May 25, 1926. 1,585,755

W. O. BORCHERDT

NODULIZATION OF MINERALS

Filed Sept. 15, 1922

Fig. 1.

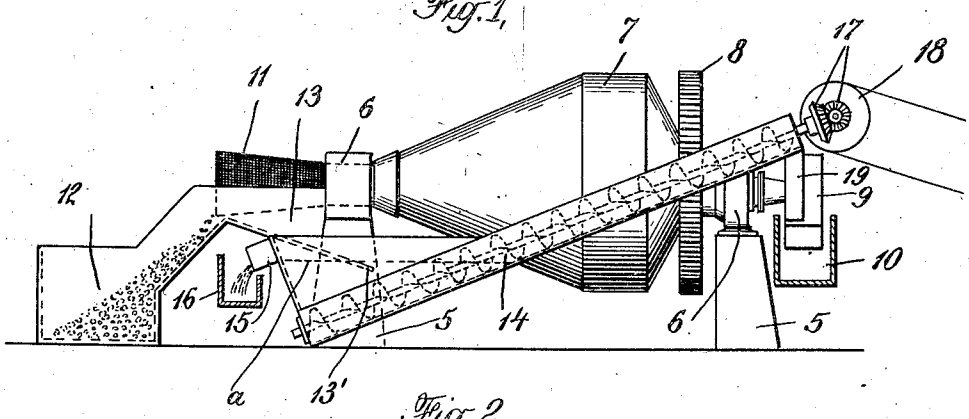


Fig. 2.

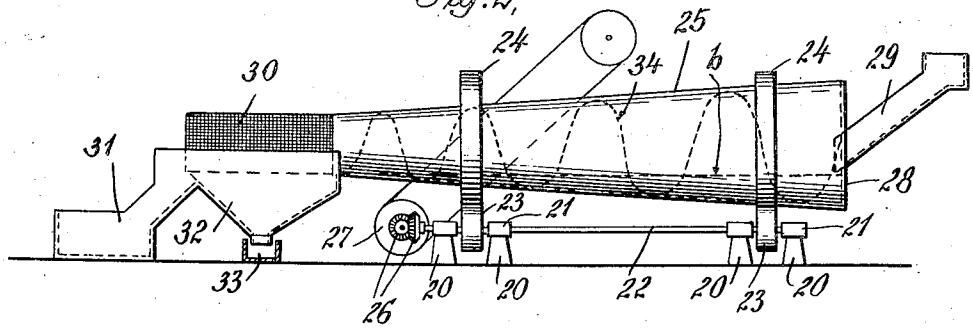


Fig. 3.

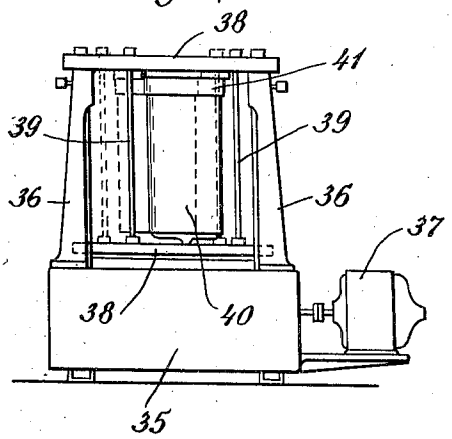
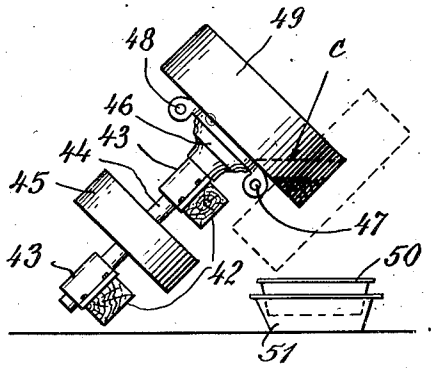


Fig. 4.



INVENTOR
Walter O. Borcherdt
BY
Pennie, Davis, Marvin & Edmonds
ATTORNEYS

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UNITED STATES PATENT OFFICE.

WALTER O. BORCHERDT, OF AUSTINVILLE, VIRGINIA, ASSIGNOR TO THE NEW JERSEY ZINC COMPANY, OF NEW YORK, N. Y., A CORPORATION OF NEW JERSEY.

NODULIZATION OF MINERALS.

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This invention relates to the nodulization of minerals, and more particularly to the nodulization of minerals associated with colloidal constituents in a mineral pulp, and has for its object the provision of certain improvements in the nodulization of minerals.

The nodulization or granulation of minerals, as a step in the concentration of ores, has heretofore been proposed, notably in the United States patents of Cattermole 763,259 and 763,260, dated June 21, 1904, and 777,273, dated December 13, 1904 and Cattermole-Sulman-Picard, 777,274, dated December 13, 1904. To the best of my knowledge, these prior proposals to nodulize minerals have been only experimentally investigated or developed, and, so far as I am aware, no practical application of these proposals has heretofore been successfully established and maintained under commercial operating conditions.

The nodulization of minerals belongs to that class of processes in which oils, fats, soaps, tars, gums and other agents are employed to effect the concentration of minerals for which they have a selective affinity. In nodulizing minerals, the selective affinity or adhesion of oils and other substances for certain minerals is employed to build up masses or nodules which are compact, dense, closely adherent and of a higher order of magnitude than the individual mineral particles. The separation of the nodules from the "unoiled" or un-nodulized minerals of the mineral mixture, usually in the form of a mineral pulp, depends upon the size and density which the nodules can be caused to attain, and, therefore, the larger they can be made, the easier, in general, will it be found to separate them from the unoiled or un-nodulized mineral particles.

The present invention contemplates, as an improvement in the nodulization of minerals, the control of the results of such processes by regulation of the kind, condition and amount of the colloidal constituents associated with the minerals in a mineral pulp. I have discovered that the colloidal constituents of minerals pulps often inhibit or exercise a deleterious influence on the nodulization of minerals, and that when only one mineral species is to be nodulized improved results may often be secured by changing the condition or the amount, or both, of the associated collidal constituents, while, in the case that several diverse mineral species are contained in the mineral pulp, control of the condition or of the amount of the associated colloidal constituents may make possible the differential nodulization of such minerals, or, where diverse minerals tend to nodulize in mixed masses, the addition of a colloidal agent, regulated in kind, condition and amount, may, likewise, render possible the differential nodulization of such minerals in the form of successive products, each consisting, respectively, of substantially one such mineral, nodulized or agglomerated into coherent masses.

In the accompanying drawing, I have diagrammatically illustrated certain types of apparatus suitable for the nodulization of minerals. Thus, Figs. 1, 2, 3 and 4 of the drawings illustrate different types of mineral nodulizing apparatus which will be described in detail hereinafter.

I have found various types of apparatus adapted for the nodulization of minerals. Thus, vessels rotated or oscillated about a substantially horizontal axis may be used, the mineral pulp and "oil" and addition agents, if any are used, being fed in at one end and the pulp containing nodulized mineral being discharged from the opposite end. The forms of such rotating or oscillating vessels may be substantially cylindrical, or spherical, or conical, or such vessels may embody combinations of such forms. The interior of such vessels may be smooth or roughened, as by lifter-bars, or the like, and the vessels may be constructed of wood or metal and lined with various substances, depending upon the characteristics of the particular mineral mixture to be treated and the results desired.

I have found that the nodulization of minerals can be very advantageously effected in ball-, tube-, or pebble-mills, intended for the grinding of minerals, and sometimes even while grinding of minerals is going on therein. Thus, I have produced in a Hardinge pebble-mill (eight feet in diameter by thirty inches cylindrical length), which was grinding ore in the usual way, nodules of galena (lead sulfide) ranging up to one and one-half inches in diameter. This nodulizing action was brought about

by feeding into the mill, with an ore pulp containing galena, an emulsion of crude coal-tar oil with ivory soap, under certain special conditions of colloid control hereinafter more particularly described. The galena nodules thus formed, although composed of particles which for the most part were finer than 200 mesh (Tyler standard screen openings) were firm and coherent, about the consistency of raw rubber, and contained 38.52% lead. Retreatment of similar material in a rotating cylinder, followed by separation of the coarse nodules from the fine un-nodulized minerals, by means of a fine mesh screen, gave a nodular concentrate containing 71% lead.

