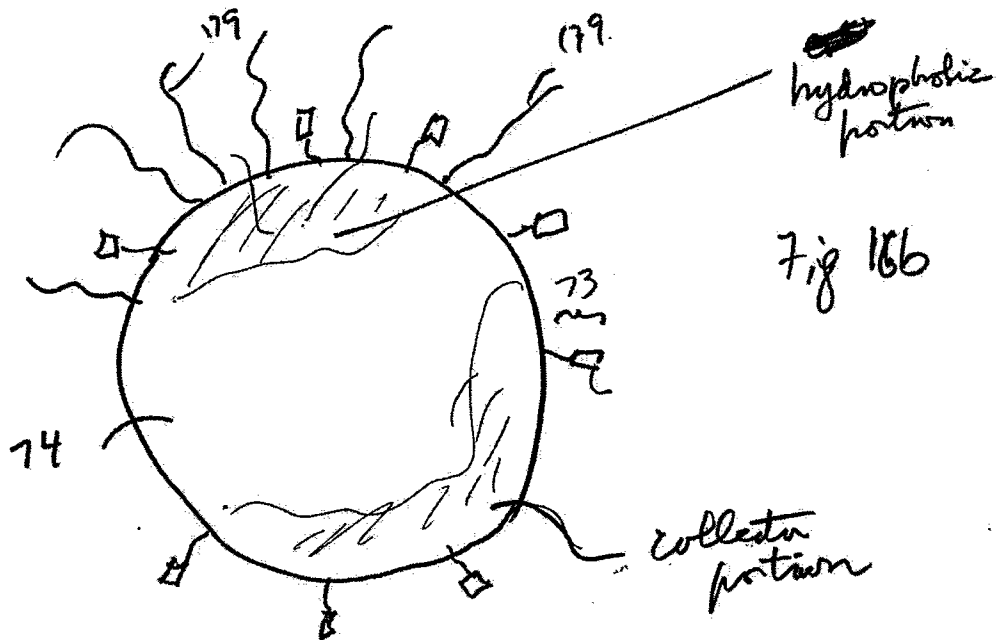
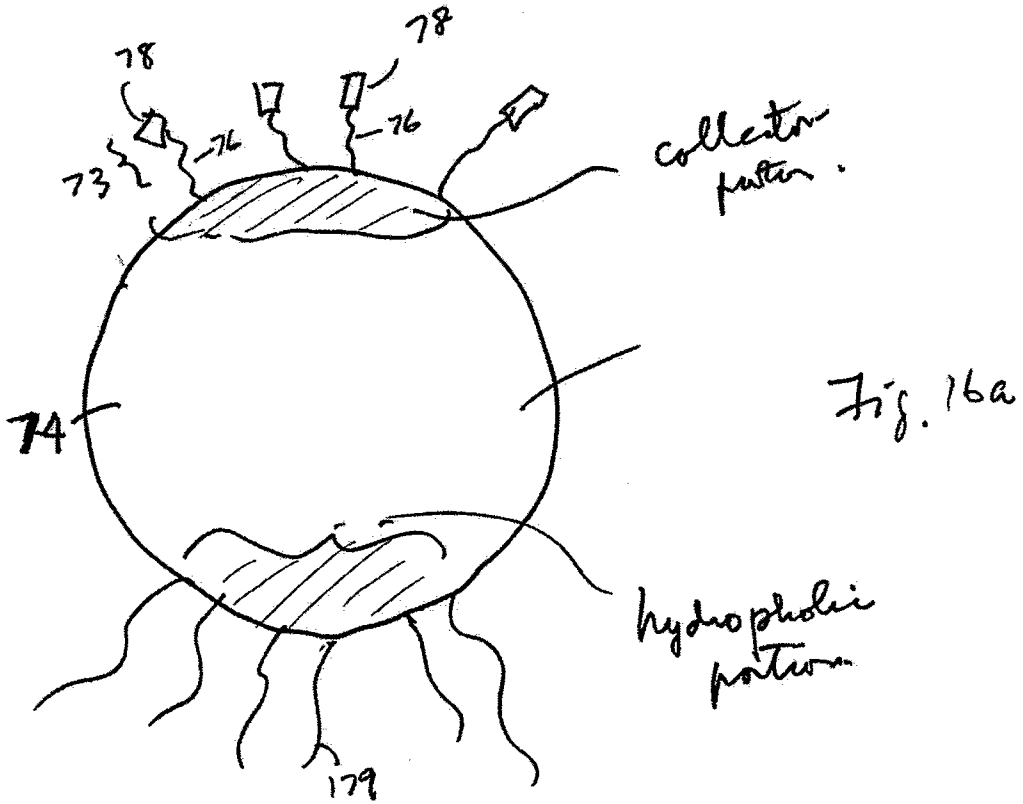


