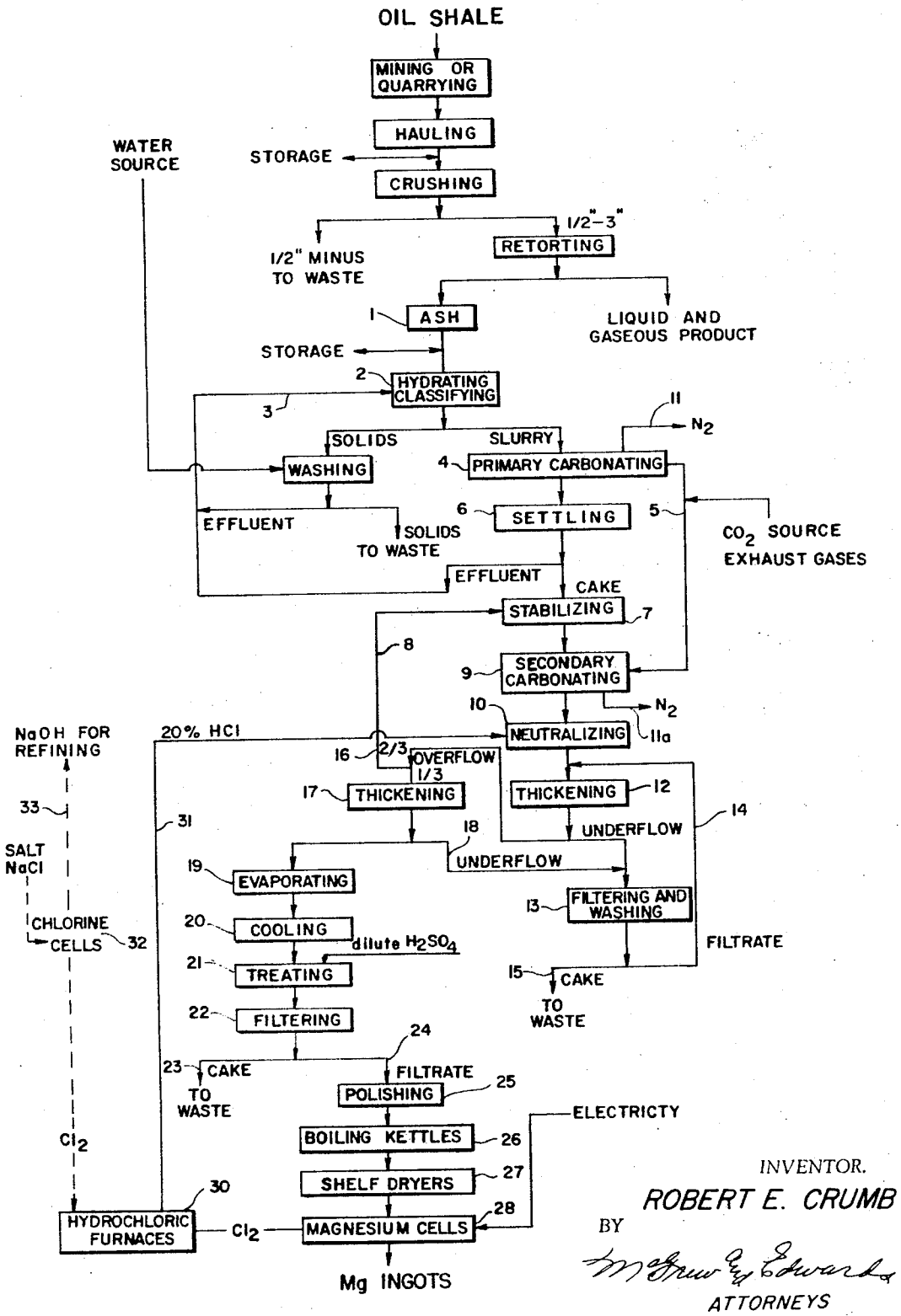
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TREATMENT OF RESIDUES OF OIL SHALE RETORTING FOR MAGNESIUM RECOVERY

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TREATMENT OF RESIDUES OF OIL SHALE RETORTING FOR MAGNESIUM RECOVERY

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This invention relates to a novel method of treating the residual material of oil shale retorting, generally designated ash, for recovery of its magnesium content to form magnesium chloride which may be further processed to yield magnesium products including metallic magnesium, magnesia, calcined dolomite, dead burned dolomite, and caustic-calcined magnesia.

