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(54) Title: METHOD FOR THE PRODUCTION OF HYDROGEN AND OTHER PRODUCTS AND DEVICE FOR CARRYING OUT THIS METHOD

(57) Abstract: Hydrogen is produced from waste aluminium by its reaction with water in the presence of sodium hydroxide as a catalyst. In addition to hydrogen, products of the reaction are also aluminium hydroxide, sodium chloride, heat and potentially electric energy. The reaction occurs in the reactor (1), and hydrogen is collected in a low-pressure hydrogen tank (3). The substance of hydrogen production, according to the invention, is that gas is successively removed from the reactor (1) and/or other accessory devices with the use of a vacuum pump (4) at a minimum pressure of 0.5 kPa before the reaction, then the reactor is filled with hydrogen of a minimum purity of 99.5%, the gas is pumped away again with a subsequent filling with hydrogen of a minimum purity of 99.5% again to a positive pressure of at least 0.1 MPa. Gas removed from the reactor and/or accessory equipment with the use of the vacuum pump (4) is exhausted to a chimney (5) and dispersed into the atmosphere. The subject of the invention is a method and device for 'the safe production of hydrogen at an industrial level and' other products as well as their purification for suitable industrial application as raw materials for other industrial production.

Method for the production of hydrogen and other products and device for carrying out this method

Field of the invention

This invention relates to a method of industrial production of hydrogen and other products from waste aluminium and devices for the method.

Background and summary of the invention

The environmentally sustainable use of waste material, in this case aluminium, (aluminium packaging, lids, tubes, closures, beverage cans etc.) is a global issue. Hydrogen production from the reaction of aluminium with water using sodium hydroxide as a catalyst is generally known. The products of the reaction are Al_2O_3 or $Al(OH_3)$ and heat. Waste aluminium can be used favourably for production. The patent file CN 183 6773 introduces a catalyst applied to aluminium waste to remove the protective layer on the surface of aluminium for an improved reaction of aluminium with water. The catalyst is a compound containing PVA, ethanol, acetone, mercury chlorides and water. According to patent file JP 2003 226502, aluminium is melted together with lithium and magnesium in order to produce alloy, then water is added. This method has a high-energy demand. A similar procedure is described in patent file RU 2356 830 in which bismuth or lead is added to the alloy in order to increase the yield, as well as in document WO 2008/17088, where aluminium and lithium alloy are used, and the generator works without electric heating.

As concerns the raw materials used for the production of hydrogen, aluminium is used in particular as well as alloys of alkali metals, aluminium alloys, magnesium alloys, lithium alloys, etc. The raw material (fuel) is in the form of dust, powder, compressed boards or cell cartridges.

As concerns the aluminium production devices, there are many of them described. Patent file US 6506 360 describes a small compact device for hydrogen production by which the fuel (ground waste aluminium) is fed to a reactor in a fuel cell where it reacts with water in the presence of NaOH as a catalyst with hydrogen and heat production. The intensity of the reaction is controlled by immersion of the fuel cell to avoid overheating of the reactor. The generated heat is not used in any way, and the hydrogen is combusted in a burner. The device may be used e.g. as a cooker, it is not suitable for hydrogen production at an industrial level.

For hydrogen production at an industrial level, the device described in patent file DE 340 1194 is used. Production takes place in a reactor in the form of a reaction of aluminium in the presence of NaOH as a catalyst with heat, hydrogen and DC current being generated while natrium-aluminate is generated as a by-product. Aluminium raw material is placed on a mesh in the reactor; NaOH and water are fed to the reactor through a central funnel then rises above the mesh where it reacts with aluminium. The hydrogen is removed and a DC electric current is taken from the electrode arranged inside the reactor. A method for the use of heat is not described in detail, but the reactor shell is fitted with a water heat exchanger used for the heating of water and cooling of the reactor at the same time. Natrium-aluminiate is described here as a raw material for use in chemical industry but it poses problems with the use, being hard to prepare it to a temper for application in the chemical industry. The main disadvantage of the reactor, however, is that at the beginning of the reaction the inner space of the reactor is full of air and may form an explosive mixture of air with hydrogen, which is dangerous and absolutely undesirable for industrial production. A similar disadvantage is attributable to other known devices for hydrogen production.