FIG. 15b

FIG. 15a



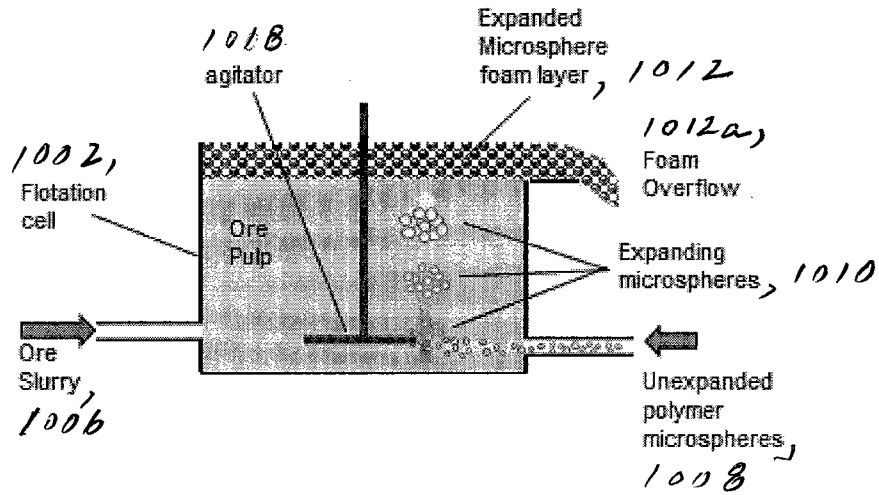


Figure 17a: Flotation cell arrangement utilizing expanding microsphere functionalized polymer 'beads'.