Twenty-five gallons per ton of oil shale as found in the Colorado, Utah and Wyoming area was found to comprise about 86% mineral constituents and 14% organic material. Analyses show that the oil shale is not a shale in the usual sense of the word but a marlstone containing more than 10% of magnesium compositions. One report analyzes the material as 48% magnesium and calcium carbonates, 21% feldspar, 13% quartz, 13% clays, and 5% other material including 1% pyrite. The recoverable oil during the extraction generally is about 66% of the oil content of the shale while 9% comes off as uncondensed gas and 9% is burned during extraction as carbon residue on the ash. Other analyses of the oil shale of the Colorado, Utah and Wyoming area show a range in magnesium content between 3.8 and 8.7%, while one report averages the magnesium content as 5.9%. From the foregoing, it is apparent that substantial quantities of magnesium products are available for recovery from the residue of oil shale refining.

At the present time, oil shale retorting in the United States has not been conducted on a commercial basis, but there are a number of programs in the nature of pilot plant operations which, if demonstrated commercially feasible, would provide large quantities of a new source of oil and corresponding large quantities of oil shale residue for treatment by the present process. Enough of such material has been available for laboratory testing to provide a reliable indication of the favorable commercial potential of the present treatment in providing a new source of magnesium products including metallic magnesium.

Up until the present time, handling of oil shale residue has generally been considered an unavoidable and costly expense in determining commercial feasibility which to some extent at least has held back the development of an oil shale industry. Consequently, the availability of a profitable use for oil shale residue indicates that a commercial oil shale operation utilizing such practice would have a substantially increased opportunity for success under present conditions.

Accordingly, it is an object of my invention to provide a simple, economical and efficient method of treating the residue material of oil shale refining to convert the magnesium content thereof into magnesium products.

Another object of the invention is to provide a control of the settling rates of slurries formed in the present treatment for the collection and segregation of the magnesium carbonate content separate from other carbonates present in the material taken for treatment.

A further object of the invention is to provide sources of regent materials in one stage of the treatment which are utilized in another stage of the treatment.

Still another object of my invention is to provide a rapid and efficient settling of flocs formed in the separation of magnesium hydrate from calcium hydrate and subsequent conversion of the magnesium hydrate to a purified and concentrated magnesium chloride solution so as to permit

treatment of a large volume of material in equipment of relatively small volume capacity.

One of the innovations of the present treatment is the retention of clay in extremely fine sizes, together with other insoluble material of similar size as a media for controlling the settling rate of flocs formed in the magnesium content of the material under treatment at various stages through the recovery operation. As a result, a rapid settling is obtained after floc formation which permits low cost handling and facilitates separations of the magnesium content from other compositions formed in the treatment.

Another innovation of the present treatment is the effective means of cleaning the liquor formed above the floc by the screening action of the associated granular material and clays on fine particles of precipitate held in suspension at settling stages of the treatment. Laboratory tests have shown the floc formed in this invention to be as much as ten times faster in settling than a corresponding untreated floc.

The practice of the invention will now be described with reference to the accompanying drawing illustrating a typical flow sheet for the treatment of the residue of oil shale refining for recovery of its magnesium content. For a better understanding, the preliminary steps of collecting and preparing the oil shale for retorting are shown in the flow sheet, but the novel features of the present treatment are in the treatment of the ash or residue following retorting. The solid residue of shale retorting shown at **1** is first subjected to size reduction and preferably this reduction is performed as a wet treatment with agitation as would be performed in stage **2** designated hydrating, classifying. While material as large as ½ inch can be treated without crushing, it is preferable to have the material introduced into stage **2** reduced to minus ⅛ inch sizes, and as shown, effluent from a subsequent stage is introduced as the liquid of the treatment performed at stage **2** as a water source and also for cooling. The mixing is controlled at stage **2** to establish a pH of about 10 or higher and if the effluent recycling does not establish the required pH, calcium hydroxide refined from material from subsequent stages of this treatment may be introduced into stage **2** to adjust the pH. The hydrating action is an exothermic reaction and would result in excessive heating if cooling were not provided at this stage.