The disadvantages of the hitherto known methods and devices for the production of hydrogen from aluminium are that the factors important for industrial production, especially safety, are not taken into account. The issue of hydrogen purity is not taken into account and because air is always present in the production device, an explosive mixture of hydrogen and oxygen may be formed with each new filling of the reactor with input raw materials, which is the most explosive at concentrations of 1 % vol. H_2 and 99 % vol. O_2, or 1 % vol. O_2 and 99 % vol. H_2. Because the purity of hydrogen produced in the described devices ranges from 94 to 98%, the formation of the explosive mixture is very likely. Another disadvantage of the known methods and devices is that the issue of hydrogen purity as well as other potential by-products, such as aluminium hydroxide or sodium chloride, are not taken into account, no issues related to the removal of impurities and waste from production are discussed, nor are recycling and regenerating of the reaction liquid, which is a matter of cardinal importance with respect to the environment. Known methods and devices also lack a sufficient solution of the use of generated heat in order to use heat optimally both for the production process itself and keeping the device at an operating temperature and the product for further use.

The task of the invention, therefore, is to establish a method and device for the production of hydrogen and other products from waste aluminium which would remove all the issues described above, which would be safe as well as suitable for the production of hydrogen at industrial levels, environmentally-friendly (waste-free), and economically effective.

The objective as specified above is achieved by the method of the production of hydrogen and other products in a reactor by the reaction of aluminium with water in the presence of sodium hydroxide or potassium hydroxide as a catalyst, according to the presented invention, the basis of which is that the reactor and/or other accessory devices are depressurized to a negative pressure at least 0.5 kPa with a vacuum pump before the reaction, the reactor is then filled with hydrogen of a minimum purity of 99.8%, the gas is pumped away again with a subsequent filling with hydrogen of a minimum purity of 99.5% again to positive pressure at least 0.1 MPa, whereas the gas removed from the reactor and/or accessory equipment using the vacuum pump is exhausted to a chimney and dispersed into the atmosphere.

The underlying idea of the invention is the increased safety of hydrogen production in which a safe level must be achieved by exhausting all air from the production device before production, when the oxygen content in the finished hydrogen does not exceed 10 ppm.

In the favourable execution of the hydrogen production according to the invention, the produced hydrogen is further purified so that the hydrogen produced in the reactor is washed in washing tank in treated service deaerated water and saturated with hydrogen. The hydrogen is fed to the washing tank through small holes to aerate in the water column.

Furthermore it is favourable when the hydrogen is fed from the washing tank for the separation of residual water in the separation tank fitted with Raschig rings where the water is precipitated and run down on the rings, then relatively dry hydrogen is collected in low-pressure hydrogen tank where the last residual water is frozen using the freezing lamellas connected to the cooler.

Following the rinsing (pumping in and out) of the reactor and other accessory devices with hydrogen, it is favourable to perform the operation from the hydrogen produced by the device itself. According to favourable execution of the method according to the invention, hydrogen is compressed from the low-pressure hydrogen tank to medium-pressure container of service hydrogen used for rinsing the reactor and other accessory devices and for saturation of the treated service water with hydrogen.

In another favourable execution of the method according to the invention, the reaction liquid is treated and reprocessed together with the first phase of aluminium hydroxide $Al(OH)_3$ production. Ferromagnetic admixtures are separated from the reaction liquid, being the mixture of water, NaOH, and aluminium particles, with the use of a solenoid in the tank, the liquid is then fed to the input of a mechanical filter where the mechanical admixtures are separated, then the liquid is fed to the input of the first precipitator of $Al(OH)_3$, where aluminium hydroxide is precipitated with the use of hydrochloric acid and the suspension thus generated is filtered for the removal of $Al(OH)_3$ and pure reaction liquid is collected and the reprocessed reaction liquid is reused for hydrogen production in the reactor.

