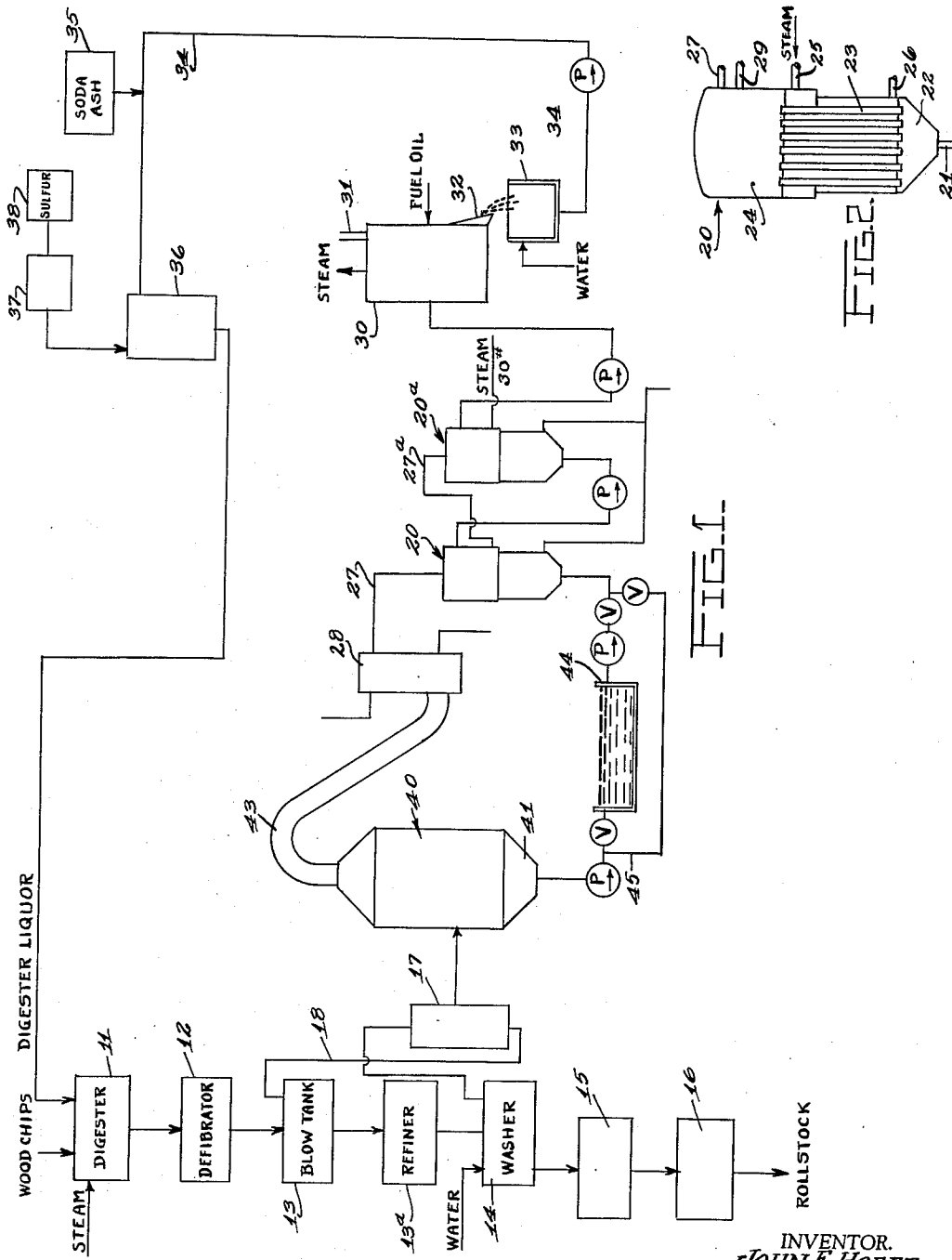


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FLASH EVAPORATION OF PULP LIQUOR
TO ELIMINATE CALCIUM SALTS
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FLASH EVAPORATION OF PULP LIQUOR TO ELIMINATE CALCIUM SALTS

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This application is a continuation-in-part of my application Serial No. 658,994, filed May 14, 1957 now abandoned.

This invention relates to the production of pulp. More specifically, this invention relates to so-called chemical processes for the production of wood pulp, which pulp is ultimately converted to paper. Even more specifically, this invention relates to a process of recovering residual chemicals utilized in the aforesaid chemical pulping operation.

