



Abstract

In a process for the production of aluminum hydroxide involving extraction of alumina from an alumina-containing ore by an aqueous alkaline solution, supplying a slurry containing the alumina-containing ore with a high solid content, which has been prepared from a small amount of an alkaline solution together with an aqueous alkaline solution which is preheated to a temperature that is high enough to have a temperature after the mixing with the slurry that is higher than the extraction temperature of alumina. Simultaneously or after the mixing feeding the mixture to an extraction apparatus comprising a tube reactor, extracting alumina from the alumina-containing ore under conditions of a temperature of 120-160°C and an extraction time within 10 minutes, separating residue from an extract solution immediately after the extraction, desilicating the extract solution, and adding seeds of aluminum hydroxide to the extract solution which is desilicated to precipitate aluminum hydroxide. By this production process, it is possible to economically produce aluminum hydroxide with little contamination by silica from an alumina-containing ore with a high content of reactive silica.

Process For Production of Aluminum Hydroxide From Ore  
Containing Alumina

The present invention relates to a process for the production of aluminum hydroxide from an ore containing alumina.

In more detail, the present invention relates to a process for the production of aluminum hydroxide, in which aluminum hydroxide can be obtained economically with little loss of alkali, a high yield of alumina, low contamination by silica and a low unit cost of energy, even when a low quality ore containing alumina (often referred to as bauxite hereafter) with a high content of soluble silica is used as the starting material in a process that is the so-called Bayer process for the production of aluminum hydroxide, wherein bauxite is dissolved in an alkali solution and the solution of sodium aluminate thus obtained is hydrolyzed to precipitate aluminum hydroxide.

The process that is most commonly employed for the production of aluminum hydroxide from bauxite is the Bayer process. This process comprises the following steps: Bauxite is treated with an alkaline solution, such as an aqueous sodium hydroxide solution or an aqueous mixture solution of sodium hydroxide and sodium carbonate to make a slurry, and the alumina contained in the bauxite is extracted as sodium aluminate (extraction step); insoluble residues such as iron oxides, silicates and titanium oxides are separated from the slurry (red mud-separation step); seeds of aluminum hydroxide are added to a clear solution of the sodium aluminate after the separation of the insoluble residues so that the aluminum hydroxide is precipitated at a temperature usually of 50-70°C and the aluminum hydroxide then precipitated is separated from the sodium aluminate solution (separation step); and a portion of the separated aluminum hydroxide is recycled as seeds while the rest of the separated aluminum hydroxide is withdrawn as a product, and the sodium aluminate solution after the separation (often referred to as a decomposing solution) is recycled as is or after condensation for use in the bauxite-dissolving step.



Usually, bauxite contains an alkali-soluble silica (often referred to as a reactive silica or  $R\text{-SiO}_2$ ), the content thereof being dependent on the place where it is mined. Accordingly, in the above extraction step, the reactive silica  
5 contained in bauxite is dissolved as well as the alumina component.

When an extract solution (sodium aluminate solution) containing the reactive silica that has been dissolved therein is subjected to the precipitation step to obtain aluminum  
10 hydroxide by the precipitation thereof, the silica in the solution is also precipitated after decomposition together with the aluminum hydroxide, which causes deterioration of the quality of the aluminum hydroxide thus obtained. Accordingly, the reactive silica in the extract solution is allowed to  
15 react with a portion of the alumina and a portion of the alkaline solution, so as to precipitate as sodalite or zeolite, which is alkali-insoluble before entering the precipitation step (desilication step), and is removed and discarded together with the iron oxides, the titanium oxides  
20 and other insoluble substances separated in the subsequent red mud-separation step.

Conventionally, in the most common practice, a residence time in the extraction step has been made as long as 30 minutes to 6 hours so as to achieve sufficient dissolution of  
25 the reactive silica and conversion of the dissolved reactive silica to desilication products before being precipitated.

However, the above-described process is not economical, since the soluble silica in the extracted solution is removed as the desilication products by using a large amount of  
30 alumina and alkali as described above.

Known processes for suppressing the loss of the alkali caused by the reactive silica in bauxite includes a process described in Japanese Patent Kokoku Publication No. 8257/1962 wherein bauxite with a high content of the reactive silica can  
35 be used by dissolving the alumina component selectively, while utilizing the difference in the solution rate into a caustic alkali or sodium aluminate solution between the alumina and

the reactive silica in the bauxite. In a process described in Japanese Patent Kokoku Publication No. 37678/1973 the extraction residue is separated by using a synthetic high molecular weight coagulant with suppressing dissolution of the reactive silica while allowing the alumina component to be dissolved sufficiently, and in a process described in Japanese Patent Kokai Publication No. 230613/1987 aluminum hydroxide is precipitated by extracting the alumina component in a tube reactor, immediately flash-cooling a mixture of the extract solution and the extraction residue, separating and removing the extraction residue, and desilicating the extract solution, from which sodium hydroxide is precipitated.

However, the process disclosed in Japanese Patent Kokoku Publication No. 8257/1962 uses two sorts of bauxite, one with a high content of the reactive silica and the other with the usual content of the reactive silica, and employs different conditions for the extraction of each bauxite. Therefore, it cannot be applied in a case in which bauxite with the usual content of the reactive silica or bauxite with the high content of the reactive silica is used alone.

The process of Japanese Patent Kokoku Publication No. 37678/1973 is an excellent invention in regard to rapid separation of the extraction residue, but no detailed description of the extraction of alumina is given on how efficiently the dissolution of the reactive silica is suppressed, and, in addition, no process is disclosed to suppress the decrease in the yield of alumina.

In Japanese Patent Kokai Publication No. 230613/1987 there is disclosed a process wherein a mixture of the extract solution and the extraction residue is flash-cooled immediately after the extraction, so as to suppress the passage of the soluble silica from the bauxite into the alkaline solution, the residue is separated off, and the extract solution is desilicated. It is said that in this process heating is carried out by directly injecting live steam into a mixing header and a tube reactor. However, in this case, a specially large evaporator is required for



keeping the water balance in the system, and so this process is not economical. When a mixed slurry comprising an aqueous alkaline solution, such as a recycled decomposing solution and bauxite is heated to an extraction temperature by using recovered steam and live steam in the mixing header, the formation of  $R-SiO_2$  takes place even during the preheating before the extraction step, so that the suppression of the formation of  $R-SiO_2$  is insufficient. In addition, since the desilication is conducted after flash-cooling at a temperature as low as 80-110°C, the reaction rate of the desilication is low and an extraordinary large apparatus for the desilication is required to be provided in order to avoid contamination with silica in the aluminum hydroxide product.

In addition, when the extract solution is kept over a long time in the desilication step, so as to decrease the silica concentration to the desired level, the alumina component in the extract solution is simultaneously precipitated as aluminum hydroxide, which is a disadvantage since the yield of alumina is decreased in the overall process even when the alumina extraction ratio from the bauxite is high.

In view of the above-described situation, the inventors of the present invention have made extensive studies for finding a process for the economical production of aluminum hydroxide from bauxite, wherein the amount of sodium hydroxide to be lost is decreased, the decrease in the alumina yield is suppressed, and aluminum hydroxide with little contamination by silica is precipitated without deterioration of the energy cost.