It is favourable for the next reprocessing of the reaction liquid and the next purification of aluminium hydroxide that a part of the reaction liquid, favourably 20% vol., and a part of the reprocessed reaction liquid, favourably 20% vol., are fed to a neutralising unit where the liquid is diluted with water in proportion of 2 : 1 and pH is brought to 7.0 using hydrochloric acid, whereas the aluminium hydroxide is precipitated and filtered out using the first $Al(OH)_3$ filter, fed to the second $Al(OH)_3$ precipitator where the previously obtained aluminium hydroxide is fed from the filter for $Al(OH)_3$ removal, new lye is added, the mixture is heated to 85 °C, HCl is added to bring the pH value to 7.0 and the suspension is then filtered at the second $Al(OH)_3$ filter, whereas the filtered lye is fed to the tank for deaeration and saturation with hydrogen and fed to the inter-tank of the reaction liquid where the used reaction liquid from the reactor is collected.

In another favourable execution of the method according to the invention, the steps towards the final purification of sodium hydroxide and separation of salt solution are performed and the salt solution will be used for the next applicable product sodium chloride so that aluminium hydroxide from the second filter $Al(OH)_3$ mixes with water in the washing tank $Al(OH)_3$ and NaCl contained in the suspension is dissolved, the suspension is then deposited, the salt solution is fed to the third $Al(OH)_3$ filter, the tank is filled with water again and the sediment is mixed after analysis in the presence of NaCl; the washing process then either repeats or the suspension is fed to the third $Al(OH)_3$ filter.

It is favourable for the final treatment and sale of aluminium hydroxide as the final product when the aluminium hydroxide, filtered out on the third $Al(OH)_3$ filter, is dried in a dryer and transferred to the packing and distribution $Al(OH)_3$ point from where it is sold to customers according to their requirements.

In another favourable execution of the method, the final sodium chloride product is ready for sale, whereas the salt aqueous solution from the third filter $Al(OH)_3$ is fed to the crystallizing device where sodium chloride is let to crystallize at temperature of 85 °C, dried in the dryer for NaCl drying and transferred to the NaCl store for dispatching.

Finally, it is favourable from the production point of view that hot water be used for operation of the device from the water heat exchanger of the reactor, which is fed to the hot service water tank, from which hot service water is fed to the hot service water tank, from which hot service water is distributed to the second $Al(OH)_3$ precipitator, NaCl crystallizing device and NaCl dryer.

The subject of the invention is also a device for hydrogen production from waste aluminium by its reaction with water in the presence of sodium hydroxide or potassium hydroxide as a catalyst, when $Al(OH)_3$ and heat are generated, including a reactor with a water heat exchanger and at least one low-pressure hydrogen tank, the basis of which lies in the fact it contains at least one service tank for treatment of reaction liquid or reaction products, whereas the inner space of the reactor, low-pressure hydrogen tank and service tank is connected to a vacuum pump and its output is fed to a chimney while at the same time, the reactor, the hydrogen tank and service tank are independently connected to the chimney via safety valves. Connection with the vacuum pump is used for rinsing the tanks and pumping gas away, a direct connection with the chimney via the safety valves is a safety measure for the case of unexpected and dangerous overpressure in the reactor or another accessory device.

In favourable execution of the device according to invention, hydrogen output from reactor is connected to the washing tank input for separation of water steams and captured lye drops and the output from the washing tank is fed to the separation tank with Raschig rinks for separation of residual water, from where hydrogen is fed to the low-pressure hydrogen tank and the precipitated water is fed to the reservoir of emergency and operation water.

It is favourable after freezing of the residual water in hydrogen when the low-pressure hydrogen tank is connected with the cooler for hydrogen cooling in low-pressure hydrogen tank.