A classifying step is performed at the discharge from stage **2** to reject coarse material, including quartz, feldspar, unreacted carbonates and clay in larger sizes with the slurry or overflow of the classification being taken as the material for subsequent use. This material comprises an aqueous solution of mineral hydrates including magnesium hydroxide, calcium hydroxide and finely divided clays, silts and unreacted particles.

The reject solids from stage **2** are washed and then passed to waste with cool effluent collected and recycled as a part of the recycle introduction shown at **3.** If excess water is available for recycle, the surplus amount may be wasted. The separated slurry in stage **2** is introduced into a primary carbonating stage **4** with a suitable source of CO_2 introduced at **5.** Usually, such a plant operation will have exhaust gases available and such exhaust gases as from the retorting operation are used as a source of CO_2 supply. Exhaust gases from currently planned retorting operations are considered waste and this treatment provides a new use for these waste gases. Otherwise, flue gas from oil shale refining, on site power generation, or other operations may be used as the CO_2 source. Carbonating towers are provided at stage **4** and if gas flow is properly controlled, the reaction is as follows:

$$CO_2+Ca(OH_2)+Mg(OH)_2\rightarrow$$

$$CaCO_3+Mg(OH)_2+H_2O+26.8 \text{ cals.}$$

Preferably, conductivity measurements are taken at first carbonation stage 4 to control the carbonation rate which should be slow enough to assure that calcium carbonate is formed in substantial quantities with minimum formation of magnesium carbonate. As the magnesium hydrate carbonates, conductivity and viscosity increase due to the formation of basic magnesium carbonate, thereby providing a basis for controlling the extent of the reaction. After carbonating at stage 4 as just described, the treated material is delivered into a settling stage 6 from which some or all of the effluent which is essentially water is returned through line 3 as the supply to stage 2, while the precipitate which contains a fast settling floc is introduced into a stabilizing stage 7. The fast settling floc of fine clay and insolubles passes with the magnesium hydroxide and calcium carbonate discharge into stabilizing stage 7 and water or solution from a subsequent stage is introduced through a line 8 to provide the liquid necessary for stabilizing the floc for treatment in secondary carbonating stage 9. This liquid contains magnesium chloride solution which may be present in a concentration of as much as 16% which tends to increase the calcuim carbonate formation. The discharge of the stabilizing stage is introduced as feed into a secondary carbonation stage to obtain a partial removal of soluble calcuim in the magnesium chloride neutralization of the magnesium hydrate and to form calcium carbonate from any other unreacted calcium in stabilizing stage 9. Through the acid introduction and the introduction of approximately 20% HCl into the discharge of the second carbonation stage 9 at neutralizing stage 10 a final pH of about 7.8 is established. This acid introduction is conducted at a slow rate so that the magnesium hydrate material will dissolve without dissolving calcium carbonate as shown in the following reaction:

$$Mg(OH)_2+2HCl \rightarrow MgCl_2+2H_2O+29.4 \text{ cal.}$$

The carbonation stage 4, stabilizing stage 7, secondary carbonation stage 9, and the subsequent neutralizing stage 10 are utilized in combination to provide a means of cleanly separating the calcium and magnesium and to provide a means of changing the magnesium into a form that may be further processed to yield magnesium products including metallic magnesium.

The first and second carbonation stages both employ the carbonating towers previously described in preferred practice and the reaction of the gas so introduced with the constituents of the slurry agitates the slurry to keep it in suspension during the carbonation reaction and produces an evolution of nitrogen which may be drawn off at the top of the towers and collected as a product of the treatment. As shown in the drawings, the nitrogen discharge is passing from the treatment through lines 11 and 11*a*.