The Hardinge mill, as is well known, consists of two hollow conical frustra of differing vertex angles, with bases opposed and joined by a relatively short hollow cylindrical section, about the substantially horizontal axis of which (with which the axes of the conical frustra coincide) the vessel, as a whole, rotates. This vessel is composed of steel plates, is lined with wear-resisting material (in the case mentioned flint pebbles set in cement), and is partly filled with flint pebbles, which, by the rotation of the mill, are continually raised and dropped back, thus grinding the ore, which is fed in at one end with water and discharged from the other end. The discharge of ground ore depends upon its suspension in water, and a species of hydraulic classification governs the delivery of the mineral particles. These facts explain the apparent paradox of large nodules forming under such circumstances. The galena, although very heavy, would, under ordinary circumstances, be discharged from the mill as soon as it was ground fine, but because of the presence of the "oil" the galena particles adhere to one another to form nodules, and, because of the peculiar rubber-like consistency of these nodules, they maintain their integrity despite the grinding action to which they are subjected.

Another factor contributing powerfully to the growth of the nodules, in the particular instance hereinbefore mentioned, was the mechanical classifier which was run in closed-circuit with the Hardinge mill. The function of this classifier was to return to the mill such particles of mineral as were discharged therefrom without being sufficiently ground. Since the nodules of galena had, so far as the classifier was concerned, the same properties as coarse ore particles, they were, if discharged from the mill, at once returned to it, and therefore continually increased in size. So powerfully was this phenomenon manifested that, on one occasion, the flint pebbles composing the grinding charge, some of these four inches in diameter, were forced from the mill by the accumulation of nodulized galena. It will readily be seen that under such conditions, it is only necessary to interpose a screen of suitable mesh between the discharge of the Hardinge mill and the mechanical classifier, whereupon the nodules of galena as soon as they are built up to a diameter exceeding the diameter of the holes in the screen are retained upon it and form a lead concentrate. The holes in the screen must obviously be larger than the largest particles of un-nodulized mineral discharged by the mill, so as to permit the free circulation of such particles for regrinding.

In Fig. 1 of the accompanying drawing I have shown diagrammatically a combination of Hardinge mill, mechanical classifier and nodule-separating screen, such as I have just described.

In this figure foundations 5 carry bearings 6 in which are rotatably supported the trunnions of the shell of a pebble mill 7. The mill is rotated by means of a gear 8, attached thereto and driven by means of a pinion from a suitable source of power. The inlet or feed end of the mill carries a feed scoop 9, the lip or lips of which, at each rotation of the mill, dip into the mineral pulp contained in a feed box 10 and convey a portion of the pulp into the hollow interior of the mill 7. The mill 7 contains a suitable wear-resisting lining and an appropriate amount of suitable size flint pebbles or metallic balls which, by the cascading resulting from the rotation of the mill, grind the mineral which is supplied thereto by the feed scoop 9.

At the discharge end of the mill a screen 11 is provided. This screen may be attached to and rotate with the discharge trunnion of the mill or it may be otherwise suitably supported and operated. It is of such dimensions and contains openings of such size that it discharges into a container 12 as over-size only mineral nodules formed as before described. The undersize product of the screen, comprising water, finely ground mineral, mineral particles which are still insufficiently ground and mineral nodules of insufficient size, is delivered by means of the casing 13, surrounding the lower half of the screen 11, to a mechanical classifier 14. The extended end 13′ of the casing-bottom 13 projects below the water line (*a*) of the mechanical classifier and assists in preventing coarse particles from being carried out of the classifier by the overflow which flows by means of a spout 15 into a launder 16, thus conveying the surplus water and the finely ground mineral suspended therein to waste, or to a place of further treatment.

The mechanical classifier 14 may advantageously consist of a tank or settling portion in which pulp may be maintained

at a level (*a*) and an inclined extended launder-portion in which is supported one or more helical conveyors of suitable diameter and pitch. These conveyors may be supported for rotation by appropriate bearings of which that at the upper end may combine the function of a stuffing box, radial and thrust bearing. Rotation of the conveyors may be accomplished by suitable gears 17 and a pulley 18.

All material which enters the mechanical classifier and which does not overflow at the spout 18 is gradually carried by the helical conveyor up the inclined launder and is discharged through the drop 19 into the feed box 10, from which, together with the initial mineral pulp fed to the apparatus, it is delivered to the mill 7 by means of the feed scoop 9.

In Fig. 2 of the accompanying drawings, there is shown another form of apparatus suitable for the practice of the process of the present invention in certain cases as, for example, when the mineral pulp has been elsewhere properly prepared for nodulization of certain of its mineral constituents. In this apparatus foundations 20 support in bearings 21 a pair of shafts 22 which carry rollers or "trundles" 23 on which are rotatably supported the tires 24 of a shell or cylinder 25. Rotation of the shafts 22 is effected by gears 26 operatively connected to an appropriately driven pulley 27.

The rotating shell 25 has at one end a head 28 which contains a central opening through which a feed launder 29 projects into the interior of the shell. At the discharge end of the shell 25 there is mounted a screen 30 rotating therewith (or, if desired, separately supported and operated) of suitable dimensions and size of openings so that mineral nodules formed in the shell by the process of the present invention may be discharged as over-size particles into a container 31, while the undersize or unnodulized material, discharged from the shell, passes through the interstices of the screen 30 into a casing 32 and thence into a launder 33 for suitable disposal.

The shape and dimensions of the shell 25 bear such a relationship to the diameter of the central opening in the head 28, that the pulp admitted into the apparatus by the launder 29 may reach a level (indicated by *b*) at which it overflows from the discharge end of the shell into the screen 30 without overflow occurring at the head end 28.

The interior of the rotating shell 25 may, if desired, be equipped with one or more helical lines of blades 34, which may be continuous or interrupted and which are so disposed as to cause the slow but continuous progression of the solids of the feed from the inlet toward the outlet end of the apparatus.

Various other types and forms of apparatus may be employed for the formation of mineral nodules. The mechanical conditions which favor a rapid building of nodules are:—sufficient agitation so that circulation takes place throughout the whole mineral pulp, but gentle enough to permit of a certain amount of stratification or segregation of the minerals, according to density and particle size, without actual lodging. Violent agitation in one part of the apparatus is not objectionable, if there is some part where the conditions afore-stated are met.

For small scale tests, I have found it convenient to use an apparatus consisting of a small, upright steel tank having a close-fitting removable cover. The mineral pulp to be treated is placed in the tank, only partly filling it, and the oil and such other agents as may be required are added and the cover is secured. This tank is then placed in a "Ro-Tap" machine (made by the W. S. Tyler Company, of Cleveland, Ohio, and intended for shaking and jarring a nest of testing screens or sieves), in place of the usual nest of sieves, the space for which it just fills. The jarring mechanism of the machine is disconnected and the machine run at the speed desired, thus giving to the tank and its contents a vanning action, or oscillation about a vertical axis, similar to that which one gives to a vanning plaque or batea when panning a sample of ore. The pulp is thus agitated and circulated, but the heavier mineral particles, as for example, galena, tend to remain near the bottom and center of the tank, without actually being permitted to lodge. Under such circumstances, provided the other conditions for nodulization are observed, certain minerals take on a coating of oil and such oil-coated particles gradually adhere to one another, forming and building up nodules, which become roughly rounded. When the action has taken place to the degree desired, the tank is removed from the "Ro-Tap" machine, the cover is removed and the pulp is washed on a sieve having meshes large enough to pass the particles of minerals which are not nodulized, but small enough to retain the nodules, which are thereby separated as a concentrate.

In Fig. 3 of the accompanying drawings, I have diagrammatically represented the apparatus described in the preceding paragraph. The "Ro-Tap" sieve shaking machine consists of a cast iron base or tank 35 supporting hollow standards 36 through which pass vertical shafts (not shown in the drawing) which are supported in suitable bearings carried by the standards 36 and are rotated in the same direction and at equal speeds by gears concealed in the base 35, where they run in oil, being driven

by means of a shaft and flexible coupling from a motor 37. These vertical shafts are connected by means of eccentrics to the two frames 38, which are held in spaced relationship by the side rods 39 so that they hold a tank or cylinder 40 and its cover 41 in place of the "nest" or group of sieves which they were designed to hold. As the vertical shafts rotate, they cause, by means of the eccentrics, an oscillating motion of the frames 38 and of the tank 40 supported thereby. In the drawings, this lateral oscillation is indicated by the dotted lines.