Another favourable execution of the device according to the invention, the issue of service hydrogen required for rinsing of the device is addressed so that the low-pressure hydrogen tank is connected to the medium-pressure service hydrogen tank via the medium-pressure compressor for washing of the reactor and operation tanks for production and treatment of hydrogen and other products for treatment of the reaction liquid.

In another favourable execution of the device according to the invention, the low-pressure hydrogen tank is connected to high-pressure hydrogen tank via high-pressure compressor from which the compressed hydrogen is fed to the filling and distributing point of hydrogen. Hydrogen can be distributed e.g. in pressure cylinders or otherwise as requested by customer. Another of potentially possible method of use of hydrogen produced and treated in this way is re-compressing and use for combustion engine in mixture with oxygen, whereas the combustion engine may drive an alternator or a generator for production of electricity sold to the distribution grid.

Another favourable executions of the device according to the invention are intended for reprocessing of the reaction liquid used (mixture of water, aluminium hydroxide and aluminium particles). In one favourable execution of the device the output of used reaction liquid from the reactor is fed to input of the container with solenoid for separation of ferromagnetic admixtures, output of which is fed to input of mechanical filter for separation of mechanical admixtures, output of which is fed to input of the first $Al(OH)_3$ precipitator for precipitation of aluminium hydroxide connected with the first container of hydrochloric acid, output of which is connected to filter input for removal of $Al(OH)_3$ and outputting clean reaction liquid is fed to the inter-tank of the reaction liquid and the output of the filtered out aluminium hydroxide is transferred for further processing.

In another favourable execution of the device according to invention the clean reaction liquid is furthermore reprocessed for reuse, whereas the output of the clean reaction liquid is connected from the inter-tank of the reaction liquid to the input of reprocessed reaction liquid tank, whereas the tank is connected with the first tank of sodium hydroxide and the output of the reprocessed reaction liquid is fed back to the reactor input from the tank.

Furthermore it is favourable when the reservoir of emergency and service water is connected with the reactor, the washing tank, the deaeration and saturation tank for deaeration of the service water and its saturation with hydrogen.

It is also favourable when the device according to the invention includes a reservoir for cooling water, which is connected with hot water heat exchanger, with washing tank and deaeration and saturation tank.

In another favourable execution of the invention the device is modified for the final purification and sale of pure aluminium hydroxide so that output of the reaction liquid from the inter-tank of the reaction liquid and reprocessed reaction liquid from the tank of the reprocessed reaction liquid is fed to the neutralizing unit connected with the second hydrochloric acid tank and output of the neutralized suspension from the neutralizing unit is fed to input of the first $Al(OH)_3$ filter output of which is connected to input of the second $Al(OH)_3$ precipitator, output of which is connected to input of the second $Al(OH)_3$ filter, output of which is fed to the input of the washing tank $Al(OH)_3$, output of which is fed to the input of the third filter $Al(OH)_3$ and the output of the separated aluminium hydroxide is fed from the third filter $Al(OH)_3$ via the dryer to packing and distributing point for sale of $Al(OH)_3$.

It is favourable from the technological point of view when the second $Al(OH)_3$ precipitator is connected to the tank of hot service water to which hot water from hot water exchanger of the reactor is fed.

It is also favourable when the second reservoir of hydrochloric acid is connected to the second $Al(OH)_3$ precipitator.

Furthermore, it is favourable when the second reservoir of sodium hydroxide is connected to the second $Al(OH)_3$ precipitator.

In another favourable execution of the device according to the invention, sodium chloride as the final product for sale is prepared. Solution of sodium chloride from the first $Al(OH)_3$ filter is fed to the NaCl crystallizing unit from which the crystallized sodium chloride transferred to NaCl store for dispatch via the NaCl dryer.

In technologically favourable execution of the invention, the NaCl crystallizing unit is formed at least from one bath with hot service water feed from hot service water tank, fitted with skimmer of salt steams terminated in a condenser.