Thus, the present invention provides a process for producing aluminum hydroxide from an alumina-containing ore which comprises the steps of: (a) mixing said alumina-

containing ore with an alkaline solution to obtain a slurry having a solids content higher than 20% by weight, and preheating said slurry at a temperature of 70-120°C, (b) mixing a preheated aqueous alkaline solution with said  
5 slurry obtained in step (a), (c) extracting alumina contained in said mixture obtained in step (b) as sodium aluminate, in a tube reactor at a temperature of 120-160°C within 10 minutes, to obtain a mixture of an extract solution of sodium aluminate and dissolution residues of  
10 reactive silica, (d) immediately separating said dissolution residues from said mixture obtained in step (c), to obtain the extract solution, (e) desilicating said extract solution to obtain a mixture of desilication product and a clear extract solution of sodium aluminate, (f) separating said  
15 desilication product from said mixture obtained in step (e), to obtain the clear extract solution, and (g) adding seeds of aluminum hydroxide to said clear extract solution to precipitate aluminum hydroxide, wherein in said alumina-containing ore 50% or more of the alumina is alumina  
20 trihydrate and the content of reactive silica is from about 0.5 to 15% by weight based on the total weight of the ore and wherein said aqueous alkaline solution in step (b) is preheated prior to mixing to achieve said extraction temperature of 120-160°C of step (c) after mixing with the  
25 slurry of step (a), provided that the case is excluded that the slurry is heated in step (a) to 120°C and is subsequently mixed with the aqueous alkaline solution preheated to 120°C, too.

In the drawings:

30 Fig. 1 shows a flow chart of an embodiment of the present invention;

Fig. 2 shows a flow chart of an embodiment of the well-known Bayer process; and



5a

Fig. 3 shows the temperature dependence of the dissolution rate coefficients of alumina and the reactive silica in bauxite into an aqueous alkaline solution.

The alumina-containing ore to be employed as a raw material in the present invention includes bauxite, laterite and other ores that contains alumina, of which the major crystal form is alumina trihydrate (usually, the content of alumina trihydrate is higher than about 50% by weight, and preferably higher than about 70% by weight, based on the total content of alumina in the ore) and which also includes the reactive silica.

There is no specific limitation on the content of the reactive silica, but it is usually from about 0.5% by weight to about 15% by weight, and commonly from about 0.5% by weight to about 10% by weight based on the ore weight. When bauxite with a high content of the reactive silica is employed, the process of the present invention provides economical advantage.

In practicing the process of the present invention with bauxite as the raw material as is or after being roughly



ground, it is formed into a slurry using a slurring solution and is then charged into a preheating apparatus as is or after being wet ground as desired.

5 A smaller particle size of the bauxite charged into the preheating apparatus is more preferable, to make the difference in separation rate between alumina and the reactive silica greater. Since a larger particle size generally allows easier separation in the separation step of the extract solution from the residue, the particle size of the bauxite is  
10 smaller than 10 mesh, and preferably smaller than 60 mesh.

The solid content of the slurring solution for the bauxite when preheated is high enough to have a slurry that allows the bauxite to be transferred, and depends on the type, the particle size and other factors of the bauxite. The solid  
15 content of the slurry is generally adjusted to be higher than about 20% by weight and preferably in a range of 30 to 65% by weight.

There is no specific limitation on the solution to be used for the preparation of the slurry, and the recycle  
20 solutions used in the Bayer process, such as a decomposing solution or its concentrate (often referred to as a recycled decomposing solution) and washing solutions of the residue and the precipitated aluminum hydroxide, may be employed. Particularly, the washing solution for the residue is more  
25 preferable, because it has a lower  $\text{Na}_2\text{O}$  concentration than that of the recycled decomposing solution and it contains a small amount of the reactive silica that is dissolved during the washing of the residue and works to suppress the transfer of the reactive silica during preheating of the bauxite slurry,  
30 and also because the reactive silica contained in the washing solution for the residue is removed by desilication in the subsequent desilication step.

Depending on the sort of bauxite, the  $\text{Na}_2\text{O}$  concentration of the slurry and the type of the preheating apparatus for the  
35 slurry, an upper limit of the temperature to preheat the bauxite slurry is about  $120^\circ\text{C}$  and preferably about  $110^\circ\text{C}$ . If the preheating temperature is higher than  $120^\circ\text{C}$ , such a

temperature is not desirable, since it allows the reactive silica to be dissolved into the slurry during the preheating of the bauxite slurry.

5 Since the extraction of the reactive silica proceeds even during the preheating of the bauxite slurry, the period required to preheat the slurry is set within 10 minutes and preferably within 5 minutes.

10 The preheating of the bauxite slurry is not necessarily required, but for the purpose of efficient utilization of heat recovered from the slurry after the extraction, it is preferable to preheat the slurry to a temperature higher than about 70°C and more preferably higher than about 80°C.

15 Usually, a preheating apparatus such as a double-tube heat exchanger or a shell-and-tube heat exchanger is used as the preheating apparatus for the bauxite slurry, since it allows little back mixing and preheats the slurry in a short time.

20 There is no specific limitation on any other aqueous alkaline solution that is mixed with the preheated bauxite slurry in the practice of the process of the present invention, and the recycled decomposing solution may be mainly used, and in addition an alkali-containing solution produced in other steps may be used as is or after condensation.

25 These aqueous alkaline solutions are generally preheated in a conventional manner, so as to reach the desired extraction temperature after being mixed with the bauxite slurry. For example, they are preheated to a temperature of 150°C to 170°C by using recovered or live steam.

30 As the preheating apparatus for the aqueous alkaline solution, indirect heating-type heat exchanges such as a double-tube, a shell-and-tube and a spiral-type heat exchanger may be employed.

35 The preheated bauxite slurry and the preheated aqueous alkaline solution are charged into an extraction apparatus separately or after being mixed together.

The mixing ratio of the preheated bauxite slurry to the preheated aqueous alkaline solution is determined depending on



factors such as the sort of bauxite, the solid content of the bauxite slurry and the composition of the decomposing solution, and adjustment is carried out so as to have a molar ratio of  $\text{Na}_2\text{O}/\text{Al}_2\text{O}_3$  of the liquid at an exit of the extraction apparatus of 1.30-1.60 and preferably 1.35-1.50.

In the present invention, the slurry is brought to an intended extraction temperature at the entrance to the extraction apparatus.

When extraction at a higher temperature is desired, the heating may comprise directly injecting some live steam into the preheated aqueous alkaline solution just before charging into the extracting apparatus, or into the mixed slurry when the bauxite slurry is mixed with a preheated aqueous alkaline solution to produce the mixed slurry just before charging into the extraction apparatus.

It is well-known that there are differences in the dissolution rates of alumina and the reactive silica contained in bauxite and the formation rate of the desilication product in the aqueous alkaline solution as described in Japanese Patent Kokoku Publication No. 8257/1962 and in Japanese Patent Kokai Publication No. 230613/1987.

