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METHOD FOR SOLVING RAW ALUMINATES OF LIME
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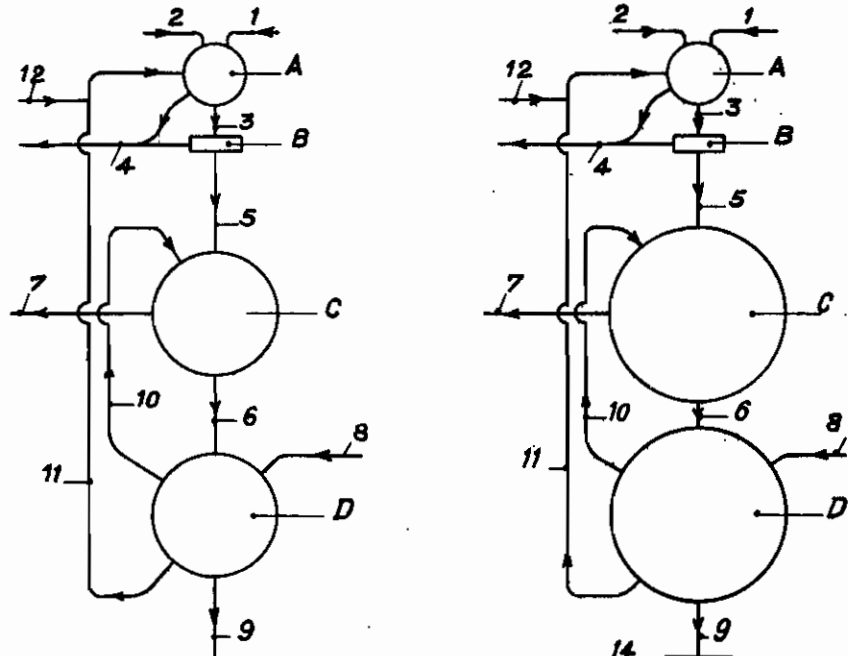


FIG. 1

FIG. 2

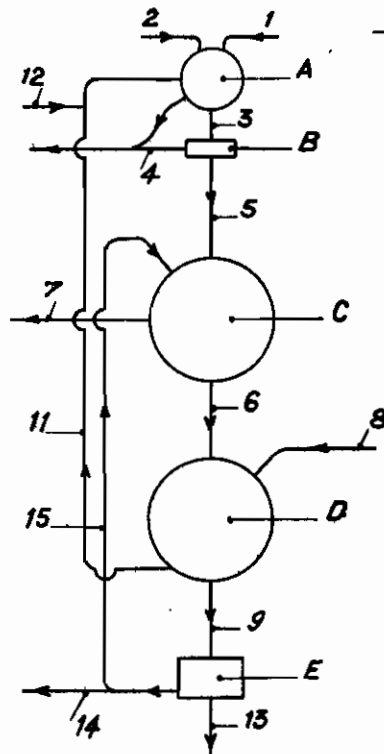


FIG. 3

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METHODS FOR SOLVING RAW ALUMINATES OF LIME IN WATER AND EVENTUALLY RECOVERING ALUMINA FROM SUCH SOLUTIONS

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When raw Aluminates of Lime are dissolved in water to extract Aluminates of Lime as a solution, a limit is rapidly reached over which efficiency falls whilst the solutions oversaturated become instable and difficult to handle.

The inventor has discovered certain new methods by which these difficulties are overcome.

According to these new methods, suitable means are used so as to insure the presence in the dissolving water of alkaline salts such as for instance caustic or carbonated alkalis. Under these conditions, higher extracting efficiencies may be reached and more stable solutions are obtained.

At the same time, certain other salts, which will be described later may be added to the solution in order to prevent silica from getting into solution and means are described to keep within proper limits the proportion of Alkali and salts which might accumulate in the dissolving liquid specially when such liquid is working in closed circuit.

The invention also includes ways and means which may be used in connection with the said solution in order to precipitate more or less completely CO_3Ca in a first operation by the purifying effect of Alkaline carbonate and later on Alumina more or less free from Calcium impurities.

The following description will explain more completely the details of the invention.

It must be clearly understood that the solutions referred to in this patent are always very diluted as opposed to the concentrated solutions usually employed in the usual technics working with Alkaline-Aluminate solutions.

The invention applies to solutions containing generally less than 5 grammes of Alumina and more often less than 1 gr. 5 of Alumina per liter whilst the usual industrial solutions of Alkaline Alumina contain generally over 20 grammes of Alumina and more often 80 to 250 grammes of Alumina per liter.