For use of all waste salt solutions it is favourable when aqueous phase from the third $Al(OH)_3$ filter is fed to the NaCl crystallizing unit.

It is favourable for power engineering use of hot water from operation when the NaCL dryer is fed by hot service water from hot service water tank.

It is favourable for power engineering use of cooling water when the device includes the cooling water reservoir to which the feed from water treatment plant, from NaCl crystallizing device and condenser is terminated and the cooling water from the reservoir is fed to the reactor, washing tank, to the deaeration and saturation tank, to the neutralizing unit and to the Al$(OH)_3$ washing tank. It is finally favourable when the reactor is fitted with an agitating device.

The benefits of the method and device for hydrogen production and for production of other products according to the invention can be seen especially in guarantee of safe operation suitable for hydrogen production under industrial conditions because all air, which could cause formation of the explosive mixture, is removed from the device before the reaction. Another benefits lie in achieving of high purity level for both produced hydrogen and aluminium hydroxide and in production of other marketable products such as sodium chloride, heat, and electricity. The operation is economic and environmentally friendly with minimum impact on environment.

Brief description of the drawings

The invention will be described in detail with the use of drawings, whereas fig. No. 1 shows technological scheme of the method and device according to the invention and fig. No. 2 schematic view of the reactor.

Detailed description of the preferred embodiments

It is understood that specific examples of the invention execution described and depicted below are shown for indicative purposes only and not as limitation of examples of the invention execution to said examples. The experts in the art will find or shall be able to derive, while using a routine experimenting, either higher or lower number of equivalents to specific executions of the invention specially described herein. These equivalents will be covered in the scope of the following patent claims as well.

The example of execution of the method for hydrogen production and device for the method is shown on figure 1.

The main input raw material for hydrogen production is waste aluminium, e.g. bottle caps, lids from yoghurts, pastes and similar products, tubes from condensed milk, packaging from chocolates, butter etc., beverage cans, cream jars, packaging of cheeses and much more. This waste material is collected in collection and gathering place 43 of aluminium located outside so-called hydrogen zone, i.e. the zone of the main production equipment where aluminium is produced. From there, aluminium is transported to sorting and crushing line 40 also located outside the hydrogen zone. Here, aluminium is manually checked to remove plastic materials, paper etc. This sorted waste is transported to an incinerator. Aluminium is then crushed into 4 - 6 mm particles and stored in crushed aluminium storage 41 that may be located outside the hydrogen zone as well.

From here, crushed aluminium is transported to filling and dosing device 7, which is already located in the hydrogen zone, and its bin and other components are air-displaced before each operation as any other device in the hydrogen zone. The bin of the filling and dosing device 7 is filled with belt conveyor; filling of crushed aluminium to the reactor 1 is automatic using a screw-dosing conveyor.

Another raw material for hydrogen production is water. Water is pumped from the water pipeline, goes through the water treatment plant 44 and collects in the reservoir 23 of the cooling water located outside the hydrogen zone, from where it is fed primarily to the reactor 1 as well as other parts of the device as described later.

The next raw material for hydrogen production is sodium hydroxide purchased and stored in the first bin 20 of sodium hydroxide in hydrogen zone from which it is fed to the tank 19 for reprocessing of the reaction liquid (mixture of sodium hydroxide and water) and then to the reactor 1. Sodium hydroxide is stored also in the second bin 37 of sodium hydroxide outside the hydrogen zone.

The last raw material required for hydrogen production according to the invention is hydrochloric acid collected in the first reservoir 15 of hydrochloric acid in the hydrogen zone and in the second reservoir 36 of hydrochloric acid outside the hydrogen zone and it is used for $Al(OH)_3$ precipitation and neutralization of the reaction liquid.