For the testing of mineral nodulization, on a somewhat larger scale, I have found it convenient to use a steel tank or drum of circular cross section having a flat bottom at one end and open at the other end. This drum has a shaft coinciding with the geometrical axis of its cylindrical portion, and the shaft is mounted in appropriate bearings. The axis of the shaft is conveniently inclined at an angle of about 45° with the horizontal, so that when a pulp sample is placed in the tank and the latter is rotated, its open end being upward, the pulp is dragged up the side and bottom of the tank to effect agitation while spilling or slopping out of the contents of the tank is prevented. The heavier mineral particles segregate in the V-shaped space formed by the side and bottom of the tank. Since, in such a device, the pulp is exposed to view, oil and other agents may readily be added and the results observed. When nodules of the desired kind and size have been formed, the rotation of the drum may be stopped and the drum tipped (a hinged joint being conveniently provided for that purpose) to remove the sample for examination or for separation of the nodules by screening or otherwise.

In Fig. 4 of the accompanying drawings, I have shown diagrammatically the apparatus described in the preceding paragraph. Frame members 42 carry bearings 43 in which is rotatably supported a shaft 44 adapted to be driven by means of a pulley 45. At the upper end of the shaft 44 and rotating therewith is a casting 46 which is hinged by means of a hinge-pin 47 and a locking pin 48 to a tank 49, the upper end of which is open. When the rotation of the apparatus is interrupted with the hinge pin 47 down, the locking pin 48 may be withdrawn and the tank 49 tipped about the hinge-pin 47 as an axis into the position shown by the dotted lines, for the discharge of its contents into a sieve 50 appropriately supported above a pan 51. When the apparatus is in operation, the pulp stands not higher than indicated by *c*, and the heavier particles of the pulp tend to segregate into the V-shaped space between the bottom and side wall of the tank.

In the preparation of a mineral mixture for recovery of one or more of its valuable minerals by nodulization, it is necessary to crush or grind the minerals as in similar concentrating operations, if this has not previously been done. The minerals must, as will be well understood by those skilled in the art, be ground fine enough to secure substantially complete release of one or more mineral species which it is desired to nodulize, while, at the same time, not reducing them needlessly. If some of the minerals are especially weak or friable, stage-grinding may be practiced perhaps with intermediate screening or other classifying steps. These operations may be performed wet or dry, depending upon the circumstances attending each case, but it may be said in general that, aside from the considerations mentioned, it will not usually be necessary to grind a given mineral mixture as fine for nodulization treatment as is required for froth-flotation concentration. Since the fineness of grinding somewhat affects the result secured by nodulization, this will, in each instance, be a proper subject for experimentation to determine the optimum condition.

Similarly, the degree of dilution of the mineral pulp, while variable with fair results through quite a wide range, should be determined for each mineral mixture to secure the best results. The pulp need not necessarily be free-flowing, but it must have sufficient liquid so that agitation is practicable. If, on the other hand, the pulp is too dilute the best results may not be secured or too much oil may be required, too much time consumed, or the capacity of the apparatus may be sacrificed.

Many selective agents are known in the art to which this invention relates, which have in common the property that they adhere under certain circumstances (which may be determined by experiment) to particles of certain mineral species and not to others, and thus serve to bind the former particles together. While, for convenience, I call these selective agents "oil", I do so knowing that many of them are not oils, and that some of them are not liquid at ordinary temperature. I have successfully used as such selective agents, with different minerals, petroleum oils, paraffin, vaseline, coal-tars, wood oils, wood tars, resins, oleic and other fatty acids, gums, soaps and greases. As is usual in such cases, each mineral of a mixture presents a special problem which may be solved by experimentation, keeping in mind the general characteristics of the mineral and of the available selective agents, and the result which is desired. In some instances, the oil may be added to the mineral pulp in the condition in which it comes on the market. In other

instances, it may be found best to emulsify the oil before use, employing for this purpose any appropriate agent and procedure. Some times it is advisable to cut the oil with alcohol, kerosene, or some other solvents, or to heat it. Often, all the oil may be added at one time to the mineral pulp, but in other instances it may be found better to add it in a number of increments or doses to secure the best results.

What are known in the art as "addition-", "minor-" or "modifying-agents" may be added to the mineral pulp to bring about or to maintain desired conditions or results. These may be acids, organic or inorganic, of which sulphuric acid is the most common, or alkaline agents, of which sodium hydroxide is the most usual, or they may be salts like copper sulphate or other chemical reagents. They may, indeed, be substances exercising no chemical activity under the circumstances in which used, but of value as aiding in the binding or stabilization of the nodules, or contributing to the hardness or permanence of the nodules. Among such substances may be mentioned coal-dust, charcoal dust, coke dust, wood-pulp and saw-dust. Such substances are generally characterized by ability to hold or adhere to the oil used, and therefore may sometimes aid in the process either by entering into the composition of the resulting mineral nodules or by acting as carriers, to them, of the oil. Other substances, also characterized by ability to take an oil-coating and thus enter into the composition of the mineral nodules, may be added to assist in the final separation or concentration of the mineral nodules or to aid in the smelting or other further beneficiation of the nodules. Thus, iron-filings or powdered magnetite may be incorporated in the formation of nodules to permit of the final separation from the pulp, by magnetic means, of nodules composed principally of non-magnetic mineral, or coal dust may similarly be added so as to secure its incorporation and intimate mixture with the mineral nodules, thus facilitating their subsequent smelting.

Besides the preparation of the mineral pulp, the apparatus employed, the selective agent, and the addition agent, if any, the formation of mineral nodules is affected by temperature and time. With each mineral pulp, it will be necessary to perform a series of tests to determine what temperature and time of treatment are best adapted to give the desired results. With some minerals and selective agents a low temperature is best, and may be secured by cooling the pulp by means of cooling-coils or by partial evaporation of the liquid of the pulp, as by means of a cooling-tower. When a temperature higher than normal is best, it may be secured by direct heating of the pulp, by injecting steam, or by the use of heating coils. Under certain circumstances, it is desirable to use as the selective agent, at least in part, a material having a melting point higher than atmospheric temperature. When it is desired simply to introduce into the pulp such an agent in liquid form, it will, of course, only be necessary to melt the agent and to add it to the pulp in a way that conduces to minute subdivision of the agent therein. When, however, it is desired that such an agent remain liquid in the pulp for a certain time, it will be necessary to heat the pulp, by some such means as those mentioned, to a temperature above the melting point of the agent, adding the agent either in molten condition or as a solid, and permitting it to melt and disperse in the pulp. After the desired action has taken place, the pulp may be again cooled. Thus, I have found it advantageous, under certain circumstances, to use ordinary paraffin, at least in part, as a selective agent. In this case, the mineral pulp was heated by direct heat applied to the containing vessel to a temperature above the melting point of paraffin and maintained at that temperature until the agitation of the selective agent with the pulp resulted in the formation of incipient nodules of the desired mineral. The pulp temperature was then slowly allowed to fall, the agitation being continued, during which the mineral nodules continued to increase in size, so that by the time the pulp temperature had fallen to that of the atmosphere, the desired mineral was combined with the paraffin into hard nodules of the desired size.

The formation of mineral nodules is ordinarily carried out as a preparatory step to a mineral concentration operation. The concentration operation may involve hydraulic classification, screening, jigging, tabling, magnetic separation or any other kind of mineral concentration to which the properties of the nodules and of the unnodulized minerals in the pulp lend themselves. Thus, the concentration may be effected by removing the nodules from the remainder of the mineral pulp or by removing the remainder of the mineral pulp from the nodules. The particular method of concentration to be chosen in a given instance will depend not only upon the ordinary considerations governing concentration, but will take into account the condition of the nodules. If these are firm and the mineral particles adhere tightly, it may be practicable to use a more rapid or rougher method than if they are soft or friable.

Should it be desirable to recover from the concentrated nodules as much as possible of the selective agent used in their formation, this may be done in various ways, as will

be understood by those skilled in the art. Thus, if a fatty acid has been employed as the selective agent, it may be recovered from the nodules, at least in part, by treating them with an alkaline agent to produce a soap, which may be decanted or otherwise separated and recovered. Where a soap has been used to form the nodules, it may be decomposed by the action of acid and the fatty acid thus released may be separated from the mineral matter by appropriate means. Appropriate solvents may also be used for the extraction and recovery of the selective agent from the nodules. Heat, directly or otherwise applied, as, for example, by cooking or steaming the nodules, may be utilized to release the selective agent from the mineral matter and thus make possible its separation and recovery therefrom.