Considering the extraction rates of alumina and the reactive silica contained in bauxite in detail, it has been understood that the dissolving reaction rate of each component follows a first order reaction, and on the rate constant of the reaction shown in Fig. 3, alumina shows a higher gradient of the rate constant of the reaction than does the reactive silica. Thus, when alumina is present in bauxite in the crystal form of alumina trihydrate (gibbsite), the alumina trihydrate is dissolved much faster than the reactive silica, so that it reaches the solubility equilibrium determined by the  $\text{Na}_2\text{O}$  concentration and the temperature; at a given  $\text{Na}_2\text{O}$  concentration, the extraction shows great temperature dependency. Accordingly, the present inventors have found that, in the process of extraction of alumina by dissolving alumina extensively from bauxite while suppressing the dissolution of the reactive silica, mixing, at the entrance of

the reactor, the bauxite slurry and the aqueous alkaline solution which have been separately preheated, so as to raise the temperature instantaneously to the temperature required for the dissolution of the alumina is more ideal than the conventionally practiced process of mixing an aqueous alkali solution with a slurry containing an alumina-containing ore at a high solid content and heating the mixed slurry to an extraction temperature.

The inventors have made extensive studies for finding a process that satisfies the above consideration and have consequently completed the present invention by preheating, in a preheating apparatus using an indirect heating manner, each of the bauxite slurry and the aqueous alkaline solution separately, mixing the preheated slurry and the preheated alkaline solution and then charging the mixture into the extraction apparatus, namely in the so-called binary fluid mode, and regulating the preheating temperature of the bauxite slurry to be as low as possible for suppressing the extraction of the reactive silica, but high enough to allow partial recovery of the applied heat, while regulating the preheating temperature of the aqueous alkaline solution which presents no problem in relation to the dissolution of silica, and high enough to allow the mixture of the preheated binary fluid mode to immediately reach the extraction temperature of the alumina.

It is of course possible that when the aqueous alkaline solution can be heated to a sufficiently high temperature, the bauxite slurry may not be preheated.

As the extraction apparatus of the alumina, a tube reactor with little back mixing is employed adiabatically. The shape of the reactor is not particularly limited. For example, it is possible to use a thermally insulated tube that transfers the mixture to the subsequent separation step as the reactor, so far as the binary fluid consisting of the preheated bauxite slurry and the preheated alkali solution is mixed for the extraction of alumina from the bauxite.

The extraction apparatus is not required to have a



heating function from its exterior, and it is recommended to raise the temperature of the slurry at the entrance of the apparatus sufficiently high to proceed with the reaction without supplying additional heat to the reactor, with the aid  
5 of thermal insulation, namely in the so-called adiabatic manner.

This is done to advantageously utilize the difference between alumina and silica in their dissolution rates in the alkaline solution. When the same quantity of heat is supplied  
10 during the same extraction time, it is more advantageous for the extraction of the same amount of alumina suppressing the dissolution of silica to have a temperature at the entrance of the extraction apparatus high enough and to allow the temperature to decrease from the entrance to the exit of the  
15 apparatus, than to keep the temperature of the slurry constant using heating means.

In the extraction apparatus, the omission of a heating means, especially means that can supply heat from the exterior, eliminates reduction of the heat transfer rate due  
20 to scaling which introduces a major problem when a tube reactor is employed, and is additionally effective in a great reduction of scaling in the apparatus used for preheating the aqueous alkaline solution and the alkali-containing ore slurry.

25 The temperature and the time required for the extraction differ depending on the sort and the particle size of the bauxite, the  $\text{Na}_2\text{O}$  and  $\text{Al}_2\text{O}_3$  concentrations in the alkaline solution, and the molar ratio of the charged bauxite and the charged alkali. The most economical conditions are determined  
30 on the basis of unit costs of the bauxite and the caustic soda, the costs of the apparatus, the performances of the separating apparatus, the efficiency of the desilication step and other factors. In general, the  $\text{Na}_2\text{O}$  concentration in the extracting solution is set at about 100 g/l - about 160 g/l,  
35 the extraction temperature (the temperature at the exit of the extraction apparatus) at about 120°C - about 160°C, and the extraction time within 10 minutes, and preferably the

extraction temperature is set at about 125°C - about 150°C and the extraction time within 5 minutes. At a higher extraction temperature and a longer extraction time than the above conditions, the objects of the present invention, namely to  
5 increase the extraction ratio of the alumina from the bauxite, to suppress the dissolution of the reactive silica and to decrease the loss of caustic soda become difficult to achieve.

The conditions of the extraction step are therefore set so as to make the extraction ratio of the alumina from the  
10 bauxite as high as possible, while keeping the dissolution of the reactive silica as small as possible. It is usual to set the conditions to obtain the extraction ratio of the alumina not lower than about 70%, and preferably not lower than about 80%, while achieving a dissolution ratio of the silica not  
15 larger than about 70% and preferably not larger than 50%.

The slurry after the extraction of the alumina is immediately transferred to a solid-liquid separation apparatus so that it is divided into the extract solution (liquid) and the dissolution residue (solid). This solid-liquid separation  
20 is carried out at almost the same temperature as the extraction temperature.

Any solid-liquid separation apparatus may be used as the solid-liquid separation apparatus in the present invention, provided that the residence times of the solid and the liquid, particularly that of the dissolution residue, are short, and  
25 the volume of the extract solution entrained with the residue is small. In general, a high-speed separation-type thickener and a centrifuge (a decanter) may be employed.

For the separation, it is possible to add a known  
30 coagulant, for example a polyacrylic acid-type high molecular weight coagulant, so that the separation of the slurry is accelerated. The amount of the coagulant added to the slurry may be in the known application range, and it is usually used in a ratio of about 0.005% - about 0.1% by weight based on the  
35 weight of the dissolution residue (on a dry basis).

It is necessary to carry out the separation in as short a time as possible, and it is usually carried out within about



10 minutes and preferably within about 5 minutes after the extraction. The separation time, here referred to, is the residence time of the dissolution residue in the separation apparatus.

5        It is understood that, since the solid-liquid separation temperature in the present invention is so high, nearly the same as the extraction temperature, the more rapid separation of the solid and the liquid is possible in comparison with the separation in the conventional process. A longer separation  
10      time is not desirable, since it allows the reactive silica to be dissolved from the residue.

      The extract solution which has been separated in the solid-liquid separation step is, as is or after indirect heating or cooling if desired, transferred to a desilication  
15      reactor (desilication step). In the desilication step, the extract solution is charged into the desilication reactor as is or after adding seeds comprising a solid silicate substance as a major component if desired, so that the dissolved silica which is the extract solution reacts with a portion of the  
20      alumina and a portion of the alkaline solution, whereby the silica is converted to an insoluble silicate substance, such as sodalite and zeolite.

      When the raw material of bauxite has a large content of the reactive silica and thus the concentration of silica in  
25      the extract solution is higher than about 10 g/l, the desilication is initiated by nuclei spontaneously formed, but for the purpose of shortening the desilication time and improving the solid-liquid separation of the desilicated product there formed, it is desirable to add the seeds of the  
30      solid silicate substance comprising sodalite or zeolite as a major component.

      There is no specific limitation on the type of the desilication reactor, provided that it provides a sufficient residence time to precipitate the reactive silica from the  
35      extract solution as the desilication product. Preferably, a reactor equipped with a multi-stage agitator with little back mixing is employed.