While any suitable thickening stage may be provided following the neutralizing treatment at stage 10, I prefer to conduct the discharge from the neutralizing treatment into a first thickener stage 12 from which the underflow discharge is passed to a filtering and washing stage 13 with the filtrate therefrom recycled through a line 14 as part of the feed to thickener stage 12. The solids discharge of the filtering and washing stage 13 is passed to waste as indicated at 15.

In preferred practice, the overflow of thickening stage 12 is split with one portion being returned through a line 16 as the liquid supply for stabilizing stage 7. The remaining portion is discharged into a second thickener stage 17 and thus all the solution introduced into the material passing from settling 6 is kept in closed circuit until it passes to subsequent treatment with the portion feeding second thickener stage 17. The underflow 18 of second thickener stage 17 combines with the other feed to filtering and washing stage 13 and the liquid content thereof also is recycled through line 14 as previously explained. The overflow of thickening stage 17 containing the more concentrated magnesium chloride material is next introduced into an evaporating stage 19, then cooled at stage 20 and is subjected to a further treatment at stage 21.

Preferably, submerged combustion is provided at stage 19 for the evaporation which concentrates the magnesium chloride to about 34%. The cooling at stage 20 avoids loss of magnesium chloride vapor and conditions the enriched magnesium chloride solution for a separation in stage 21 which effects removal of any calcium content as sulfate by dilute sulfuric acid introduction. The acid is added slowly in quantities determined by stoichiometric determination in what amounts to a batch treatment with agitation provided and the proportioning is checked at regular intervals during the acid addition.

When the reaction has progressed to an end point in treatment stage 21, the material is discharged to a filtering stage 22 with calcium carbonate and precipitated gypsum removed, together with other finely divided insolubles as a waste product as shown at 23. The filtrate of filtrering stage 22 is a relatively pure and concentrated magnesium chloride solution which is then ready for conversion to metallic magnesium or to other magnesium products by procedures already in use in the art. In the production of metallic magnesium as shown in the flow sheet, these procedures include a pulping stage 25, boiling kettles 26, shelf dryers 27 and finally introduction into magnesium cells 28 for an electrolytic conversion forming magnesium ingots as one final product, as indicated at 29, while evolved chlorine gas is delivered into a hydrochloric acid furnace as shown at 30 with one portion of the evolved hydrochloric acid delivered through a line 31 as the hydrochloric acid supply to neutralizing stage 10. In addition to producing hydrochloric acid to deliver into the hydrochloric acid furnace 30, the chlorine cells 32 convert salt brine (NaCl) into NaOH as a material for further refining as shown at 33.

Any of the finely divided clays or other suspensions remaining with the solution in the overflow passing from second thickening stage 17 is effectively removed with the waste material in the final filtering stage 22. The final filtrate of this separation analyzes about 75% $MgCl_3$, 3% MgO, .75% CaCl and 1% NaCl. While the procedure for conversion of the concentrated magnesium chloride to metallic magnesium as shown in the flow sheet is a preferred procedure, other treatments known in the art may be utilized in the final conversion to produce a final high grade magnesium product.

The treatment practices set forth in the foregoing description are directed to the recovery of the magnesium content of oil shale residue for its final production as a high grade magnesium product of the type described hereinbefore. It is recognized that the material taken for treatment includes lithium and thallium which are known to be present in trace quantities with the magnesium in the various steps of the present process. Consequently, where it is desired to recover the lithium or thallium content as a final product the preparation steps of the present process may be utilized to the final stages where the magnesium chloride content is separated from the thallium and lithium content associated with the magnesium hydrate and magnesium chloride in the earlier steps of the treatment.