Since my present invention is applicable to the preparation for nodulization of many kinds of mineral mixtures, I wish to be understood when referring to " mineral pulp" as including in this term mixtures of natural or artificial minerals with a liquid, and, therefore, comprehending ores, tailings, middlings, concentrates, smeltery slags, flue dusts, fumes, furnace products, manufactured materials, foundry or factory sweepings or similar débris, coal, coke, sand, gravel, concrete, aggregate, rock crushed for agricultural purposes or for fertilizer manufacture, oil shale, oil rock, oil sand, etc., when mixed with a liquid to form a pulp, and regardless of whether or not the mineral mixture exists as a pulp before or after the treatment contemplated by the present invention.

The word "mineral" as herein used, is to be understood as including inorganic substances of substantially constant chemical composition occurring naturally in the crust of the earth; such inorganic but artificial substances analogous in structure and use to natural minerals, and which, by extension of thought, are in practice classed as minerals, and also such substances found in the earth as are organic in the sense that they are supposed to owe their origin to the plant or animal life of past geological ages, but are now classed as mineral. It will therefore be understood that I intend to include in the word "mineral" not only the well recognized natural minerals, metallic and non-metallic, but also metals, elements, smeltery slags, refractory materials, abrasive substances, glass, ashes, flue dusts, foundry or factory sweepings or similar débris, coal, coke, bitumens, petroleum oils, etc.

It is well known that colloids and colloidal slimes, both organic and inorganic, often are present in mineral pulp, and when present in considerable amount, may have an unfavorable effect upon the concentration of such mineral pulp. When considerable amounts of colloids or colloidal slimes are thus present, it is usually necessary to operate in a more dilute pulp. The colloidal matters present in a mineral pulp are probably derived for the most part from the gangue or non-valuable particles of the mineral mixture, although it is not unlikely that valuable mineral particles may also be present in the pulp in the form of colloids. Such colloidal matters may also be introduced with the milling water which is used to form the mineral pulp, and this source of colloidal matters may be considerable during periods of heavy rainfall when surface waters containing mud and other suspended matters, and heavily charged with both organic and inorganic colloids, run into the source from which the milling water is customarily taken.

The colloidal matters may be present as pure colloids, organic or inorganic, or in a state bordering on the so-called "coarse suspensions". Throughout this specification and the appended claims, I intend to embrace in the expressions "colloids", "colloidal slimes" and "colloidal constituents", both true colloids and those quasi or borderland substances which may not be truly colloidal but partake of the qualities of or resemble, colloids, and without regard to the sources from which such colloidal matters are derived. Thus, for the purposes of the present invention, the colloidal constituents may be considered as ranging from just above the molecular size upward through the class of so-called suspensoids, which, while possibly not true colloids, still, because of their relatively large specific surface, exihibit some, if not all, of the properties of colloids, and are capable of existing in both the sol or gel state, or of being dispersed and coagulated, or flocculated and deflocculated. By a colloidal slime, therefore, I mean a material which is not necessarily a true colloid, but exhibits colloidal characteristics to a sufficient degree to make it amenable to the manipulation hereinafter described.

While it has heretofore been proposed to treat mineral pulps in various ways for the purpose of overcoming or minimizing the prejudicial effect of colloidal matter upon some contemplated mineral treatment operation, the injurious effect of colloidal matter upon the nodulization of minerals has not been investigated and, as far as I am aware, has not heretofore been even recognized. As heretofore stated, I have found that the presence of colloidal matters in a mineral pulp usually exercises a prejudicial or deleterious influence on the nodulization of particular mineral constituents of the pulp and the present invention is particularly directed towards controlling the action or influence of colloidal matters upon mineral nodulization.

As the result of my investigations, I believe that the injurious action on the nodulizing operation of colloidal matters present in the mineral pulp may result from their presence in the mineral pulp, or may be due to their attachment to, or adsorption by, certain minerals of the pulp, or the reagents introduced into the pulp to effect or assist nodulization, or may be due to their combination, chemically, with such reagents, thus neutralizing them or delaying or inhibiting the action which they are intended to bring about, or may be due to their affecting the density or viscosity of the pulp, the settling rate of the mineral particles, the liquid-holding capacity of the mineral particles, the entanglement or other form of aggregation of the mineral particles, or in other and less obvious ways. It is my belief that these colloidal matters may interfere with nodulizing operations whether they exist in a flocculated (or coagulated) or in a deflocculated (or dispersed) condition, but I have found that in general their action is less marked when dispersed or deflocculated.

When the colloidal constitutents of a mineral pulp are flocculated, and owe their deleterious influence on the nodulization of the minerals to this condition, and especially when they are of such a kind as to be only mildly objectionable, or are present in slight amount, it may be unnecessary to actually remove or withdraw them from the pulp, and a simple deflocculation or dispersion of these colloidal constituents may suffice to overcome their inhibitory tendency and to permit the nodulization to proceed. In some cases, where two or more valuable mineral species are to be removed from a mineral pulp by successive nodulization treatments, it may suffice to deflocculate or disperse the colloidal constituents of the pulp to render one such mineral species amenable to nodulization, and, after the nodulization and removal, by an appropriate concentrating step, of that mineral species, the colloidal constituents may be further deflocculated or the continued deflocculated condition of the colloidal constituents may be taken advantage of to effect their removal or withdrawal from the pulp to the extent required to permit the nodulization of a second valuable mineral species. Regardless of whether deflocculation or dispersion of the colloidal constituents is followed by withdrawal of such constituents from the mineral pulp, the improvements which characterize the present invention are of advantage in bringing about the deflocculation or dispersion of the colloidal constituents as a preparatory step to mineral nodulization.

The present invention, in one of its aspects, contemplates, as an improvement in the nodulization of minerals, and as a preliminary step to the nodulization operation proper, the removal, in whole or in part, of colloidal constituents from a mineral mixture or pulp, and in its preferred form, the invention, in this aspect, contemplates the removal of such colloidal constituents in a dispersed or deflocculated condition. The colloidal constituents may be removed from the mineral pulp in various ways. For example, the colloidal constituents, preferably in a dispersed or deflocculated condition, may be removed from the mineral pulp by sedimentation and decantation. The colloidal constituents (whether flocculated or deflocculated) may be removed from the mineral pulp by a preliminary flotation operation in which a froth or scum containing part or the whole of the colloidal constituents, with a relatively small proportion of the valuable minerals contained in the pulp, is separated from the bulk of the mineral pulp. After the removal of the colloidal constituents in accordance with the principles of the present invention, the mineral pulp thus freed of the removed colloidal constituents is subjected to a nodulization operation in accordance with any appropriate practice. In another of its aspects, the present invention contemplates the dispersion or deflocculation of the colloidal constituents of a mineral pulp without necessarily removing the dispersed or deflocculated colloidal constituents from the mineral pulp, as a preparatory step to a mineral nodulization operation.

The removal, by sedimentation and decantation, from the mineral pulp, of the colloidal constituents, depends for its effectiveness upon the relative difference in the rate of settling or sedimentation of the mineral particles and the colloidal constituents. For this reason, it is desirable to cause the colloidal constituents (where their removal is to be effected by decantation) to settle at a much slower rate than the mineral particles in the mineral pulp, whereby after a predetermined settling of the mineral particles, any desired portion of the supernatant liquor containing the slower-settling colloidal constituents can be decanted in any suitable way to effect the removal from the mineral pulp of the desired quantity of the colloidal constituents. In this connection, the present invention contemplates the dispersion or deflocculation of the colloidal constituents so as to cause them to settle at a very much slower rate than would be the case if they were coagulated or flocculated, so that they will remain in more or less permanent suspension in quiet pulp, thus permitting settling or sedimentation of the sands and slimes containing the valuable minerals, and decantation, by displacement or otherwise, of the liquid containing the suspended colloids or colloidal slimes.

The colloidal constituents of mineral pulps are rarely, if ever, naturally deflocculated and dispersed to their maximum possible extent. Since aggregated or flocculated colloid masses act like solid particles of greater magnitude, the removal of the partially flocculated colloidal constituents of a mineral pulp by means of settling processes, or even by washing with water on tables or vanners, is generally incomplete and inadequate. The agencies which promote the flocculation of the colloidal constituents of a mineral pulp also in general seem to promote the adsorption or other form of attachment which exists between such colloidal constituents and the granular constituents of the mineral pulp. It follows, therefore, that when the colloidal constituents of a mineral pulp have been thoroughly deflocculated and minutely dispersed, they no longer exist in the form of aggregates, resembling the coarser solid particles of the pulp, but behave more like substances in solution, and are, in fact, spoken of as being in colloidal solution, in which condition the forces tending to maintain them in suspension are greater than the effect of gravity, thereby greatly facilitating their separation by sedimentation and decantation, and as, at the same time, their adsorption or other bond for the coarser solid particles of the mineral pulp is weakened, the removal of such colloidal constituents from the mineral pulp is greatly facilitated over what is possible in their natural partially flocculated condition.