The conditions of the desilication change depending on whether the heat-recovery step from the extract solution carried out by, for example, flash evaporation, is carried out before or after the desilication step, and so they cannot be fixed simply. However, the conditions are set at about 80°C - about 160°C of the desilication temperature and about 15 minutes - about 10 hours of the treating time, and preferably at about 115°C - about 160°C of the temperature and about 15 minutes - about 5 hours of the time, and more preferably at about 120°C - 140°C of the temperature and about 0.5 - 3 hours of the time. The higher the treating temperature, the faster the desilication rate, and the less the amount of aluminum hydroxide precipitated during the desilication treatment.

However, since the higher treating temperature requires a pressure apparatus, the conditions of the desilication are selected from an economical viewpoint.

After the desilication treatment, the extract solution is cooled, if desired, and solid-liquid separated into the desilication product and the clear sodium aluminate solution. The solution is transferred to a precipitation step for the aluminum hydroxide.

Cooling of the extract solution is carried out by using a flash evaporator or an indirect heat exchanger. When a flash evaporator is used, flashed steam is used as recovered steam to preheat the bauxite slurry and the recycled decomposing solution. When an indirect heat exchanger is used, it is also used to preheat the bauxite slurry and the recycled decomposing solution.

In the process of the present invention, the cooling of the extract solution may be carried out either immediately after the separation of the extract solution from the dissolution residue or after the desilication treatment.

The separation of the desilication product from the extract solution may be carried out by using a thickener, a centrifuge or a filter alone, or optionally in combination. When a portion of the separated desilication product is reused



as the seeds in the desilication treatment, it is recommended to reactivate the seeds by a process such as grinding, sieving and washing before recycling to the desilication step.

Especially, it is noted that grinding the obtained

5 desilication product by using, for example, a ball mill, and using it as the seeds, which meet the conditions that will be described hereinafter, can greatly shorten the time required for the desilication treatment.

10 The desilication product used as the seeds depends on the desilication temperature, the concentration of the soluble silica in the extract solution, the desilication time and other factors. The desilication product having an average particle size of about 1  $\mu\text{m}$  - about 30  $\mu\text{m}$ , and preferably about 5  $\mu\text{m}$  - about 20  $\mu\text{m}$ , may usually be used as the seeds,  
15 and the amount of the seeds added may be selected from a range of about 5 g/l - about 150 g/l, and preferably from that of about 20 g/l - about 100 g/l.

On the other hand, the dissolution residue that has been separated in the solid-liquid separation step in the process  
20 of this invention is cooled and washed to recover the extract solution entrained with the dissolution residue. Cooling of the residue is carried out by using a flash evaporator or an indirect heat exchanger. The flashed steam from the flash evaporation is used as the recovered steam to preheat the  
25 bauxite slurry and the recycled decomposing solution, and the recovered heat in the indirect heat exchanger is also used to preheat the bauxite slurry and the recycled decomposing solution. There is no particular limitation on the type of the apparatus to be used for washing and draining the  
30 dissolution residue. When the residue with a high soda content is washed, a high-speed thickener, a centrifuge or a filter that can prevent R-SiO<sub>2</sub> from dissolving out from the residue during the washing, may be used alone or optionally in a combination thereof.

35 The present invention will now be described in detail with reference to the accompanying drawings, but the present invention is not limited by the following description.

Fig. 1 shows a flow chart of an embodiment in which the process of the present invention is practiced and Fig. 2 shows a flow chart of the conventional process known as the Bayer process. In the figures, the numeral 50 stands for a slurry-preparation vessel comprising a ball mill, 51-55 for preheaters, 57 for an extraction apparatus, 58 for a solid-liquid separation apparatus, 59 for a desilication reaction vessel, 60-62 for flash evaporators for cooling, 63 for a solid-liquid separation apparatus, 64 for a grinder, 1 for a bauxite stream, 2 for a recycled decomposing solution stream and 3-47 for lines (conduits).

In Fig. 1, numeral 2 denotes the recycled decomposing solution, which is supplied and divided into the lines 3 and 4. Bauxite is supplied through the line 1 to the ball mill 50 and is ground and mixed in the ball mill, together with the recycled decomposing solution supplied through the line 3, so that a transferable slurry is prepared therefrom. Then, the slurry is transferred through the line 5 into preheaters 51 and 52, each of which usually comprises a double tube heat exchanger and each of which is so constructed that heat is supplied from the flash evaporators for cooling 62 or 61 through the lines 31 or 32, whereby the slurry is preheated to the desired temperature.

The main stream of the recycled decomposing solution through line 4 is transferred through the lines 8, 9 and 10 into the preheaters 53, 54 and 55, each of which usually comprises a shell and tube heat exchanger, and each of which is so constructed that heat is supplied from the flash evaporators for cooling 62, 61 or 60 through the lines 29, 28 or 27 whereby the stream is preheated. Then, the stream is transferred through the line 10 into the preheater 56 which usually comprises a shell and tube heat exchanger and which is so constructed that heat is supplied by live steam through the line 26 whereby the stream is further preheated. A portion of the live steam flowing through the line 26 may be fed directly into the decomposing solution, but it is preferable to use it in an indirect heating manner in the preheater 56, so that the



water balance in the system is maintained, the amount of steam consumed is decreased and the size of the evaporator is made small. The preheating temperature in the preheater 56 is not particularly limited, and the preheating is carried out to reach the desired extraction temperature of the alumina when the solution is mixed with the bauxite-containing slurry through the line 7 on the supply into the extraction apparatus.

The preheated bauxite slurry and the preheated decomposing solution are transferred through the lines 7 and 11, respectively, mixed together, and supplied to the extraction apparatus 57 through the line 12.

A tube reactor with little back mixing may be used as the extraction apparatus 57, and the extraction temperature is generally in a range of about 120°C - about 160°C.

In the extraction apparatus 57, the slurry in which the alumina component is the ore has been extracted as sodium aluminate is withdrawn immediately through the line 13 and fed into the solid-liquid separation apparatus 58 for the separation of the residue from the extract solution, so as to prevent the transfer of silica from the residue into the extract solution.

Any known high molecular weight coagulant may be added to the slurry that is fed into the solid-liquid separation apparatus 58 at a point of the line 13 for the purpose of the improvement of the separation efficiency.

The type of the solid-liquid separation apparatus 58 is not specifically limited provided that the solid-liquid separation is carried out in as short a time as possible, and the residence time of the residue in the apparatus is usually within about 10 minutes. Usually, a high speed separation-type thickener or a centrifuge is employed.

The slurry fed into the solid-liquid separation apparatus 58 is divided into the dissolution residue (red mud) and the extract solution, and the residue (red mud) is transferred through the line 15 to apparatus (not shown) to treat the dissolution residue, which is discharged after the recovery of

heat and alkali.