Three broad classes of pulp manufacture are commonly utilized in the production of paper. The oldest type of process involves the separation of the fibers constituting the wood entirely by mechanical treatment, such as grinding or tearing. Another type of fiber separation is effected entirely by chemical digestion in which the wood chips are literally cooked in an aqueous solution of chemicals to soften or remove the ligneous or non-cellulosic encrustant and bonding materials which hold the innumerable tiny cellulose fibers together, producing so-called chemical pulps. A third type of pulp production is accomplished partly by chemical digestion and partly by mechanical treatment. The chemical pulping operations known in the art include the "soda" pulping process utilizing an alkaline solution of sodium hydroxide, the sulfite process utilizing an acid solution of an alkali metal (sodium, potassium, etc.), sulfite, the sulfate or "Kraft" process, and the so-called "semi-chemical" processes in which the cooking liquor includes a buffering agent to reduce the drastic acid or alkaline action.

It is economically desirable to recover the chemicals utilized in the above referred to processes, and it is with this phase that this invention is most directly concerned for an alkaline process. The recovery of the chemicals necessitates at some stage of the process the stripping off of excess water, usually by evaporation, utilizing for reasons of thermal efficiency multiple effect evaporators. Unfortunately, however, it has been found that in the evaporation step a deposit of a salt or other complex organic material forms on the walls of the tubes of the evaporator. This precipitation in the form of a deposit or coating seriously impedes the heat transfer within the evaporator whereby insufficient water is removed, adversely affecting the later steps of the chemical recovery or, in fact, impeding the flow of the process liquid there-through.

Prior to the present invention, the removal of the deposited coating in a semi-chemical process operating on the alkaline side required the undesirable procedure of disconnecting the evaporators and soaking the interior thereof with an acid solution. In more serious situations, that is, where the coating was too thick to be attacked by the acid, it was necessary to actually bore out the interior of the tubes.

Accordingly, it is an object of the present invention to provide a more continuously operable process for the recovery of chemicals from chemical pulp produced by an alkaline semi-chemical pulping process.

It is likewise an object of this invention to provide an improvement in the process of recovering chemicals, which improvement eliminates the necessity of frequent time-consuming and costly shut-downs for acid cleaning of evaporator components.

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These and other objects of this invention will become apparent from the following detailed description, taken in conjunction with the annexed sheet of drawings on which is presented for purposes of illustration only, a preferred embodiment of this invention.

In the drawings:

FIG. 1 is a flow diagram illustrating in partially schematic form a pulping process incorporating a chemical recovery process modified by the improvement of this invention.

FIG. 2 is an enlarged sectional view of an evaporator utilized in the chemical recovery step.

Basically, this invention constitutes the discovery that precipitation in the form of a coating on the components of an evaporator may be substantially eliminated by cooling the process liquid at the same or reduced pressure prior to evaporation.

Referring now more specifically to the drawings, there will be disclosed and explained in considerable detail the improvement representing this invention as incorporated into a specific semi-chemical pulping process in which sodium sulfite constitutes the pulping or digesting chemical, and sodium carbonate constitutes a buffering agent.

Wood chips (about $\frac{3}{4}$ " in size) are fed at a rate of about 50,000 lbs. per hour into a pair of continuous digesters 11. Each digester consists of six 24" diameter, 20' long pipes (not shown), which are horizontally disposed and stacked in vertical array. Each of the pipes contains a conveyor screw which propels the chips longitudinally along the 20' length. Alternate ends of the pipes are connected in downward fashion to the pipe lying beneath, thereby serving to propel the chips in alternately opposite directions through the pipes. Steam under pressure of 170 lbs. per square inch gauge is also introduced into the reactor, effecting a temperature therein of about 375° F. The digesting or cooking liquor is contemporaneously fed into the digesters at a total rate of about 80 gallons per minute. The liquor is essentially an aqueous solution of sodium sulfite and sodium carbonate in the respective concentrations of 0.294 lb. (expressed as Na_2O) and 0.233 lb. (expressed as Na_2O) per gallon of solution. The carbonate serves as a buffer for acids released during digestion. The pH within the digester measures from 8.5 to 10.0. From the digester, the chemically attacked wood and the spent digesting liquor pass to a defibrator 12 which effects a mechanical shearing and tearing of the chemically attacked wood chips. The mixture then passes to a blow tank 13 which is essentially a large expansion tower where the pulp is diluted from about 35% pulp solids (consistency) to about 4.5% pulp solids. The latter is conducted through a refiner 13a to prepare the fibers for washing. The pulp solution is then conducted to a washing operation 14, where water is fed countercurrent to the flow of pulp and liquid, leaching out residual chemicals and various organic complexes produced during the digesting operation. Vacuum drums are conveniently employed in this operation for separating the pulp from the bulk of liquid, including spent digesting liquor. The separated pulp, measuring about 20% solids (consistency), passes thence to conventional pulp processing equipment including refiners 15, Fourdrinier paper-making machine 16, or the like, which converts the pulp into paper in the form of roll stock.