Even when the colloidal constituents of the mineral pulp are originally deflocculated or have been reflocculated early in the treatment of the pulp, they may have become flocculated during the treatment to which the pulp is subjected, or agents may have been added which cause them to flocculate and in such cases the same general method of treatment is applied to secure deflocculation, in accordance with the principles of this invention, as would be applied to a pulp containing naturally flocculated colloidal constituents.

The present invention accordingly contemplates, as a preliminary step to the nodulization of one or more mineral species associated in a mineral pulp with an objectionable amount of colloids, the treatment of the mineral pulp with a deflocculating or dispersing agent in order to convert the colloids into a deflocculated or dispersed condition (provided they are not already present in such a state of dispersion or deflocculation), and separating or removing the dispersed or deflocculated colloids, in whole or in part, by decantation, or otherwise, from the mineral pulp prior to the nodulization operation. As a result of this removal of the colloids in a dispersed or deflocculated state, the mineral pulp is thereby freed from such colloidal matter, to the desired extent, so that the nodulization operation can thereafter be carried out without being prejudiced or inhibited by the colloidal constituents which have been removed.

I have found further that, for certain purposes, it is desirable to retain part of the colloidal constituents in the mineral pulp, and that, when a proper amount of such constituents is present, it is possible to effect a differential nodulization of one or more mineral species in the mineral pulp, while the nodulization of another or other mineral species is retarded or inhibited by the colloids remaining in the mineral pulp; and that, thereafter, by a further removal of a part or all of the remaining colloids, in the manner hereinbefore referred to, nodulization of one or more such other mineral species can be effected.

As a result of the investigations which I have made, I have been led to believe that colloidal adsorption takes place upon metallic surfaces and upon the surfaces of sulfides and other minerals, but that the strength of the adsorption varies considerably, depending upon the character of the colloid, its relative concentration, the kind and character of adsorbing material, and its temperature and condition of electrical charge. I do not, however, desire to limit myself by any theoretical explanation of the principles underlying the present invention. Whatever may be the correct explanation of the prejudicial effect of colloids when present, and of the advantages resulting from their removal, the process of the present invention involves, in one of its aspects, the separation or removal from the mineral pulp of the colloids in a dispersed or deflocculated condition, and in whole or in part, whether adsorbed by or otherwise combined or admixed with the minerals), as a preliminary or preparatory step to a mineral nodulization operation.

If the mineral pulp contains the colloids or colloidal slimes in a naturally sufficiently dispersed condition, then the treatment with a dispersing or deflocculating agent may not be necessary and the mineral pulp may be subjected directly to nodulization or to differential sedimentation or decantation for the removal of the colloidal constituents to the desired extent. With the removal of the colloidal slimes there will, of course, also be removed a corresponding portion of the liquid of the mineral pulp, together with such constitituents as are dissolved therein.

If the colloidal slimes of the mineral pulp are not naturally sufficiently dispersed (as is generally the case in actual practice), the mineral pulp is treated with a dispersing or deflocculating agent to bring about the

desired dispersion or deflocculation, after which, if their presence is inhibitory to nodulization, decantation (or other appropriate procedure) is employed for the purpose of removing a portion or the whole of the dispersed colloidal constituents and accompanying liquid containing the added agent or agents. The dispersing agent which I have used to particular advantage with many mineral mixtures is sodium silicate, but many other agents are available for effecting the desired dispersion or deflocculation of the colloidal constituents. Using sodium silicate, I have found that good results are obtained with a small amount, for example five per cent down to a fraction of one per cent of the sodium silicate per ton (dry weight) of the mineral mixture being treated. The dispersing or deflocculating agent should be properly chosen with reference to the colloidal properties of the mineral mixture and in accordance with the known principles of colloid chemistry so that the desired deflocculation or dispersion will take place. The nature of the dispersing agent will accordingly vary somewhat with different mineral mixtures, because the colloidal constituents vary, in some cases being of a basic character and in others of an acid character, and in some cases being positively charged, and in other cases being negatively charged. The dispersing agent may thus be of an acid character, in case the colloidal constituents are such as are dispersed by an acid reagent, or of an alkaline character, if the preliminary tests indicate this to be desirable. The agent or agents may themselves partake of a colloidal character as, for example, silicic acid or sodium or potassium silicates, or soaps which also display acid or alkaline characteristics. In addition to the agents hereinbefore mentioned, I have in practice successfully employed gum arabic (acacia), foundry molasses, tri-sodium phosphate, etc., as colloid dispersing agents.

The dispersion of the colloids (whether adsorbed by the mineral particles or otherwise coagulated or flocculated), may be promoted, or even brought about, to a greater or less extent, by rapid circulation and agitation of the pulp, which will serve to distribute the deflocculating agent, if any is used, and cause abrasion of the mineral particles with each other and with floccules or coagules of colloidal matter in which the mineral particles may be enmeshed, so that the separated and dispersed colloids may be more readily removed by decantation. Increase or decrease in temperature may similarly be of assistance in bringing the colloids into a state permitting their removal from the mineral pulp. The optimum temperature, in the case of any particular mineral mixture, for effecting dispersion of the colloidal constituents contained in the mineral mixture may be determined by tests, in which the other factors are held constant and the temperature varied through a wide range. Where this optimum temperature is higher than the normal temperature of the mineral pulp, the mineral pulp may be heated to the desired temperature by direct heating or by the use of steam-heating coils, or by steam blown into the pulp, and where this optimum temperature is lower than the normal temperature of the mineral pulp, the pulp may be cooled by dilution with cold water, by cooling coils, by cooling towers, etc.

I have found that the necessary distribution of the dispersing or deflocculating agent through the mass of the mineral mixture and the contemplated dispersion or deflocculation of the colloids or collidal slimes present in the mineral mixture can be very conveniently and effectively brought about by adding the deflocculating or dispersing agent to the mineral pulp at some point prior to the admission of the mineral mixture to the ball-, or pebble-mills, or other fine-grinding machines. Such machines almost invariably form a part of the equipment of concentrating plants. By so adding the deflocculating or dispersing agent to the mineral mixture ahead of the fine-grinding mills, the necessary admixture is secured without inconvenience or added expense, and the dispersion or deflocculation of the colloids or colloidal slimes may take place under the most favorable conditions of temperature and violent agitation. Under such conditions floccules or coagules are readily broken up and prevented from re-forming, or particles already coated with colloids or enmeshed within floccules are cleaned or released. Such colloids as are released from a solid or indurated condition by the grinding are immediately placed in the dispersed or deflocculated state, and the fresh mineral surfaces exposed by the grinding are prevented from being coated with inhibitory coatings of colloidal material. This procedure may, with some mineral mixtures, be sufficient to effect the desired degree of deflocculation without the use of a deflocculating agent, provided the decantation of the colloidal constituents is effected immediately after the pulp leaves the grinding machine, it being, of course, understood that the removal by decantation of the colloidal constituents in a dispersed state must take place when the mineral pulp is relatively quiescent, and cannot be satisfactorily carried out while the pulp is undergoing such agitation as will interfere with the desired settling of the non-colloidal constituents.

Whatever may be the preliminary treatment, or combination of treatments, to

which the mineral pulp is subjected for the dispersion or deflocculation of its colloids, (in case such preliminary dispersion is necessary), these colloids are, according to one aspect of the present invention, removed (by decantation or otherwise) in a dispersed condition from the mineral pulp to the extent necessary to prevent them from interfering with the subsequent treatment of the mineral pulp. Such removal of the colloids in a dispersed condition may take place in tanks such as those of the Dorr, Allen or Callow types. With the overflow from such tanks there will be removed a corresponding amount of liquid so that the mineral mixture will become thickened. So much of the liquid may in fact be removed that only sufficient liquid and accompanying slimes remain to permit the handling of the pulp as by pumping and its preparation for the next step in the process.

After the deflocculated or dispersed colloids or colloidal slimes have been removed to the desired extent, that is, in whole or in part, depending upon the result desired, the remaining mineral pulp, which is now in a more concentrated state with respect to its solid phase, may in certain cases be directly subjected to a nodulization operation, and in other cases may be further thickened or diluted and then subjected to the nodulization operation. The removal of the colloids from the mineral mixture often enables the mineral mixture to be treated in a state of greater density, that is, in a more concentrated form with respect to its solid phase, with the result that an increased tonnage of mineral mixture can be handled by a given plant.