At the same time, the solutions used according to this invention do not contain more than five grammes Alkali calculated as CO_3Na^2 and contain more generally less than one gramme and further the molecular proportion of Alkali is at a maximum equal and generally inferior to the molecular quantity of Alumina getting into solution. When Aluminates of Lime are solved in water deprived of Alkaline salts, dissolution becomes more and more difficult as the concentration of the solution increases; at the same time, the stability of such oversaturated solution decreases, with the result that a limit is quickly reached when efficiency begins to fall down.

In the presence of Alkali, the soluble Aluminate of Lime is transformed partially (and eventually totally) into very soluble Alkaline Aluminate so

that oversaturation of the Aluminate of Lime is easily avoided and stable solutions are obtained.

Further when stable solutions are used, it is possible to effect the dissolutions at temperatures which are not permissible with less stable or unstable solutions. For instance, dissolution under the conditions described may be carried at temperatures averaging and even exceeding 60° Cent., and, as Aluminates of Lime are more completely, more easily and more quickly extracted in hot solution, a substantial advantage is secured.

Only small quantities of alkali can be used because experimentation shows that if Silica is to be avoided the alkaline content can only be present as a fraction of the Alumina dissolved in the liquid. For instance, 0,200 to 0,400 only (counted as CO_3Na^2 or the equivalent molecular quantity of CO_3K^2) can be used in a solution containing 1 gr. of Alumina per liter if one does not accept that Silica will also be dissolved in a proportion which would be detrimental in most cases. This proportion of 0,200 to 0,400 of CO_3Na^2 for 1 gr. of Alumina is equivalent to only 0,19 to 0,38 molecule of Alkali for 1 molecule of Alumina in solution. The inventor has discovered that this limit can be substantially raised on condition that the solution contains also other salts which act to stop silica from getting into solution. As an instance salts like Alkali or Earth-Alkali Sulfides, Sulfates and Chlorides separately or in mixture give the desired result.

It must be noted here that owing to equilibrium laws governing solutions containing at the same time Alkali and Earth-Alkali all the salts present will divide into a necessary proportion of Alkali salts and earth-alkali salt of each sort.

As an example, a solution giving excellent results contained per liter:

Alkali (counted as $\text{Na}_2\text{O} + \text{K}_2\text{O}$)	---	0,700 to 0,900
Sulfur combined as sulfides	-----	0,150 to 0,180
SO_3 combined as sulfates	-----	0,200 to 0,250

Generally, under these new conditions with a solving liquid containing not more than 0g,800 to 0gr,900 Alkali carbonate counted as CO_3Na^2 before dissolving the raw aluminate and giving out solutions with about 1 gr. Alumina per liter after dissolution, the quantity of silica solved is practically negligible.

With higher molecular proportion of Alkali to Alumina, it is still possible to have only an acceptable proportion of Silica in the solution whilst the equilibrium solution may contain all its Alumina as Alkaline Aluminate with practically no Alkaline earth aluminate in solution.

In order to get solving liquid containing the elements which have been described, two ways may be employed: the salts may be added to the solving water or these salts or their constituents may be brought in (totally or partially) by the

raw materials to be solved, which may be chosen so that they will contain automatically the desired stuffs.

In order to better understand this point, it must be explained that, under industrial conditions the solving liquid is utilized in a closed circuit organized as follows: the solving liquid is mixed and agitated with the raw material to be solved, exhausted residues are separated, the clean solution is treated (generally by CO² injection) in order to separate Alumina as a precipitate and the solving liquid free from Alumina, and eventually of other precipitated elements (such as CO²Ca) goes back to dissolve again a new quantity of raw material.

If the raw material does not contain the additional salts which must be present in the solving liquid, these must be regularly added in small proportion to make up for the unavoidable losses of the circuit.

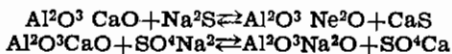
If, on the contrary, the additional salts are automatically brought in by the raw materials it may happen that they will accumulate in the circuit and exceed in the long run the desired proportions, in this case, a proportion of the solving liquid may be regularly taken off and replaced by fresh water in order to keep the solvent solution within the proper limits.

As an example of a raw material containing, at the same time as soluble aluminate of lime the salts necessary for the invention, the following analysis is given:

SiO ² -----	21,95
Fe ² O ³ -----	5,57
Al ² O ³ -----	11,74
CaO-----	56,97
SO ³ -----	0,60
S-----	1,59
Alkalis as Na ² O-----	0,15
Alkalis as K ² O-----	0,55

It has been found that the solving liquid may be, in certain cases, automatically kept within the proper limits for certain salts and eventually for all the salts and this is a great simplification.