As noted hereinbefore the presence of the clay and other insolubles in fine sizes which are carried with the magnesium content through the successive stages until separation at the thickener stage are effective not only in inducing a fast settling of the material formed into flocs but also in exerting a cleaning action on the liquor standing above the flocs when flocs are formed with the result that effective settling is attained at a greatly accelerated rate compared with the normal settling rate of such material. Consequently, it is recognized that the inclusion of a minor quantity of the clay and other insoluble fines as an inert material associated with other reactive material tending to form flocs provides an effec-

tive control to induce a rapid settling of such floc-forming material. Therefore, it is within the invention concept of the present invention to use the finely divided inert material as a settling aid for floc-forming material in treatments other than those utilized in the present process. Other changes and modifications may be availed of within the spirit and scope of the invention as set forth in the hereunto appended claims.

What I claim is:

1. The method of treating the ash residue of oil shale retorting which comprises forming a finely divided residue of oil shale retorting into an aqueous slurry containing magnesium hydrate at a pH of about 10, said slurry containing most of the magnesium and calcium content of said residue and a substantial amount of clays and other insolubles in finer sizes with coarser sizes of quartz, feldpars, unreacted carbonates and clays removed, passing said slurry through a first carbonation stage to establish a pH of about 8, separating at least a portion of effluent from the solids of the discharge of first carbonation and recycling the separated effluent to the slurry formation stage, stabilizing the separated solids from first carbonation containing the magnesium hydrate and fine clays with overflow solution from a thickening stage, subjecting the pulp so formed to a second carbonation treatment for partial removal of soluble calcium, neutralizing the pulp from second carbonation by acid addition, introducing the neutralized pulp into the thickener stage, discharging the underflow of thickening containing calcium carbonate and fine clay from the treatment, returning a portion of the acidified overflow of the thickening stage to said stabilizing stage, separating the thickener underflow at a filtration stage, recycling the separated filtrate to the thickening stage, evaporating another portion of the thickener overflow containing substantially no suspended solids thereby increasing concentration of the magnesium chloride content, introducing sulfuric acid into the solution at a slow rate so as to form the calcium content into sulfate, filtering the material after acid addition, discharging the cake to waste, and subjecting the separated filtrate to a treatment to convert the magnesium chloride content to a high grade magnesium product and to evolve chlorine in vapor form as a product of the treatment.

2. A method as defined in claim 1, in which at least some of the evolved chlorine is formed into hydrochloric acid solution and recycled through the neutralizing stage of the treatment.

3. A method as defined in claim 1, in which nitrogen evolved at the carbonation stages is discharged as a product of the treatment.

4. A method as defined in claim 1, in which hydrochloric acid is introduced in the neutralizing stage in a concentration of at least 20%.

5. A method as defined in claim 1, in which the material introduced into the first and second carbonation stages is passed through carbonating towers countercurrent to a flow of CO_2 gas therein.

6. A method as defined in claim 1 in which the separated efficulent recycled to the stabilizing stage is a magnesium chloride solution at a concentration of about 16%.

7. A methods as defined in claim 1 in which a pH of about 7.8 is established at the neutralizing stage.

8. The method of treating the ash residue of oil shale retorting which comprises introducing a finely divided residue of oil shale retorting into a hydrating stage to form magnesium hydrate at a pH of about 10, classifying the resulting slurry and discharging coarser sizes of quartz, feldspars, unreacted carbonates and clays from the treatment, conducting the remaining material to a first carbonation stage establishing a pH of about 8 in the solution, separating at least a portion of the effluent from solids of the discharge of first carbonation and recycing the separated effluent to the slurry formation stage, stabilizing the separated solids from first carbonation containing the magnesium hydrate and fine clays with overflow solution from a thickening stage, subjecting the pulp so formed to a second carbonation treatment for partial removal of soluble calcium, neutralizing the pulp from second carbonation by acid addition, introducing the neutralized pulp into the thickener stage, discharging the underflow of thickening containing calcium carbonate and fine clay from the treatment, returning a portion of the acidified overflow of the thickening stage to said stabilizing stage, separating the thickener underflow at a filtration stage, recycling the separated filtrate to the thickening stage, evaporating another portion of the thickener overflow containing substantially no suspended solids thereby increasing concentration of the magnesium chloride content, introducing sulfuric acid to the solution at a slow rate so as to form the calcium content into sulfate, filtering the material after acid addition, discharging the cake to waste, and subjecting the separated filtrate to a treatment to convert the magnesium chloride content to a high grade magnesium product and to evolve chlorine in vapor form as a product of the treatment.