The filtrate from the pulp washing 14 passes to a temporary hold-up tank 17. This filtrate is commonly referred to as black or spent liquor and, at this state, is at about 180° F. It contains about 10% solids consisting primarily of residual chemicals, but including various organic complexes, salts, and the like. Some of the filtrate is recirculated from the hold-up tank through the line 18

to the blow tank 13. Conventionally, the filtrate is next pumped at about 200 gallons per minute directly to a series of evaporators 20 and 20a, one of which is shown as an enlarged section in FIG. 2. The liquid enters the evaporator through an inlet tube 21 (FIG. 2) located in the bottom of the evaporator, and entering first a conical portion 22. When the conical portion is filled with the liquid, the liquid then proceeds up through a plurality of upstanding tubes 23 leading through a heat exchanging chamber to an upper cylindrical chamber 24. Steam or vapor from preceding effects enters a side inlet tube 25 and circulates about the outside of the tubes 23, the condensate passing out through tube 26. The heat converts some of the liquid passing through the tubes 23 into vapor or steam which passes out the chamber 24 through tube 27 which is connected to a barometric condenser 28 (FIG. 1), or to the next evaporator via line 27a. The remainder of the liquid leaves the chamber 24 through the tube 29 and passes to the succeeding evaporator. For simplicity of illustration, only two evaporators have been shown in FIG. 1; however, a greater number may be conveniently employed in the interest of thermal efficiency. As can be seen by referring to FIG. 1, the steam from evaporator 20a passes to evaporator 20 and thence to the barometric condenser 28. The process liquid being evaporated flows in reverse direction from the evaporator 20 to the evaporator 20a.

The number of evaporators may be chosen from a consideration of the thermal efficiency of the evaporation step and also should be sufficient either in number or effective heat transfer area to convert the 10% solids solution filtrate to a solution containing about 45% to 50% solids. In the operation described herein, it was found that five evaporators, connected in series, were adequate to meet these requirements when the last evaporator was fed with steam under 30 lbs. pressure.

The concentrated solution leaving the last evaporator is pumped at about 40 to 50 gallons per minute to a recovery furnace 30. Fuel oil is also fed to the furnace as a primary source of ignition. Some of the solids contained in the solution fed to the furnace are combustible and these are burned. The hot products of combustion are used to generate steam before passing to the smoke stack 31. The non-combustibles comprising essentially the chemicals utilized in the process are melted to form what is commonly referred to as a smelt. The smelt flows out the bottom 32 of the furnace into a smelt dissolving tank 33 supplied with water. The smelt substantially dissolves in the water forming a green liquor consisting primarily of sodium carbonate together with the lesser amounts of sodium sulfide and other salts. The green liquor so formed flows from the bottom of the dissolving tank and is circulated through the line 34. A tank 35 contains dissolved soda ash and supplies make-up sodium carbonate solution to the line 34 as required to bring the concentration of the liquid up to the value specified hereinbefore. The liquor then passes to a sulfiting tank 36 which is essentially a large Raschig-ring packed absorption tower into which is introduced concurrently therewith sulfur dioxide gas proceeding from a sulfur burner 37 supplied by a source of sulfur 38. The amount of sulfur burnt is controlled so as to provide sufficient sulfur dioxide to adjust the concentration of the sodium sulfite in the liquor solution to the value specified hereinbefore. The liquid, as such, is referred to as sulfited liquor or digester liquor and is reintroduced into the digester.