As regards sulfides and sulfates the regulation is automatic because the sulfide and the sulfate of Calcium cannot exceed a very limited solubility whilst on the other hand the Alkaline sulfides and sulfates have their solubility limited in the presence of Aluminate of Lime, according to the following equations:



The result is that Na²S and SO⁴Na² cannot accumulate over the limit where they are transformed into the calcium equivalent salts and in their turn the Calcium salts are precipitated with the residue as soon as they exceed their limit of solubility and, eventually as sulfo Aluminate of Lime.

As regards the Alkalis, their concentration may also be limited in the case where CO² is used to separate Alumina, as the inventor has found that under proper condition alkalis may be precipitated partially together with the Alumina, probably as a double Carbonate of Alkali and Alumina.

For instance, with an industrial lye containing per liter 0gr,600 of potash and 0gr,100 of Soda (counted as K²O and Na²O) with 1 gr. of Alumina treated by CO² at a temperature of 50 to 60° Cent, the Alkalis are partially precipitated together with the Alumina.

This is a very interesting way to automatically

control alkalis content in the lyes and further when the raw material contain alkalis (as it is often the case) this method has in addition the advantage of recuperating a valuable material.

Alkaline concentration may also be limited by other means. It has been controlled that silica is soluble only when Alkalis exist in the solution as free caustic alkalis or as ionisable salts such as the carbonates. On the contrary, silica is not dissolved by alkali salts when they are practically not ionisable unless relatively high concentrations are reached. This gives the possibility of regulating the alkaline ionisable concentration within the desired limits as it is easy to convert in proper proportion ionisable salts into non ionisable salts by very simple means.

The desired result will be obtained if the alkaline ionisable salts are transformed into chlorine or sulfates and this may be conveniently realized by an addition of the corresponding acids (HCl or SO⁴H²) or more economically by adding earth alkaline chlorine or sulfate which give by double decomposition CO²Ca and the desired alkaline chlorine or sulfate in the part of the circuit where the alkalis necessarily exist in the carbonated state.

When using carbonic acid precipitation, it has been found that the best condition for the solving liquid returning in circuit to dissolve a new quantity of raw-material is reached when the solution is near the point where phenolphthaleine is just discoloured. If the solving liquid is alkaline, efficiency is lower and if it is acid, efficiency falls again.

When the described methods are used, the invention gives solutions which contain alumina dissolved as a mixture of alkaline aluminates and earth alkaly aluminates and at the limit in the state of alkaline aluminate alone.

Precipitation of alumina from the said solution is carried by CO². Now it is well known that precipitation of alkaline aluminates by CO² at temperatures inferior to 75/80° Centigrade even in the presence of seeding alumina gives only gelatinous and more or less colloidal precipitates which are very difficult to filter and to utilize. The inventor has now found that with the diluted solutions which he uses it is possible to obtain, without heating the lyes at the specified temperature (75 to 80°), precipitates of very good quality easy to filter and to handle.

These precipitates of good quality are obtained when precipitation is carried over and over again in the presence of the precipitates formed in successive operations continuously agitated and kept or sent back, continuously, in the reaction vessel until suitable quality is reached. Under these conditions, it has been found that the final precipitate becomes more and more dense and easy to filter and to handle.

As an example, one will describe batch operation. A first batch of solution is treated by CO² and after decantation the clear mother-lye is separated whilst the whole precipitate remains in the carbonating tank. A new supply of solution is admitted in the tank and treated by CO² whilst the first precipitate is agitated in the new solution. Decantation follows and separation of the mother-lye: the whole precipitate (from the two operations) remaining in the tank. This succession of operation is continued until suitable quality is obtained.

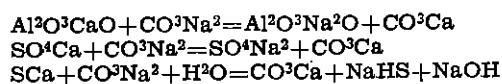
Of course, instead of batch operations, a continuous circuit may be utilized for instance by combining a carbonating vessel and a decanting

tank. In this case, the precipitate from the decanting tank is continuously pumped back into the carbonating vessel until proper grade of precipitate is obtained after which the precipitate may be utilized or the circuit regulated so that a fraction of the precipitate goes back to carbonation as a seed whilst another fraction is taken off and utilized.