9. A process as defined in claim 8 in which the reject solids are washed before passing to waste and the affluent is recycled as part of the liquid supply to the hydrating stage.

10. The method of treating the ash residue of oil shale retorting which comprises forming a finely divided residue of oil shale retorting into an aqueous slurry containing magnesium hydrate at a pH of about 10, said slurry containing most of the magnesium and calcium content of said residue and a substantial amount of clays and other insolubes in finer sizes with coarser sizes of quartz, feldspars, unreacted carbonates and clays removed, passing said slurry through a first carbonation stage to establish a pH of about 8, separating at least a portion of the effluent from solids of the discharge of first carbonation and recycling the separated effluent to the slurry formation stage, stabilizing the separated solids from first carbonation containing the magnesim hydrate and fine clays with overflow solution from a thickening stage, subjecting the pulp so formed to a second carbonation treatment for partial removal of soluble calcium, neutralizing the pulp from second carbonation by acid addition, introducing the neutralized pulp into a first thickener stage, the underflow of said thickening stage containing calcium carbonate and fine clay into a filtration stage, returning a portion of the acidified overflow of said thickening stage to said stabilizing stage, introducing the remaining portion of said thickener overflow into a second thickening stage, introducing the underflow of the second thickener stage into the feed to the filtration stage following the first thickening stage, recycling the separated filtrate of said filtration stage as feed to the first thickening stage, evaporating the overflow of said second thickener stage containing substantially no suspended solids thereby increasing concentration of the magnesium chloride content, introducing sulfuric acid to the solution at a slow rate so as to form the calcium content into sulfate, filtering the material after acid addition, discharging the cake to waste, and subjecting the separated filtrate to a treatment to convert the magnesium chloride content to a high grade magnesium product and to evolve chlorine in vapor form as a product of the treatment.

11. In a method of treating the ash residue of oil shale retorting, the steps of forming a finely divided residue of oil shale retorting into an aqueous slurry containing most of the magnesium and calcium content of said residue and a substantial amount of clays and other insolubles in finer sizes with coarser sizes of quartz, feldspars, unreacted carbonates and clays removed, passing said slurry through a first carbonation stage to establish a pH of about 8, separating at least a portion of effluent from the solids of the discharge of first carbonation and recycling the separated effluent to the slurry formation stage, stabilizing the separated solids from first carbonation containing the mag-

nesium hydrate and fine clays with some overflow solution from a thickening stage, subjecting the pulp so formed to a second carbonation treatment for partial removal of soluble calcium, neutralizing the pulp from second carbonation by acid addition, introducing the neutralized pulp into the thickener stage, discharging the underflow of thickening containing calcium carbonate and fine clay from the treatment, and discharging the remaining thickener overflow as a product for subsequent treatment.

12. In a method of treating the ash residue of oil shale retorting, the steps of forming a finely divided residue of oil shale retorting into an aqueous slurry containing magnesium hydrate at a pH of about 10, said slurry containing most of the magnesium and calcium content of said residue and a substantial amount of clays and other insolubles in finer sizes with coarser sizes of quartz, feldspars, unreacted carbonates and clays removed, passing said slurry through a first carbonation stage to establish a pH of about 8, separating at least a portion of effluent from the solids of the discharge of first carbonation and recycling the separated effluent to the slurry formation stage, stabilizing the separated solids from first carbonation containing the magnesium hydrate and fine clays with some overflow solution from a thickening stage, subjecting the pulp so formed to a second carbonation treatment for partial removal of soluble calcium, neutralizing the pulp from second carbonation by acid addition, introducing the neutralized pulp into the thickener stage, controlling floc formation and accelerating the settling rate of precipitated solids in the neutralized pulp at the thickening stage by maintaining the fine clay in association therewith, discharging the underflow of thickening containing calcium carbonate and fine clay from the treatment, and discharging the remaining thickener overflow as a product for subsequent treatment.

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