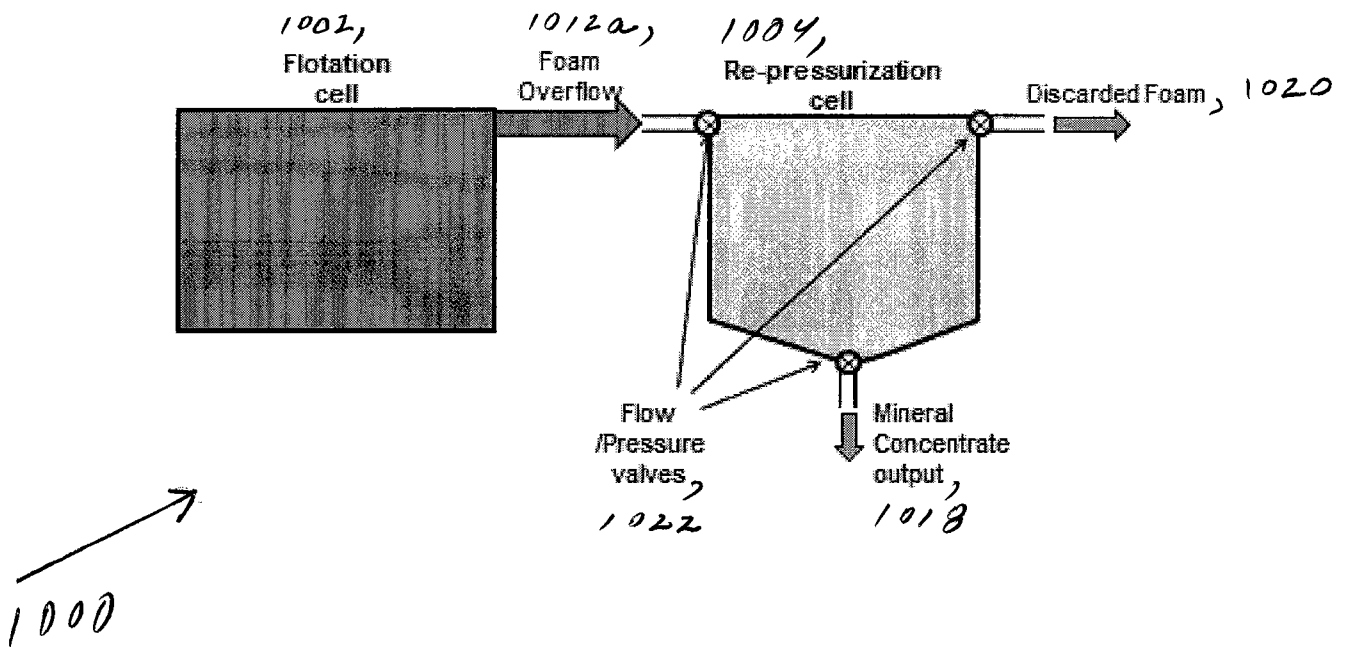


Figure 17b. A conceptual implementation of the re-pressurization cell for the recovery of minerals from the expanded polymer microsphere 'foam'.

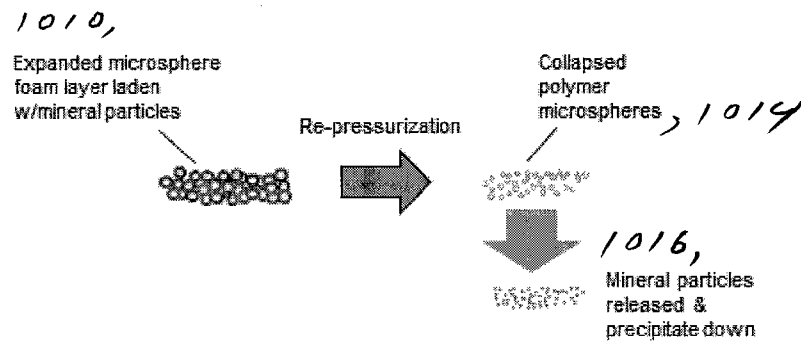


Figure 17c. Principle of the re-pressurization induced collapse of the expanded polymer microspheres and release of the attached mineral particles.