The colloidal slimes which are separated from the mineral pulp are commonly of a character such that they may be run to waste. In case, however, these slimes carry sufficient values, they may be themselves subjected to a further treatment for the recovery of the values therefrom. For example, they may be subjected to a flotation treatment, for the separation of valuable minerals therefrom, or they may be subjected to other appropriate treatment for the recovery of values.

The liquid accompanying the removed colloids may be separated and recovered for re-use. The colloids contained therein may thus be coagulated, and settled or filtered out. The liquid separated from the colloids may be purified, if necessary, to free it from dissolved salts prejudicial to the maintenance of the desired state of dispersion of the mineral mixture to which it may be subsequently added.

If the original mineral mixture contains several valuable ingredients, such as sulfides, the removal of the colloidal constituents may be carried out in a number of stages in order to take advantage of the selective inhibition of the colloids or colloidal slimes toward the nodulization of certain of the minerals. For example, in a mixed sulfide mineral mixture, containing sulfides of lead, zinc and iron, which it is desired to treat by the nodulization process, the mineral mixture may be treated for the removal of a portion only of the colloidal slimes, in the manner hereinbefore described, so that there will be retained sufficient of the colloids to prevent any considerable nodulization of the iron and zinc sulfides, while permitting the nodulization of the lead sulfide, so that a lead concentrate can be obtained, relatively free from zinc and iron. The remaining mineral pulp may then be treated for the removal of an additional portion of the colloids, whereby nodulization of the zinc, or nodulization of the zinc and iron, may be readily effected. Where the zinc is nodulized without nodulization of the iron, a still further removal of the colloids from the remaining mineral pulp may then be effected in order to permit nodulization of the iron sulfide. In carrying out differential nodulization of different minerals, advantage may also be taken, in each case, of the well known selective qualities of certain oils, or other agents, for the various minerals, such selective qualities supplementing the selectively inhibitory action of the colloidal constituents.

It will be understood that mineral mixtures other than lead and zinc ores can be treated in a similar manner and with proper selection of the agent or agents added for bringing about or maintaining the dispersed state of the colloids (where the addition of such agent or agents is necessary for this purpose), depending upon the so-called colloidal charge, (whether electro-positive or electro-negative), of the constituents of the mineral mixture being treated, this treatment being based upon tests made in accordance with the general principles of colloid chemistry. The agent or agents may thus be of an acid character, in case the colloidal constituents are such as are dispersed by an acid reagent, or of an alkaline character, if the preliminary tests indicate this to be desirable. The agent or agents may themselves partake of a colloidal character, as, for example, silicic acid or sodium or potassium silicates, or soaps which also display acid or alkaline characteristics, or they may be organic colloids, for example, gum arabic (acacia), in small amounts, may be added to promote the desired dispersion and separation of the colloids.

It will be seen that this aspect of the present invention involves the separation of colloidal constituents from the mineral mixture, prior to nodulization, so that the nodulization operation is carried out without interference therefrom, or with such regulated

action of the remaining colloids as is desirable for the particular object in view, as in case a differential nodulization of certain minerals is desired. This preliminary separation may be readily effected by a simple over-flow or decantation of the dispersed colloids, liquid being subsequently added to dilute the pulp, if necessary to secure the desired results. Where the colloids are not already present in a sufficiently dispersed state a suitable agent for bringing them into such a state may be added, and the separation thereafter effected. In each case there is separated from the mineral mixture, along with the separated colloids, a corresponding amount of the liquid with its dissolved constituents so that the mineral mixture is thereby freed from any objectionable constituents contained therein. This liquid, however, after a suitable purification, may be returned to the operation and used over and over again. The decantation may be carried out on the counter-current principle by the use of a series of tanks arranged for counter-flow of the mineral pulp and of the overflow, so that a more or less complete separation of the colloids may be effected and the amount thereof regulated.

Where the mineral pulp contains, in solution in the liquid thereof, substances which prevent dispersion or deflocculation of the colloids, such substances may be in part or in whole removed, as, for example, by the removal of the liquid from the mineral pulp prior to the dispersion or deflocculation treatment, or they may be otherwise neutralized and rendered harmless by methods and agents which are generally known, and can be regulated by simple tests. For example, an excessive quantity of magnesium sulfate or of some other electrolyte in the mineral pulp may interfere with the proper action of sodium silicate as a dispersing agent. Such a condition may be corrected by washing the mineral mixture for the removal of soluble salts. Where the mineral pulp is acid or where there is latent acidity, due to the occlusion of sulfur dioxide, an alkali may be added to correct the acidity, whereby the sodium silicate is enabled to act in the desired manner.

In some mineral mixtures, containing more than one valuable mineral, which it is desired to nodulize differentially, there may be present naturally insufficient inhibitory collodial matter to permit of such differential nodulization, and, as a consequence, even with the nicest choice of selective nodulizing agents and of addition agents the valuable minerals may nodulize simultaneously, forming mixed-mineral nodules. In such instances the addition of colloidal matter regulated in kind, condition and amount, may make possible the nodulization of one such valuable mineral while the nodulization of the other is substantially inhibited. After the first mineral has been nodulized and removed from the pulp by a concentration operation, in the desired way, the pulp may then be treated to deflocculate or disperse the added colloidal matter, which may then be removed to the extent desired, by decantation or otherwise, and the second valuable mineral may then be nodulized likewise and recovered from the pulp by a concentrating operation.

The colloidal matter thus added to inhibit the nodulization of one valuable mineral in a pulp, while permitting the nodulization of another, may be either organic or inorganic in composition, and it may be added in either a flocculated or deflocculated or in either the sol or gel state. In each specific instance it will be necessary to perform experiments to determine the colloidal matters which are effective in producing the desired inhibitory action, and which of them it is best to use. By similar experiments it will be determined in what state the colloidal matter should be added, and how much should be used, bearing in mind the subsequent treatment to which the ore-pulp and the valuable minerals are to be subjected. Among the colloidal agents which I have found effective in certain instances, are, the colloidal part of clays, earths, ground ore or rock, acacia, saponin, agar-agar, hemoglobin, glue, goat's blood extract, tannin and milk casein. Many similar substances are known to exercise a deleterious influence on the adhesion of "oil" to minerals, and such colloidal substances should be experimented with systematically when searching for a substance which will be effective in inhibiting the nodulization of one valuable mineral while permitting the nodulization of another.

In the application of this feature of the present invention, as, likewise in the application of its other features, advantage is to be taken of the known action of other agents and means, which may, on the one hand, increase the tendency of one of the valuable minerals to nodulize, or, on the other hand, decrease the tendency to nodulize of the other valuable mineral. For example, in the case of a certain ore containing galena and sphalerite, I have found that sulfur dioxide in solution in the pulp aids in preventing the nodulization of the sphalerite, when used in connection with a colloidal slime derived from a ground ore, the galena nodulizing, with the aid of appropriate agents, to the practical exclusion of the sphalerite. After the galena has thus been nodulized and by means of a suitable concentrating step has been removed from the pulp, the latter is treated with an alkaline agent, to neutralize the sulfur dioxide, following which the added colloidal

constituent is removed as herein described, whereupon it becomes possible, by the use of suitable selective and addition agents, to nodulize the sphalerite and to remove it from the pulp. Many addition agents act one way toward one valuable mineral, and in the other way toward a second valuable mineral. In some instances advantage may be taken of this fact by using a single addition agent to enhance the nodulization of one valuable mineral in a pulp and inhibit that of another.

Some mixed-mineral concentrates may be treated to peculiar advantage by the last-described variant of the process of the present invention. For example, if the mixed-mineral concentrate contains two valuable minerals, both amenable to nodulization, but insufficient colloidal matter to inhibit the nodulization of one of them, a colloidal agent may be added to the concentrate pulp, together with such other agent or agents as may be necessary, sufficient in kind, condition and amount to substantially inhibit the nodulization of one of the minerals while permitting the nodulization of the other. The nodulized mineral may then be removed from the concentrate pulp, and the remainder of the pulp, freed, if necessary from water and the added colloidal agent, may be, itself, a finished product.

I have discovered that when mineral pulps are prepared for nodulization treatment according to the principles of the present invention, that it is often possible by nodulization to secure a more complete differential separation of one valuable mineral from another than has so far commonly been found possible by the known methods of froth flotation. It is, accordingly, often possible to retreat, by the herein described methods, the mixed-mineral concentrate resulting from froth flotation of a mixed-mineral pulp, and to produce therefrom secondary concentrates of a higher order of purity.