Generally, the solutions obtained according to the invention contain a proportion of lime which is precipitated together with the alumina under CO_2 action as only in very exceptional cases the circuits may be organized so as to contain all the alumina as alkaline aluminate. (For instance, when raw materials very poor in silica are used or when a certain proportion of silica will not be detrimental or when solutions are obtained in a very diluted state e. g. less than half a gramme of alumina per liter.)

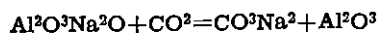
The inventor has however found that it is possible and advantageous to obtain directly a precipitate of alumina containing practically no lime or only a small proportion of lime. This result will be obtained by adding to the solutions (obtained from the raw material according to the invention) before precipitating the alumina by CO_2 a proper proportion of alkaline carbonates (with or without bicarbonates).

Under these conditions all the calcium salts present into the solution will be transformed into CO_3Ca and replaced by soluble alkaline salts as follow:



The solution so treated and separated by known means from solid CO_3Ca is then treated by CO_2 and the Alumina recovered contains practically no Calcium salt.

The addition of Alkaline Carbonate into the solution may be realized simply by taking back a proper fraction of the mother-lye from the precipitation of Al^2O^3 by CO_2 in a partially closed circuit. This is possible because when the carbonating operation treats a lye previously deprived of CO_3Ca according to the proposed method, the mother-lye from carbonation contains Alkaline Carbonate according to the equation



This alkaline Carbonate can therefore be used as a free source of reactive for the proposed operation.

Practically it will be better to send back an excess of mother-lye to avoid exact regulation and it is preferred to avoid an excess of alkaline bicarbonate which can be easily realized by proper regulation of the carbonation operation or by suitable corrections.

Figs. 1, 2 and 3 give schematic examples of certain methods of working out the invention.

Fig. 1 illustrates the case where the raw Aluminate does not bring in the necessary additional salts and more specially does not contain Alkaline salts or does not contain enough alkaline salts.

A is the dissolving tank.

B consists with filters or decanters or both.

C is the precipitating device for CO_3Ca by Alkaline Carbonate coming back from D.

The pipes are numbered 1 to 12.

The precipitating device C will generally comprise a mixing vessel and a decanting tank to separate the precipitate with eventually a finishing filter.

D shows the carbonating device where Al^2O^3 is precipitated. This carbonating device will generally comprise a carbonating vessel where the reaction takes place and a decanting tank to separate the Alumina with eventually a finishing filter. The raw Aluminate goes through 1 into A whilst the supplementary salts are introduced at 2. As the circuit is closed, after the first quantity necessary to get the desired proportion in the circuit salts are only injected to make up the losses.

The solution from A goes off by 3 and 5 through B to C. The residual muds are sent off by 4.

The clear solution is received in C through 5 and is mixed there with the epurating mother-lye coming back from D through 10.

The lime carbonate is evacuated by 7. The purified solution goes into D by 6.

D receives CO_2 necessary for the carbonation through 8, Alumina is extracted through 9 and the mother-lye goes back partly through 10 to C as a purifier and partly through 11 to A to act again as a solving liquid.

Make-up water is admitted at 12.

Fig. 2 illustrates the case where the raw Aluminate contains the desired Alkaline salts so that the circuit would get progressively more and more rich in Alkalis and where regulation is realized by precipitating the Alkalis as explained by regulating the carbonating operation so as to precipitate the excess of Alkalis probably as double carbonate of Alumina and Alkalis. The references are the same as fig. 1 except that E is a boiler where the complex precipitates of Alumina and alkalis are decomposed by heat action into insoluble Alumina and soluble Alkaline Carbonate.

This boiler receives through 9 the precipitate and delivers the Alumina through 13 and the dissolved Alkaline Carbonate through 14.

The rest of the circuit does not differ from Fig. 1.

Fig. III illustrates the case where the precipitation of CO_3Ca in C instead of being obtained through sending back the diluted mother-lye as in fig. 1 and 2 is realized by sending back through 15 a proper proportion of the more concentrated Alkaline Carbonate recovered in E.

Of course, these three examples are not given as a limitation to equivalent ways of realizing the invention. For instance, The regulation of the proportion of ionisable alkalis may be realised by a proper addition, in the mother-lye going back to dissolution, of the salts or acids which have been described or by replacing a given proportion of mother-lye taken away by fresh water.

It will be evidently understood that precipitates obtained from the different steps, such as CO_3Ca , mixtures of CO_3Ca and Alumina or mixtures of Carbonates of Alumina and Alkalis in different grades may be used to any industrial purpose for which they are suitable, without getting out of the scope of the invention although this is more specially intended to be used for the manufacture of Alumina.

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