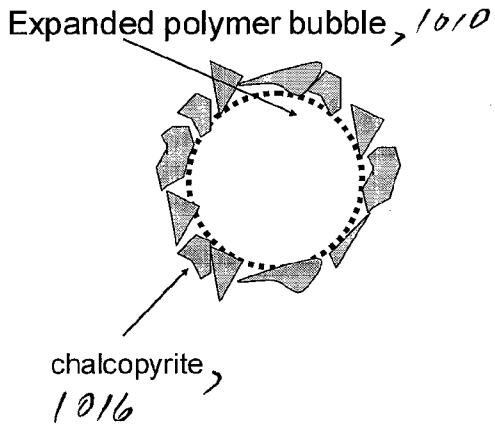


Figure 18a

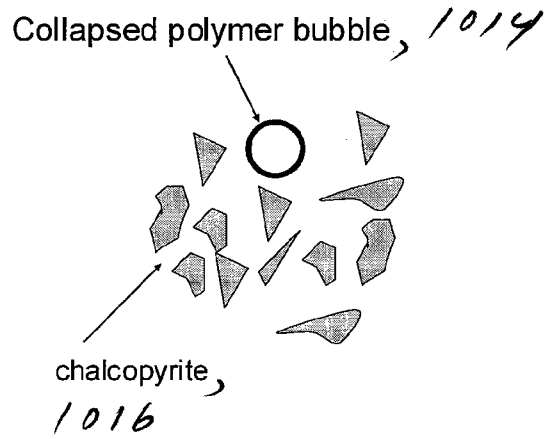


Figure 18b

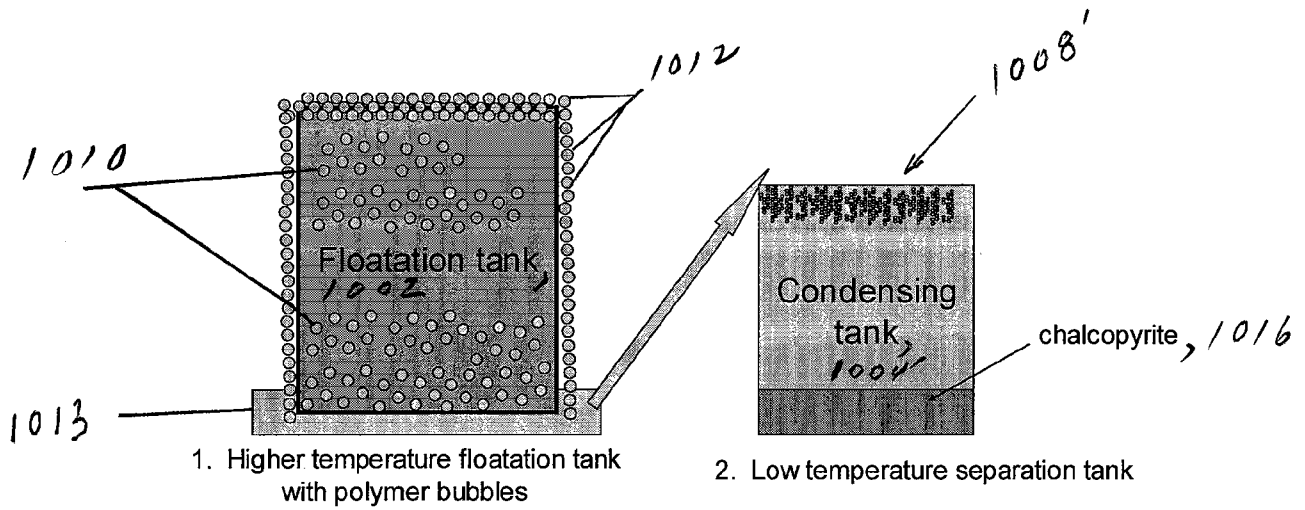


Figure 18c

**INTERNATIONAL SEARCH REPORT**

International application No.  
PCT/US2013/034762

**A. CLASSIFICATION OF SUBJECT MATTER**  
 IPC(8) - B03D 1/02 (2013.01)  
 USPC - 209/163  
 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) - B03D 1/00, 1/02, 1/10, 103/02 (2013.01)  
 USPC - 209/162-164, 901, 902; 210/200, 703-706, 776, 800

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched  
 CPC - B03D 1/001, 1/016, 1/02, 1/023, 1/08, 1/10, 1/14 (2013.01)

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)  
 Orbit.com, Google Patents, Public AppFT and PatFT, Google.com

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2003/0104359 A1 (CUTHBERTSON et al) 05 June 2003 (05.06.2003) entire document	40, 46
Y		1-39, 41-45, 47-50
Y	SCHRAMM, L. Emulsions, Foams, and Suspensions, Weinheim: Wiley-VCH, 2005, ISBN-13 978-3-527-30743-2. [retrieved on 27.06.2013]. Retrieved from the Internet: <URL:http://image.sciencenet.cn/olddata/kexue.com.cn/bbs/upload/9076Emulsions%20Foams%20and%20Suspensions%20-%20Fundamentals%20and%20Applications.pdf>. Chapter 3	1-39, 41-44, 47-49
Y	US 2005/0161406 A1 (EADES et al) 28 July 2005 (28.07.2005) entire document	3, 13, 14, 19, 29, 30, 33, 39, 45
Y	US 2010/0159225 A1 (HODJAT et al) 24 June 2010 (24.06.2010) entire document	4-8, 12, 16, 20-28, 31, 32, 38, 44, 47
Y	US 4,874,507 A (WHITLOCK) 17 October 1989 (17.10.1989) entire document	8, 24
Y	US 2001/0020603 A1 (MOOREHEAD et al) 13 September 2001 (13.09.2001) entire document	12, 28, 47
Y	US 2003/0217953 A1 (XU et al) 27 November 2003 (27.11.2003) entire document	48-50

Further documents are listed in the continuation of Box C.

\* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance	"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
"E" earlier application or patent but published on or after the international filing date	"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
"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)	"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
"O" document referring to an oral disclosure, use, exhibition or other means	"&" document member of the same patent family
"P" document published prior to the international filing date but later than the priority date claimed	

Date of the actual completion of the international search 27 June 2013	Date of mailing of the international search report <b>11 JUL 2013</b>
Name and mailing address of the ISA/US Mail Stop PCT, Attn: ISA/US, Commissioner for Patents P.O. Box 1450, Alexandria, Virginia 22313-1450 Facsimile No. 571-273-3201	Authorized officer: Blaine R. Copenheaver  PCT Helpdesk: 571-272-4300 PCT OSP: 571-272-7774