I claim:

1. The method of improving the nodulization of minerals associated with colloidal constituents in a mineral pulp, which comprises removing collodial constituents to a desired extent from the mineral pulp, and thereafter subjecting the remaining mineral pulp to a nodulization operation in which such colloidal constituents as have been removed from the pulp would if present exert a deleterious effect.

2. The method of improving the nodulization of minerals associated with normally flocculated colloidal constituents in a mineral pulp, which comprises removing colloidal constituents from the mineral pulp to a desired extent, and thereafter subjecting the remaining mineral pulp to a nodulization operation in which such colloidal constituents as have been removed from the pulp would if present exert a deleterious effect.

3. The method of improving the nodulization of minerals associated with normally flocculated colloidal constituents in a mineral pulp, which comprises removing colloidal constituents to a desired extent from the mineral pulp, said removal of colloidal constituents being preceded by the step of dispersing or deflocculating colloidal matter which would otherwise be present in the pulp in a flocculated condition, and thereafter subjecting the remaining mineral pulp to a nodulization operation in which such colloidal constituents as have been removed from the pulp would if present exert a deleterious effect.

4. The method of improving the nodulization of minerals associated with colloidal constituents in a mineral pulp, which comprises adding to the mineral pulp a dispersing or deflocculating agent for promoting dispersion or deflocculation of colloidal constituents in the mineral pulp, removing dispersed or deflocculated colloidal constituents to a desired extent from the mineral pulp, and thereafter subjecting the remaining mineral pulp to a nodulization operation in which such colloidal constituents as have been removed from the pulp would if present exert a deleterious effect.

5. The method of improving the nodulization of minerals associated with colloidal constituents in a mineral pulp, which comprises adding to the mineral pulp a dispersing or deflocculating agent for promoting dispersion or deflocculation of colloidal constituents in the pulp, subjecting the mineral pulp to a decantation treatment for the removal therefrom to a desired extent of dispersed or deflocculated colloidal constituents together with a corresponding portion of the liquid of the pulp, and thereafter subjecting the remaining mineral pulp to a nodulization operation in which such colloidal constituents as have been removed from the pulp would if present exert a deleterious effect.

6. The method of improving the nodulization of minerals associated with colloidal constituents in a mineral pulp, which comprises agitating and regulating the temperature of the mineral pulp for promoting dispersion or deflocculation of colloidal constituents in the pulp, removing dispersed or deflocculated colloidal constituents to a desired extent from the mineral pulp, and thereafter subjecting the remaining mineral pulp to a nodulization operation in which such colloidal constituents as have been removed from the pulp would if present exert a deleterious effect.

7. The method of improving the nodulization of minerals associated with normally

flocculated colloidal constituents in a mineral pulp, which comprises agitating the mineral pulp for promoting dispersion or deflocculation of colloidal constituents in the pulp, removing the dispersed or deflocculated colloidal constituents to a desired extent from the mineral pulp, and thereafter subjecting the remaining mineral pulp to a nodulization operation in which such colloidal constituents as have been removed from the pulp would if present exert a deleterious effect.

8. The method of improving the nodulization of minerals associated with colloidal constituents in a mineral pulp, which comprises regulating the temperature of the mineral pulp for promoting dispersion or deflocculation of colloidal constituents in the pulp, removing dispersed or deflocculated colloidal constituents to a desired extent from the mineral pulp, and thereafter subjecting the remaining mineral pulp to a nodulization operation in which such colloidal constituents as have been removed from the pulp would if present exert a deleterious effect.

9. The method of improving the nodulization of minerals associated with colloidal constituents in a mineral pulp, which comprises removing colloidal constituents in desired amount from the mineral pulp, subjecting the mineral pulp thus freed of the removed colloidal constituents to a nodulization operation, separating the resulting nodules from the mineral pulp removing a further amount of colloidal constituents from the remaining mineral pulp, and thereafter subjecting such remaining mineral pulp thus freed of such further amount of the colloidal constituents to a further nodulization operation.

10. The method of improving the nodulization of minerals associated with colloidal constituents in a mineral pulp, which comprises removing such portion of the colloidal constituents from the mineral pulp as to promote the nodulization of one valuable mineral species of the pulp while substantially inhibiting the nodulization of other normally nodulizable valuable mineral species of the pulp, and thereafter subjecting the mineral pulp thus partially freed of colloidal constituents to a nodulization operation wherein one valuable mineral species of the pulp is nodulized while the nodulization of other valuable mineral species of the pulp is substantially inhibited.

11. The method of improving the nodulization of minerals associated with colloidal constituents in a mineral pulp, which comprises removing a portion of the colloidal constituents from the mineral pulp, subjecting the mineral pulp thus partially freed of colloidal constituents to a nodulization operation wherein one valuable mineral species of the pulp is nodulized while the nodulization of other valuable mineral species of the pulp is substantially inhibited, separating the resulting nodules from the mineral pulp, thereafter withdrawing from the remaining mineral pulp another portion of its colloidal constituents, and subjecting such remaining mineral pulp thus further freed of colloidal constituents to a nodulization operation wherein another of the valuable mineral species of the pulp is nodulized.

12. The method of improving the nodulization of minerals associated with colloidal constituents in a mineral pulp, which comprises removing such portion of the colloidal constituents in a dispersed or deflocculated condition from the mineral pulp as to promote the nodulization of one valuable mineral species of the pulp while substantially inhibiting the nodulization of other normally nodulizable valuable mineral species of the pulp, and thereafter subjecting the mineral pulp thus partially freed of collodial constituents to a nodulization operation wherein one valuable mineral species of the pulp is nodulized while the nodulization of other valuable mineral species of the pulp is substantially inhibited.

13. The method of improving the nodulization of minerals associated with colloidal constituents in a mineral pulp, which comprises removing a portion of the colloidal constituents in a dispersed or deflocculated condition from the mineral pulp, subjecting the mineral pulp thus partially freed of colloidal constituents to a nodulization operation wherein one of the valuable mineral species of the pulp is nodulized while the nodulization of other valuable mineral species of the pulp is substantially inhibited, separating the resulting nodules from the mineral pulp, thereafter removing from the remaining mineral pulp another portion of its colloidal constituents in a dispersed or deflocculated condition, and subjecting such remaining mineral pulp thus further freed of colloidal constituents to a nodulization operation wherein another valuable mineral species of the pulp is nodulized.

14. The method of improving the nodulization of minerals associated with colloidal constituents in a mineral pulp, which comprises dispersing or deflocculating the colloidal constituents to such an extent as to promote the nodulization of one valuable mineral species of the pulp while substantially inhibiting the nodulization of other normally nodulizable valuable mineral species of the pulp, and thereafter subjecting the thus treated mineral pulp to a nodulization operation wherein one valuable mineral species of the pulp is nodulized while the nodulization of other valuable mineral species of the pulp is substantially inhibited.

15. The method of improving the nodu-

lization of minerals associated with colloidal constituents in a mineral pulp, which comprises dispersing or deflocculating to a desired extent such colloidal constituents, and subjecting the thus treated pulp to a nodulization operation wherein one valuable mineral species of the pulp is nodulized while the nodulization of other valuable mineral species of the pulp is substantially inhibited, separating the resulting nodules from the mineral pulp, thereafter further dispersing or deflocculating the colloidal constituents of the mineral pulp, and subjecting the thus further treated mineral pulp to a nodulization operation wherein another valuable mineral species of the pulp is nodulized.

16. The method of improving the nodulization of minerals associated with colloidal constituents in a mineral pulp, which comprises dispersing or deflocculating to a desired extent such colloidal constituents, subjecting the thus treated mineral pulp to a nodulization operation wherein one valuable mineral species of the pulp is nodulized while the nodulization of other valuable mineral species of the pulp is substantially inhibited, separating the resulting nodules from the mineral pulp, thereafter removing the colloidal constituents to the desired extent from the mineral pulp, and subjecting the pulp thus freed from the removed colloidal constituents to a nodulization operation wherein another valuable mineral species of the pulp is nodulized.

17. The method of improving the differential nodulization of minerals in a mineral pulp, which comprises adding to the mineral pulp a colloidal material permitting the nodulization of one mineral species of the pulp while substantially inhibiting the nodulization of the other normally nodulizable mineral species of the pulp, subjecting the pulp to a nodulization operation, and separating the resulting nodules from the pulp.