On the other hand, the extract solution is introduced into the desilication reactor 59 through the line 14, where it is held until a desired amount of the silica component dissolved in the extract solution is converted to the desilication product. As the desilication reactor 59, a tank equipped with an agitating means is generally used. In the desilication treatment, a solid silicate substance is added as seeds through line 25 for the purpose of accelerating the reaction. As the seeds, a solid silicate substance commercially available may be employed by feeding from the outside of the process, but generally the desilication product that is separated in the subsequent step is recycled, used as is, or after an activating treatment for seeds, such as washing and grinding. The treatment temperature in the desilication reactor 59 is in a range of about 115°C - about 160°C, and the treatment time is about 15 minutes - about 5 hours and preferably the temperature is about 120°C - about 140°C and the time is about 0.5 hour - about 3 hours. The average particle size of the desilication product to be used as the seeds is about 1  $\mu\text{m}$  - about 30  $\mu\text{m}$  and the amount to be added is about 5 g/l - about 150 g/l.

In the desilication reactor 59, silica dissolved in the extract solution is precipitated as the desilication product, so that an extract solution containing a desilication product, the silica concentration of which is lowered as desired, is produced. Such an extract solution is withdrawn through the line 16, passed to flash evaporators 60, 61 and 62 for cooling through lines 17 and 18, cooled there and then transferred to the solid-liquid separation apparatus 63 through line 19 for separating the desilication product.

The steam recovered in the flash evaporators 60, 61 and 62 is used for preheating the main stream of the recycled decomposing solution as above described, that is the aqueous alkaline solution, and the bauxite-containing slurry.

The slurry that is fed through the line 19 into the solid-liquid separation apparatus 63 is divided into the



desilication product and the clear extract solution (sodium aluminate solution), and the desilication product is recovered from line 23 through line 21.

5 Since the desilication product thus obtained contains a small amount of impurities, such as iron oxides and titanium oxides, it is withdrawn from the line 23 and can be used effectively for known applications, such as catalysts and inorganic fillers. A portion of the desilication product is introduced into the grinder 64 to grind it to a desired  
10 particle size for reuse as seeds in the desilication reactor 59.

The clear extract solution that has been separated in the solid-liquid separation apparatus 63 is transferred into a precipitation step (not shown) of aluminum hydroxide through  
15 line 20. The seeds are added to the extract solution for precipitating aluminum hydroxide, which is separated while the decomposing solution separated from aluminum hydroxide is recycled through the line 2.

Fig. 2 shows one example of the conventional Bayer  
20 process for the extraction of alumina from bauxite. In Fig. 2, the recycled decomposing solution is introduced through the line 2 into the slurry preparation vessel 50, in which bauxite introduced through the line 1 is ground so that a slurry is formed before it is transferred to the preheaters  
25 51 and 52 and then the extraction apparatus 57 through lines 32, 33 and 34. Heat recovered in the flash evaporators 62, 61 and 60 from the slurry after the extraction is supplied to the preheaters 51 and 52 and the extraction apparatus 57 through lines 47, 46 and 45, as in the case of Fig. 1. Live steam is  
30 also introduced into the extraction apparatus 57 through line 44, so that the slurry is heated to a desired temperature for the extraction of alumina, and thus the alumina is extracted from the bauxite. After the extraction treatment, the slurry is withdrawn through line 35 and subjected to the heat  
35 recovery in the flash evaporators 60, 61 and 62. It is then fed through line 38 into the solid-liquid separation apparatus 58 where it is divided into the extract solution and the

residue. The extract solution is introduced to the desilication reactor 59 through line 40, and introduced to the solid-liquid separation apparatus 63 through line 41 after the desilication treatment where the clear solution of sodium aluminate is separated from the desilication product. The desilication product is withdrawn from the system through line 42 and a portion thereof is recycled as seeds.

In both Figs. 1 and 2, specific number of flash evaporators for cooling, the preheater of the decomposing solution and the preheater for the slurry are shown, but any desired numbers of these pieces of apparatus may actually be employed.

According to the process of the present invention, the dissolution of the reactive silica can be markedly suppressed in comparison with the conventional process without substantially lowering the extraction ratio of alumina when the alumina is extracted from bauxite. It is, therefore, possible to greatly decrease the loss of caustic soda and alumina, which loss is caused by the removal of the dissolved reactive silica in the form of the desilication product. By employing the binary fluid mode of the indirect heating for the preheating of the slurry, and the process for alumina extraction using the adiabatic reactor (reactor without heating means), it is also possible to decrease extensively the loss of caustic soda and alumina without a decrease of the heat transfer rate due to the scaling and without a deterioration in the energy unit that is derived from evaporation and the other processing steps required to keep the water balance, in comparison with the conventional process in which live steam is used for heating and alumina is extracted while heated to the extracting temperature of the alumina in the reactor. Furthermore, when the desilication treatment is carried out immediately after the separation of the dissolution residue, namely when the desilication treatment is applied at a high temperature before cooling the extract solution in the present process, a faster desilication rate in comparison with the conventional process is allowed,



and the desilication apparatus can thus be made smaller and the amount of the precipitated alumina in the desilication step decreased. Thus, a remarkable suppression of the decrease of the yield of alumina can be expected.

5 Thus, there is provided a process for the economical production of aluminum hydroxide with little contamination by silica from the alumina-containing ore with a high content of the reactive silica that has been difficult to use, and therefore the industrial value of the present invention is  
10 great.

#### EXAMPLES

The process of the present invention will now be described in detail with reference to the Examples, but the process of the present invention is not limited by such  
15 Examples.

#### [Example 1]

By using the apparatus shown in Fig. 1, alumina was extracted from bauxite having an analytical composition (in % by weight) as shown in Table 1.

20 Table 1

T-SiO <sub>2</sub>	R-SiO <sub>2</sub>	T-Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	TiO <sub>2</sub>
5.5	4.1	50.3	14.6	2.0

Bauxite was fed through the line 1 and the recycled  
25 decomposing solution having concentrations of 152 g/l of Na<sub>2</sub>O and 82 g/l of Al<sub>2</sub>O<sub>3</sub> was fed through the line 3 to the slurry preparation vessel 50 comprising a ball mill so as to have a slurry of which the bauxite content was 600 g/l and the bauxite was ground there. The slurry of the ground bauxite  
30 was then preheated from 70°C to 95°C at a temperature-increasing rate of 7°C/min. using the steam recovered from the slurry after the extraction, which was supplied through the lines 31 and 30 in the double-tube heat exchangers 51 and 52 having a tube diameter of 25 mm and a tube length of 360 m (51  
35 + 52) by passing the slurry at a flow rate of 1.7 m/sec. The preheating time of the slurry was 3.5 minutes.

On the other hand, the recycled decomposing solution through the line 4 was preheated to 104°C by using the steam recovered from the slurry after the extraction, which was supplied through the lines 29, 28 and 27. Furthermore, live steam was injected into the outer tube side of the double-tubes through the line 26 so as to preheat the solution to 160°C by indirect heating.

The bauxite slurry leaving the double-tube heat exchanger 52 was introduced to the line 12 through the line 7 together with the recycled decomposing solution preheated in the shell-and-tube heat exchanger from the line 11, and the slurry and the solution were mixed. The resultant mixed solution was then fed into the extraction step 57 comprising a tube reactor having a tube diameter of 40 mm and a tube length of 290 m at a flow rate of 2.1 m/sec. where alumina was extracted adiabatically (without heating from the outside) in a short time.

The temperature of the slurry at the exit of the extraction step 57 was 130°C and the extraction time was 2.3 minutes.