In the operation as just described, it is found that a precipitate in the form of a coating is deposited on the inside of the tubes 23 of the evaporator 20. A similar deposit is formed on the interior of the tubes of the other evaporators as well. This deposit seriously reduces the effective coefficient of heat transfer so that insufficient water is removed. The deposit on the inside of the tubes also reduces the sectional area of the tube, increasing the difficulty of pumping. While the exact nature of the

deposit formed as a coating in the tubes is not known and, while it is not desired to be bound by any theory advanced herein, it is believed quite likely that the principal component of the precipitate or deposit is calcium oxalate. This would be likely formed due to the presence of the calcium ion in the water, wood, and wood bark, as supplied, and the release of long chain fatty acids, including oxalic acid, by the chemical attack of the ligneous component of the wood in the digestion step. Calcium carbonate is also believed contained in the deposit. The precipitate or deposit may well also consist of a variety of salts and organic complexes which would be likely to precipitate under the conditions. In any event, in carrying out the chemical recovery operation as described herein, it was found necessary to remove the deposit every four to six weeks to avoid loss of thermal efficiency. To do this, it is necessary to disconnect the evaporators and acid clean the interior of the tubes thereof with hydrochloric acid wash. The cleaning operation takes an appreciable period of time, e.g., about ten hours and, in addition, consumes a sizable quantity of the costly acid.

In the improvement of the process constituting one embodiment of this invention, the filtrate liquid is pumped at its temperature of about 180° F. from the hold-up tank 17 to a hollow, upstanding, cylindrical flash tank 40, having a conical bottom portion 41 serving to facilitate flow of the liquid therefrom. The liquid is introduced into the tank through the side wall. The tank, which is otherwise sealed from the atmosphere, is connected by conduit 43 connected at the top to a barometric condenser 28, serving to pull an exhaust, maintaining vacuum conditions within the cylindrical tank. The temperature within the tank is maintained appreciably below that of the entering process liquid by permitting the hot, entering liquor to flash to the saturation temperature corresponding to the reduced pressure. A vacuum measuring 20" of mercury and a temperature of 162° F. has been found to effectively accomplish the purposes of the invention. The size of the tank should be such that the liquid entering at a rate of about 80 gallons per minute will be freely projected into the interior of the tank. Employing the aforesaid flow rate, it has been found that a tank 9' to 10' in diameter and having an overall height of about 17' to 20' is suitable. A head of liquid sufficient to intercept the entering stream is undesirable as, obviously, the stream would not then freely pass into the atmosphere created by the establishment of the noted temperature and vacuum conditions. Rather, the liquid is allowed to immediately pass out the bottom of the tank and is conveniently pumped via line 45 to the evaporator 20 for removal of water in the same manner as described hereinbefore. A settling tank 44 is advantageously employed between the flash tank 40 and the first evaporator in order to allow hold-up and settling of the process liquid following exposure to the zone of reduced pressure and temperature.

Carrying out the process as described, but modified as described in the preceding paragraph, it was found that even after ten months of essentially continuous operation of multiple effect evaporators, there had not been built-up any serious deposit of precipitate in the form of a coating on the evaporator tubes. As a consequence, no acid soaking and washing has been required. This elimination of the deposit or coating, through the practice of this invention, practically eliminates the amount of down time heretofore required to acid wash the evaporators. Further savings in cost are also effected by the fact that the expensive acid consumption is likewise avoided. Furthermore, the overall thermal efficiency of the operation has been increased thereby.

The foregoing descriptive material was clearly set forth in the specification of such earlier application.

As described hereinabove, the coating or scale which previously formed on all effects of the multiple-effect evaporators exhibits compositional differences in each effect. It was found in the feed or cold effect that the

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scale consists essentially of calcium oxalate which is known to be more soluble in hot water than in cold. The scale in the hot or first effect was observed to consist of essentially calcium sulfite known to be more soluble in cold water. In other words, the latter salt exhibits an inverse solubility. Scale collected from the intermediate stages of the evaporators contains mixtures of these prescribed salts as might be expected.

In the preferred embodiment of the present invention set forth hereinabove, flash tank 40 is utilized primarily to cool the hot spent process of liquor from about 180° F. to a temperature more nearly equal to the temperature in the last effect of the evaporators, i.e., that temperature being equivalent to 24" to 26" of mercury vacuum. Flashing the hot spent process liquor to cool the same thereby causing precipitation of detrimental deposits in a settling tank prior to evaporation has considerably improved the operation of the evaporators.