18. The method of improving the differential nodulization of minerals in a mineral pulp, which comprises adding to the mineral pulp a colloidal material permitting the nodulization of one mineral species of the pulp while substantially inhibiting the nodulization of the other normally nodulizable mineral species of the pulp, subjecting the pulp to a nodulization operation, separating the resulting nodules from the pulp, removing colloidal constituents to a desired extent from the remaining pulp, and thereafter subjecting the remaining pulp thus freed of the removed colloidal constituents to a further nodulization operation.

19. The method of improving the nodulization of minerals which comprises adding to a mineral pulp containing a plurality of valuable mineral species a colloidal material substantially inhibitory toward the nodulization of one or more valuable mineral species of the pulp while permitting the nodulization of another or other valuable mineral species of the pulp, subjecting the thus treated pulp to a nodulization operation wherein the last mentioned valuable mineral species of the pulp is nodulized while the nodulization of the first mentioned valuable mineral species of the pulp is substantially inhibited, separating the resulting nodules from the pulp, withdrawing the added colloidal material to a desired extent from the remaining pulp, and subjecting the remaining pulp to a further separative treatment in which such colloids as have been removed therefrom would, if present, exert a deleterious effect.

20. The method of improving the nodulization of minerals which comprises adding to a mineral pulp containing a plurality of valuable mineral species a colloidal material substantially inhibitory toward the nodulization of one or more valuable mineral species of the pulp while permitting the nodulization of another or other valuable mineral species of the pulp, subjecting the thus treated pulp to a nodulization operation wherein the last mentioned valuable mineral species of the pulp is nodulized while the nodulization of the first mentioned valuable mineral species of the pulp is substantially inhibited, separating the resulting nodules from the pulp, removing the added colloidal matter to a desired extent from the remaining pulp, and thereafter subjecting the pulp thus freed of the removed colloidal material to a nodulization operation wherein another valuable mineral species of the pulp is nodulized.

21. The method of improving the nodulization of minerals which comprises adding to a mineral pulp containing a plurality of valuable minerals a colloidal material substantially inhibitory toward the nodulization of all but one of such minerals, subjecting the thus treated pulp to a nodulization operation in order to nodulize one of the minerals thereof, separating the resulting nodules from the pulp, removing from the remaining mineral pulp to a desired extent the added colloidal material in a dispersed or deflocculated condition, and subjecting the remaining pulp to a further separative treatment in which such colloids as have been removed therefrom would, if present, exert a deleterious effect.

22. The method of improving the nodulization of minerals which comprises adding to a mineral pulp containing a plurality of valuable mineral species a colloidal material substantially inhibitory toward the nodulization of one or more valuable mineral species of the pulp while permitting the nodulization of another or other valuable mineral species of the pulp, subjecting the thus

treated pulp to a nodulization operation wherein the last mentioned valuable mineral species of the pulp is nodulized while the nodulization of the first mentioned valuable mineral species of the pulp is substantially inhibited, separating the resulting nodules from the pulp, removing from the remaining mineral pulp to a desired extent the added colloidal material in a dispersed or deflocculated condition, and thereafter subjecting the remaining mineral pulp thus freed of the removed colloidal material to a nodulization operation wherein another mineral species of the pulp is nodulized.

23. The method of improving the nodulization of minerals which comprises adding to a mineral pulp containing a plurality of valuable minerals a colloidal material substantially inhibitory toward the nodulization of all but one of such minerals, subjecting the thus treated pulp to a nodulization operation in order to nodulize one of the minerals thereof, separating the resulting nodules from the pulp, dispersing or deflocculating to a desired extent the added colloidal material in the remaining pulp, and thereafter subjecting the thus treated remaining mineral pulp to a further mineral treatment operation.

24. The method of improving the nodulization of minerals which comprises adding to a mineral pulp containing a plurality of valuable mineral species a colloidal material substantially inhibitory toward the nodulization of one or more valuable mineral species of the pulp while permitting nodulization of another or other valuable mineral species of the pulp, subjecting the thus treated pulp to a nodulization operation wherein the last mentioned valuable mineral species of the pulp is nodulized while the nodulization of the first mentioned valuable mineral species of the pulp is substantially inhibited, separating the resulting nodules from the pulp, dispersing or deflocculating to a desired extent the added colloidal material in the remaining pulp, and thereafter subjecting the thus treated remaining pulp to a nodulization operation wherein another valuable mineral species is nodulized.

25. The method of improving the nodulization of minerals associated with colloidal constituents in a mineral pulp, which comprises adding to the mineral pulp a dispersing or deflocculating agent for promoting dispersion or deflocculation of the colloidal constituents of the mineral pulp, removing a part of the dispersed or deflocculated colloidal constituents from the mineral pulp, subjecting the mineral pulp thus freed of the removed colloidal constituents to a nodulization operation wherein one valuable mineral species of the pulp is nodulized, separating the resulting nodules from the pulp, removing from the remaining mineral pulp a further amount of the colloidal constituents therein, and thereafter subjecting such remaining mineral pulp thus freed of such further amount of the colloidal constituents to a further nodulization operation wherein another valuable mineral species of the pulp is nodulized.

26. The method of improving the nodulization of minerals associated with colloidal constituents in a mineral pulp, which comprises removing a part of the colloidal constituents from the mineral pulp, subjecting the mineral pulp thus freed of the removed colloidal constituents to a nodulization operation wherein a valuable mineral species of the pulp is nodulized, separating the resulting nodules from the pulp, adding to the remaining mineral pulp a dispersing or deflocculating agent for promoting dispersion or deflocculation of the colloidal constituents remaining therein, removing the dispersed or deflocculated colloidal constituents to a desired extent from said remaining mineral pulp, and thereafter subjecting such remaining mineral pulp thus freed of the removed colloidal constituents to a further nodulization operation wherein another valuable mineral species of the pulp is nodulized.

27. The method of improving the nodulization of minerals associated with colloidal constituents in a mineral pulp, which comprises treating the mineral pulp with sodium silicate for promoting dispersion or deflocculation of the colloidal constituents, removing the dispersed or deflocculated colloidal constituents to a desired extent from the mineral pulp, and thereafter subjecting the mineral pulp thus freed of the removed colloidal constituents to a nodulization operation.

28. The method of effecting the differential nodulization of lead and zinc sulfides from minerals containing the same and associated in a mineral pulp with colloidal constituents, which comprises removing from the pulp a portion of the colloidal constituents to permit nodulization of the lead sulfide while substantially inhibiting nodulization of the zinc sulfide, subjecting the pulp to a nodulization operation to effect nodulization of the lead sulfide, removing from the remaining pulp a further portion of the colloidal constituents therein to permit nodulization of the zinc sulfide, and subjecting such remaining pulp to a further nodulization operation to effect nodulization of the zinc sulfide.

29. The method of improving the nodulization of minerals associated with normally flocculated colloidal constituents in a mineral pulp, which comprises removing colloidal constituents to a desired extent from the mineral pulp by decantation in the course of which a portion of the liquid

forming the pulp is also removed, said removal of colloidal constituents being preceded by the step of dispersing or deflocculating colloidal matter which would otherwise be present in the pulp in a flocculated condition, and thereafter subjecting the remaining mineral pulp to a nodulization operation in which such colloidal constituents as have been removed from the pulp would if present exert a deleterious effect.

30. The method of improving the nodulization of minerals associated with colloidal constituents in a mineral pulp, which comprises removing colloidal constituents to a desired extent from the mineral pulp by decantation in the course of which a portion of the water forming the pulp is also removed, said removal of colloidal constituents being preceded by the step of adding to the mineral pulp a dispersing or deflocculating agent for promoting dispersion or deflocculation of colloidal constituents therein, and thereafter subjecting the remaining mineral pulp to a nodulization operation in which such colloidal constituents as have been removed from the pulp would if present exert a deleterious effect.

31. The method of improving the nodulization of minerals associated with colloidal constituents in a mineral pulp, which comprises removing colloidal constituents to a desired extent from the mineral pulp, said removal of colloidal constituents being preceded by the step of dispersing or deflocculating colloidal matter which would otherwise be present in the pulp in a flocculated condition, thereafter subjecting the remaining mineral pulp to a nodulization operation in which such colloidal constituents as have been removed from the pulp would if present exert a deleterious effect, removing colloidal constituents from the now remaining mineral pulp, and thereafter subjecting the remaining mineral pulp to a further nodulization operation in which such colloidal constituents as have been removed therefrom would if present exert a deleterious effect.

In testimony whereof I affix my signature.

WALTER O. BORCHERDT.