For the purpose of measuring the extraction ratio of alumina and the dissolution ratio of R-SiO<sub>2</sub> from the bauxite, samples of the slurry were withdrawn from a sampling port at an exit of the extraction step 57, and quenched with a flasher, and the bauxite residue was immediately separated. Based on a chemical analysis of the residue, the extraction ratio of Al<sub>2</sub>O<sub>3</sub> and the dissolution ratio of R-SiO<sub>2</sub> were calculated. The results are shown in Table 2.

[Comparative Example 1]

Using the apparatus shown in Fig. 2, alumina was extracted with the same recycled decomposing solution and the same bauxite as in Example 1.

The recycled decomposing solution was added to bauxite to have a bauxite concentration in the slurry of 600 g/l, and the slurry was subjected to the grinding treatment in the ball mill to have a particle size of 60 mesh. The slurry of the ground bauxite was mixed with the rest of the recycled



decomposing solution and heated from 70°C to 130°C at a temperature-increasing rate of 7°C/min. in the preheaters 51, 52, and the extraction apparatus 57 which comprised the double-tube heat exchangers having a tube diameter of 40 mm and a total tube length (51+52+57) of 1070 m, by using the recovered steam through the lines 47, 46 and 45 and live steam through the line 44, so that the  $\text{Al}_2\text{O}_3$  in the bauxite was extracted. In the same manner as in Example 1, the extraction ratio of the alumina and the dissolution ratio of R-SiO<sub>2</sub> from the bauxite were calculated. The results are also shown in Table 2.

[Comparative Example 2]

The same process as in Comparative Example 1 was used, except that the total length of the tubes of the double-tube heat exchangers was 730 m, so that the residence time of the slurry in the preheaters and reactors was 5.8 min. The extraction ratios of alumina and of the R-SiO<sub>2</sub> from the bauxite were calculated. The results are shown in Table 2.

[Comparative Example 3]

The extraction was carried out in an autoclave for 60 minutes by using the same starting extraction solution, the same bauxite, the same amount of bauxite added and the same extraction temperature as in Example 1. The extraction ratios of the alumina and of the R-SiO<sub>2</sub> from the bauxite in the slurry were calculated. The results are also shown in Table 2.

Table 2

	Extraction Temp. °C	Extraction Time (min.)	Extraction Ratio of $\text{Al}_2\text{O}_3$ , %		Extraction Ratio of $\text{R-SiO}_2$ , %	Loss of $\text{Na}_2\text{O}$
			Extracted	Effective		
Example 1	130	3.5+2.3	91	88	40	27
Comparative Example 1	130	8.5	92	88	47	31
Comparative Example 2	130	5.8	89	85	45	31
Comparative Example 3	140	60	96	88	100	67

The extraction time show in the above table means the temperature-increasing time of the bauxite slurry and the residence time in the extraction apparatus to which the slurry was supplied.

"Extracted" in the column of the Extraction ratio of  $\text{Al}_2\text{O}_3$  means the ratio of the extracted alumina at the exit of the extraction apparatus and "Effective" means the ratio of the available alumina calculated by converting the amount of  $\text{R-SiO}_2$  dissolved in the extract solution to an amount of the desilication product and correcting by subtracting an amount of alumina lost as the desilication product from "Extracted".

The amount of the loss of  $\text{Na}_2\text{O}$  was obtained by converting the amount of  $\text{R-SiO}_2$  dissolved into the extract solution to an amount of the desilication product and by calculating the amount of soda lost therefrom, and the unit is (kg/t- $\text{Al}_2\text{O}_3$ ).  
[Example 2]

The slurry leaving the tube reactor 57 of Example 1 was mixed with a high molecular weight coagulant with a ratio of 0.04% by weight based on the residue and then introduced into the high-speed thickener 58 so that the bauxite residue was immediately separated. The concentration of  $\text{R-SiO}_2$  in the extract solution was 3 g/l.

The extract solution was fed into the desilication reactor 59, and the seeds of the desilication product, the



average particle size of which had been adjusted beforehand to 10  $\mu\text{m}$  were added in a ratio of 50 g/l and the desilication was carried out at a temperature of 126°C for 120 minutes. The desilicated slurry was introduced into the flash evaporators 60-62 and cooled to a temperature of 100°C, and the desilication product was separated in the gravity solid-liquid separator 63. A portion of the desilication product was taken out for reuse as seeds, and added to the desilication reactor with a ratio of 50 g/l after adjusting the particle size in the ball mill 64. The rest of the desilication product was mixed with the bauxite residue which was separated in the high-speed thickener, withdrawn through the line 15 and cooled in a cooler (not shown), and the mixture was washed in a multi-stage counter current washer (not shown) to recover the sodium aluminate attaching to the residue. The extract solution separated in the solid-liquid separator 63 was transferred into a clarifying filter (not shown) through the line 20, and then introduced into a precipitation step so that aluminum hydroxide was precipitated. The concentration of R-SiO<sub>2</sub> in the extract solution leaving the solid-liquid separator 63 was 0.6 g/l, which means that the desilication was carried out satisfactorily.

[Comparative Example 4]

The slurry leaving the shell-and-tube reactor of Comparative Example 1 was fed into the flash evaporators 60-62 and quenched to a temperature of 100°C. The same amount of the same coagulant as in Example 2 was added to the cooled slurry and the mixture was immediately divided into the extract solution and the bauxite residue in the high-speed thickener 58. The extract solution was introduced into the desilication reactor 59 and the seeds of the desilication product, average particle size of which had been adjusted beforehand to 10  $\mu\text{m}$ , were added to the extract solution in a ratio of 50 g/l. The desilication was carried out at a temperature of 100°C for 750 minutes. The extract solution after the desilication treatment was then fed to the gravity solid-liquid separator 63 through the line 41 where the

desilication product was separated. A portion of the product was taken out and recycled as the seeds for the desilication reactor 59 after the adjustment of the particle size. The rest of the desilication product was taken out through the line 42 and mixed with the bauxite that was separated in the high-speed thickener 58, and withdrawn through the line 39, and the resultant mixture was washed in a multi-stage counter current washer (not shown) for recovering the sodium aluminate attaching to the residue. The extract solution separated in the solid-liquid separator 63 was introduced into a clarifying filter (not shown) through the line 43, and fed into the precipitation step so that aluminum hydroxide was precipitated.

The concentration of  $R-SiO_2$  in the extract solution leaving the solid-liquid separator 63 was 0.6 g/l, which indicates that the desilication was carried out satisfactorily. (In the above conventional process shown in Fig. 2, although a high-speed thickener was used as the solid-liquid separator 58 and the desilication product was activated by grinding in the ball mill, these are only for reasonable comparison with the effects of Example 1, but do not mean that, in the conventional process, the high-speed thickener has been employed as the solid-liquid separator 58, nor that the desilication product has been activated to make the seeds in the ball mill.)

The operational conditions in each step in Example 2 and Comparative Example 4 are shown in Table 3. The extraction ratio of  $Al_2O_3$  and the dissolution ratio of  $R-SiO_2$  calculated from the chemical analyses on the dissolution residue sampled from the exit of the tube reactor 57 and the bauxite residue sampled from the exit of the residue washer are shown in Table 4.