With regard to the theory involved in obtaining precipitation of primarily calcium salts by cooling, the following hypothesis has evolved based upon present knowledge. The cooking liquor contains a mixture of sodium sulfite, sodium carbonate, sodium sulfide and minor quantities of other compounds of sodium, sulfur and oxygen. This mixture forms an excellent buffer solution that resists change in hydrogen ion concentration upon the addition of acids or alkalis. The spent liquors are believed to contain some of these chemicals in unchanged form as well as other organic and inorganic compounds of sodium. These include sulfonated lignin, oxalic acid and sulfurous acid. Since the spent liquor is still alkaline, these acidic materials would exist in the form of salts and would be highly ionized. Analyses of the spent liquor have indicated calcium contents much higher than possible in water. This may be explained by the known dispersing action of sodium lignosulfonates. The spent process or black liquor provides an organic solution which exhibits properties of having unusual solubilizing power for calcium in any form. It has been found with tube and shell-type heat exchangers that if the hot spent liquor is cooled slightly, of the order of about 20° F., precipitation of the calcium as a scale would form. It was found that if the calcium would precipitate on cooling in a heat exchanger, it should also be expected to precipitate if cooled by any other manner except by dilution with water. As described in the prior application the mechanism of the deposition as deduced by reasoning was found to be valid due to calcium salts being precipitated in the flash tank when the temperature of the solution is lowered. It was also found that if the solution was concentrated at the same time that it was cooled, sufficient calcium would be precipitated so that the carrying power of the liquor would be sufficient to eliminate the precipitation of scale in any effect of the evaporators. In other words, the calcium content of the liquor would then be reduced to such an extent that the solvent action of the liquor is then great enough to keep the remaining calcium in solution. The flash tank offers the advantages in that large amounts of crystals can be present to start crystallization and scaling in a location of the operator's choosing, i.e., a vessel having extensive surfaces in which precipitated deposits are unobjectionable. Other methods of cooling the spent liquor in a vessel or container may similarly be employed. In these cases the liquor is in contact with precipitated seed crystals which produces the same beneficial results. Normal tube and shell heat exchangers are generally unsuitable for long term continuous service because their relatively small diameter tubes become plugged. The liquor can be allowed to cool slowly in an open tank to obtain the same effect, however, the volume of liquor in a conventional paper making process is so great that tremendous tanks would be required.

The spent liquor resembles a supersaturated solution and crystallization can be induced therein by relatively

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small changes in state such as temperature. In the case of the particular spent liquor described, a sudden relatively small change in temperature initiates the crystallization and precipitation of calcium salts. Once started the crystallization normally continues until the liquor constitutes no more than a normal saturated solution of the remaining salt. The liquor behaves in a manner similar to a colloidal suspension and the organic materials present act as stabilizing agents. As is known some colloidal solutions or suspensions are sensitive to small changes in temperature or pressure. The spent liquor behaves in such a manner as to indicate that the quantity of calcium present is insufficient to precipitate both the salts of normal solubility and those of inverted solubility. Thus, if the solution is cooled the salt of normal solubility is preferentially precipitated. This reaction reduces the calcium content in the remaining liquor to the extent that the salt of inverted solubility does not exceed the carrying power of the liquor even though it is concentrated several fold in the subsequent vacuum evaporators.

The present invention involves cooling the hot spent process liquor in a vessel of such configuration and dimensions that the precipitation of scale or deposits does not interfere with its normal function. In addition to the flash tank, a cooling tank can be used but a large individual vessel or series of vessels are then needed. A large heat-exchanger having mechanical means for removal of deposits can also be employed to cool the liquor. Also a spray tower which does not unduly dilute the liquor can be used for cooling. Cooling by any of the aforesaid means does not result in subsequent fouling or plugging of tubes of relatively small diameter that are difficult or expensive to clean. The spent liquor represents a solution that is believed to be in a state of considerable instability. The fact that the solution is so highly buffered rules out any appreciable change in pH as the result of removing acidic compounds in the flash tank or other cooling vessel.