Table 3

	Example 2	Comparative Example 4
Bauxite Slurry: Preheat temp. (°C) Extraction temp. (°C)	70 - 95 130	70 - 130 130
Residence Time: Preheat Part (min.) Extract Step (min.)	3.5 2.5	8.5 0
Liquid Composition at Exit of Extraction Step: Na <sub>2</sub> O (g/l) Al <sub>2</sub> O <sub>3</sub> (g/l) Na <sub>2</sub> O/Al <sub>2</sub> O <sub>3</sub> (molar ratio) SiO <sub>2</sub> (g/l)	136 160 1.40 3	136 160 1.40 3
Liquid Composition in Desilication Reactor: Na <sub>2</sub> O (g/l) Al <sub>2</sub> O <sub>3</sub> (g/l) Na <sub>2</sub> O/Al <sub>2</sub> O <sub>3</sub> (molar ratio) SiO <sub>2</sub> (g/l)	133 156 1.40 0.6	138 158 1.44 0.6
Desilication Conditions: Temperature (°C) Time (min.) Amount of Seeds (g/l)	126 120 50	100 750 50

Table 4

Extraction and Dissolution Ratios	Example 2	Comparative Example 4
At Exit of Extraction Apparatus (alumina) (%)	91	92
At Exit of Multi-stage Counter-current Washer (alumina) (%)	88	84
At Exit of Extraction Apparatus (R-SiO <sub>2</sub> ) (%)	40	47
At Exit of Multi-stage Counter-current Washer (R-SiO <sub>2</sub> ) (%)	45	52

Table 4 shows that the extraction ratio of alumina at the exit of the multi-stage counter current washer in Comparative Example 4 was smaller by 4% than that of Example 2. This is due to the loss of alumina caused by its precipitation in the desilication step.

[Example 3]

In Example 2, a portion of the desilication product was ground in the ball mill 64 to be reused as seeds and then recycled to the desilication reactor. The variation of the concentration of R-SiO<sub>2</sub> in the extract solution depending on the particle size of the seeds and the recycling times was studied. The results are shown in Table 5.

[Comparative Example 5]

In Example 2, a portion of the desilication product was reused as the seeds without grinding, as in Example 3. The desilication product was recycled to the desilication reactor, and the variation of the concentration of R-SiO<sub>2</sub> in the extract solution depending on the particle size of the seeds and the recycling times was studied. The results are included in

Table 5.



Table 5

Recycle Time of Seeds		Example 3	Comparative Example 5
1	Average Particle Size of Seeds ( $\mu\text{m}$ )	10	11
	Specific Surface Area ( $\text{m}^2/\text{g}$ )	2	2
	R-SiO <sub>2</sub> in Extract Solution (g/l)	0.6	0.6
5	Average Particle Size of Seeds ( $\mu\text{m}$ )	10	14
	Specific Surface Area ( $\text{m}^2/\text{g}$ )	2	1.1
	R-SiO <sub>2</sub> in Extract Solution (g/l)	0.6	0.8
30	Average Particle Size of Seeds ( $\mu\text{m}$ )	10	35
	Specific Surface Area ( $\text{m}^2/\text{g}$ )	2	0.2
	R-SiO <sub>2</sub> in Extract Solution (g/l)	0.6	1.2

## CLAIMS:

1. A process for producing aluminum hydroxide from an alumina-containing ore which comprises the steps of:
- 5 (a) mixing said alumina-containing ore with an alkaline solution to obtain a slurry having a solids content higher than 20% by weight, and preheating said slurry at a temperature of 70-120°C,
- 10 (b) mixing a preheated aqueous alkaline solution with said slurry obtained in step (a),
- (c) extracting alumina contained in said mixture obtained in step (b) as sodium aluminate, in a tube reactor at a temperature of 120-160°C within 10 minutes, to obtain a
- 15 mixture of an extract solution of sodium aluminate and dissolution residues of reactive silica,
- (d) immediately separating said dissolution residues from said mixture obtained in step (c), to obtain the extract solution,
- 20 (e) desilicating said extract solution to obtain a mixture of desilication product and a clear extract solution of sodium aluminate,
- (f) separating said desilication product from said mixture obtained in step (e), to obtain the clear extract
- 25 solution, and
- (g) adding seeds of aluminum hydroxide to said clear extract solution to precipitate aluminum hydroxide, wherein in said alumina-containing ore 50% or more of the alumina is alumina trihydrate and the content of reactive silica is
- 30 from about 0.5 to 15% by weight based on the total weight of the ore and
- wherein said aqueous alkaline solution in step (b) is preheated prior to mixing to achieve said extraction



temperature of 120-160°C of step (c) after mixing with the slurry of step (a), provided that the case is excluded that the slurry is heated in step (a) to 120°C and is subsequently mixed with the aqueous alkaline solution  
5 preheated to 120°C, too.

2. The process according to claim 1, wherein step (c) is carried out within 5 minutes.

3. The process according to claim 1 or 2, wherein step (c) is carried out at a temperature of 125-150°C.

10 4. The process according to claim 1, 2 or 3, wherein the extraction ratio of alumina is not less than about 70% and the dissolution ratio of the reactive silica is not greater than about 70%.

15 5. The process according to claim 4, wherein the extraction ratio of alumina is not less than about 80% and the dissolution ratio of the reactive silica is not greater than about 50%.

20 6. The process according to any one of claims 1 to 5, wherein said slurry obtained in step (a) is preheated to a temperature of 80-110°C, prior to mixing with said aqueous alkaline solution in step (b).

7. The process according to any one of claims 1 to 6, further comprising the step of:

25 (h) grinding said desilication product separated in step (f),

wherein step (e) comprises adding said ground desilication product obtained in step (h) and desilicating said extract solution to obtain the mixture of the

desilication product and the clear extract solution of sodium aluminate.

8. The process according to any of claims 1 to 7,  
5 wherein 70% or more of the alumina in said alumina-containing ore is alumina trihydrate.

9. The process according to any of claims 1 to 8,  
wherein the content of reactive silica in said alumina-  
10 containing ore is from about 0.5 to 10% by weight based on the total weight of the ore.

10. The process according to any one of claims 1 to 9,  
wherein the solid content of the slurry is 30 to 65% by  
15 weight.

11. The process according to any one of claims 1 to  
10, wherein said extract solution is desilicated at a  
temperature of about 80 to 160°C for about 15 minutes to 10  
20 hours.

12. The process according to claim 11, wherein said  
extract solution is desilicated at a temperature of about  
115 to 160°C for about 15  
25 minutes to 5 hours.

13. The process according to claim 12, wherein said  
extract solution is desilicated at a temperature of about  
120 to 140°C for about 0.5 to 3 hours.



Fig. 1

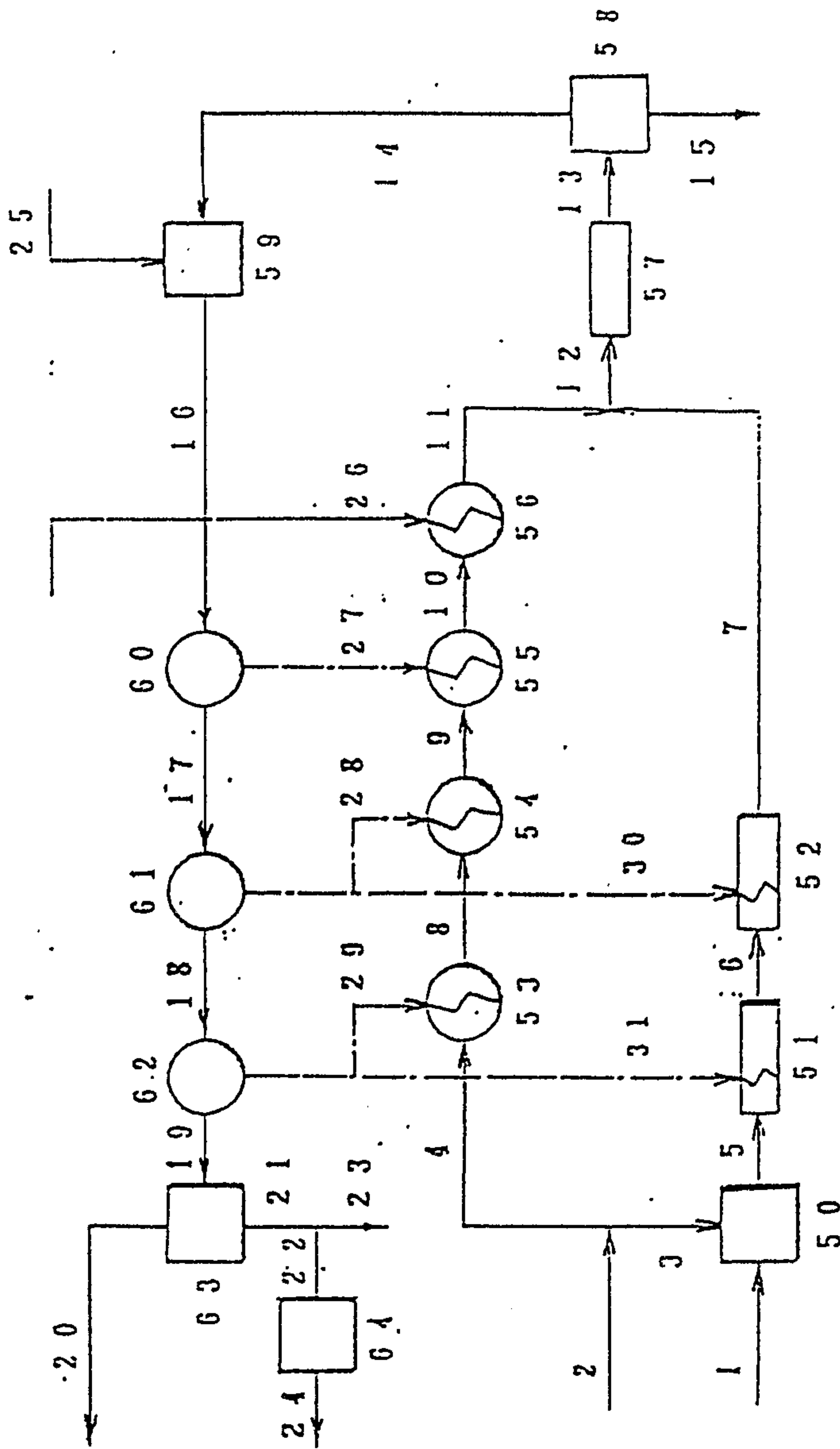


Fig. 2

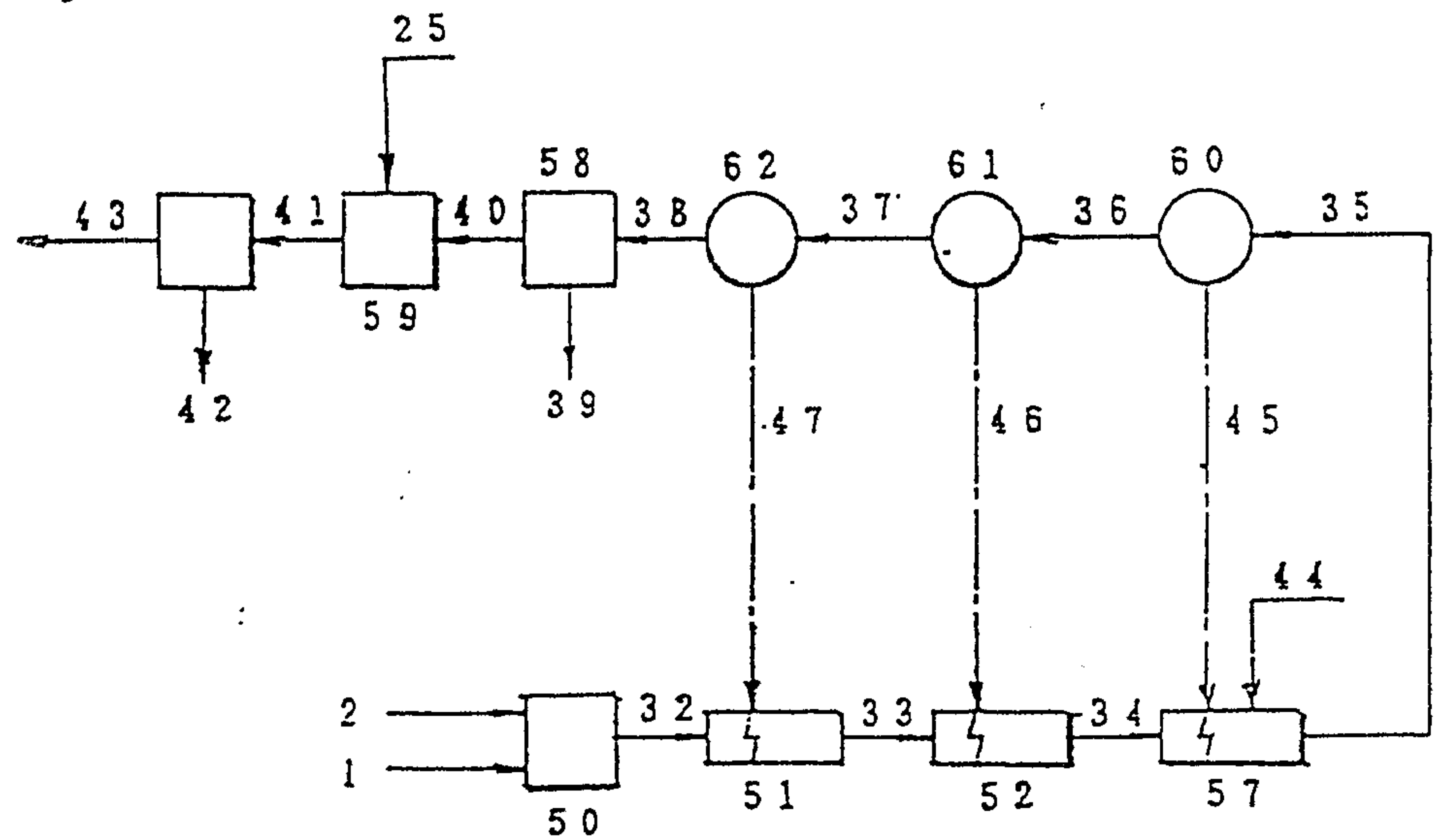


Fig.3