Thus, as described hereinabove a substantial portion of the calcium cations are precipitated out of the spent process liquor prior to evaporation. The precipitation of the deposit-forming material as calcium oxalate, calcium carbonate and calcium sulfite is preferably conducted in a vessel having sufficiently extended surfaces on which accumulation of such deposits is unobjectionable. The spent process liquor is preferably cooled about 20° F. or more below the existing temperature of the liquor to effect precipitation. After such precipitation the remaining liquor contains insufficient calcium cations to react with sulfite anions to cause adverse precipitation of calcium sulfite during subsequent thermal evaporation even to producing a concentrated solution containing up to about 50% by weight total solids.

Various modifications may be resorted to within the spirit and scope of this invention, it being intended to be limited only to the extent expressed in the appended claims.

I claim:

1. In the process of recovering chemicals from chemical pulp produced by an alkaline pulping process comprising separation of the pulp from spent process liquor containing a major portion of residual chemicals including calcium cations and oxalate, carbonate and sulfite anions, followed by evaporation of said process liquor to remove excess water and thereby form a concentrated solution of said residual chemicals; the improvement which comprises lowering the temperature of the hot spent process liquor at least 20° F., by injection into an evacuated flashing zone of essentially reduced pressure and temperature conditions, to eliminate the major portion of said calcium cations and oxalate and carbonate anions by precipitation prior to concentration of precipitant-free liquor by evaporation.

2. The process in accordance with claim 1 including

the step of lowering the temperature of said process liquor through a sufficient range to effect precipitation of essentially all calcium oxalate and calcium carbonate.

3. In the process of recovering chemicals from chemical pulp produced by an alkaline pulping process comprising separation of pulp from aqueous spent process liquor containing a major portion of residual chemicals including calcium cations and oxalate, carbonate and sulfite anions, followed by evaporation of said process liquor to remove excess water and thereby form a concentrated solution of said residual chemicals; the improvement which comprises the steps of taking the said process liquor which contains oxalate and carbonate anions approaching saturation at a temperature of about 180° F. and cooling said process liquor at least 18° to 20° F., by injection into an evacuated flashing zone of essentially reduced pressure and temperature conditions, to effect precipitation of essentially all calcium oxalate and calcium carbonate prior to evaporation of the remaining cooled process liquor.

4. In the process of recovering chemicals from chemical pulp produced by an alkaline pulping process comprising separation of pulp from aqueous hot spent process liquid containing a major portion of residual chemicals, followed by evaporation to remove excess water and thereby form a concentrated solution of said residual chemicals, said process liquid containing calcium cations and oxalate, carbonate and sulfite anions; the improvement which comprises the intermediate step of lowering the temperature of the hot spent process liquid at least 20° F., by injection into an evacuated flashing zone of essentially reduced pressure and temperature conditions, thereby precipitating calcium oxalate and calcium carbonate from said process liquid.

5. The method of concentrating the residual chemical content of aqueous spent alkaline pulping liquor prior to thermal concentration thereof by evaporation characterized by rapidly cooling the hot spent liquor by injection into an evacuated flashing zone of essentially reduced pressure and temperature conditions, to effect precipitation of essentially calcium salts, separating the precipitated calcium salts from said liquor, and evaporating the re-

maining liquor containing insufficient calcium cations to precipitate as calcium oxalate and sulfite during subsequent thermal concentration.

6. The method of concentrating the residual chemical content of aqueous hot spent pulping liquor produced by an alkaline pulping process prior to thermal concentration thereof by evaporation characterized by the injection of the hot spent process liquor into an evacuated flashing zone of essentially reduced pressure and temperature conditions to effect precipitation and separation of calcium salt constituents from the liquor prior to its concentration by evaporation.

7. The method in accordance with claim 6, further characterized by the subjection of the said liquor to a pressure essentially less than atmospheric in the said zone.

8. The method in accordance with claim 6, further characterized by the gravity separation of the effluent from the said zone into calcium salt and liquor components and subjection of the liquor component only to thermal concentration.

9. The method of concentrating the residual chemical content of aqueous hot spent alkaline pulping liquor prior to thermal concentration thereof by evaporation including the steps of reducing the temperature of the hot spent liquor by injection into an evacuated flashing zone of essentially reduced pressure and temperature conditions to effect precipitation of essentially calcium salts, the remaining liquor after cooling containing insufficient calcium cations to exceed the solubility of calcium sulfite at any stage of subsequent evaporation and concentration up to about 50% total solids.

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