The hydrogen production occurs in the hydrogen zone depicted on figure 1 as the area delimited with dashed line and includes all important devices used for production of hydrogen, particularly the reactor 1. The reactor 1 is a closed container in which known chemical reaction for hydrogen production occurs:

$$2Al + 6H_2O + NaOH \rightarrow 2Al(OH)_3 + 6H + HEAT$$

Aluminium is charged to the reactor 1 from the filling and dosing device 7 fitted with the screw-dosing conveyor. The reactor 1 is filled up to 50% of its volume by 50% aqueous solution of sodium hydroxide. Another execution may use potassium hydroxide. The reaction in the reactor 1 occurs under continuous stirring and because this is strong exothermic reaction, excessive heat must be removed with the use of active water cooling through water heat exchanger 2 in the doubled shell of the reactor 1. Hot water is fed further to operation or for other use (for sale). In the reactor 1, operation temperature at max. 85 °C is maintained. Hydrogen generated in the reactor 1 is removed for washing in the washing tank 6 and the reaction liquid (mixture of H_2O and NaOH with aluminium residues) is removed for separation of metal particles to the tank with solenoid 11. In case of any failure, e.g. in case of power supply failure with potential spontaneous increase of pressure or temperature, the reaction must be interrupted immediately by feeding of cold water from the reservoir 13 of the emergency and service water and charge of more aluminium from the filling and dosing line 7 is stopped. The reactor 1 is designed to negative pressure at least 0,5 kPa and positive pressure 1 MPa.

For execution according to figure 2, the reactor 1 is a lockable tank fitted with screwing upper flange 47 with various recesses for control, with aluminium input 48 from the filling and dosing line 7, safety valve 49 with output to collection pipeline K of chimney 5, hydrogen output 50 fed to washing tank 6, rinsing output 51 fed to the vacuum pump 4. There is side input of the reaction liquid inside the reactor 1, reaction liquid output and emergency and operation water supply. In the lower part of the reactor 1 there is agitating device 52 driven by electric motor.

The reactor 1 as well as filling and dosing line 7, as well as all other devices in so-called hydrogen zone are interconnected with the vacuum pump 4 so that inputs from each device are fed to the collection pipeline VP. With the use of the vacuum pump 4 the production line must be successively (tank by tank) air-displaced to negative pressure about 1.3 kPa and subsequently filled with pure hydrogen of at least 99.5% purity before each time the production line is started or after opening of a tank during operation. This is hydrogen identified as "H_2 rinse" taken from medium-pressure reservoir 24 of the service hydrogen and distributed to each reservoir in the hydrogen zone. Then, each reservoir in the hydrogen zone is air-displaced again and filled with "H_2 rinse" hydrogen to positive pressure of 0,1 MPa. All exhausted air as well as rinse hydrogen is taken to the chimney 5 to which the output from the vacuum pump 4 terminates. This process is necessary for safety reasons; exhausting of all air must provide oxygen contents in finished produced hydrogen under 10 ppm.

The chimney 5 consists of tube of inner diameter of 150 mm and height over the highest point of the technological device of the production line including roof. The chimney 5 is not and must not be fitted with terminal burner. Fed mixture of hydrogen and air is exhausted to atmosphere, whereas released hydrogen rises upright and therefore may not accumulate to a phase of explosive mixture, i.e. 1 – 99 % H/O_2. Exhausted hydrogen is not a substance causing greenhouse effect, is neither poisonous nor toxic and not explosive if diluted to high proportion. Environment is not exposed to smell, airborne particles etc.

Direct output from the reactor 1 is fed to the chimney 5 through the safety valve (used for relieving of dangerous overpressure) and the collection pipeline K of the chimney 5 has terminated outputs from each device and tank in the hydrogen zone fitted with safety valves and they are used for exhaust of dangerous positive pressure.

An important feature of the production process according to the invention is purification of the generated hydrogen. Hydrogen from the reactor 1 is fed to the washing tank 6, which is 70% filled with treated oxygen-free from the reservoir 13 of the emergency and service water. The remaining 30% of the volume of the washing tank 6 consists of washed hydrogen. Hydrogen is fed to the washing tank 6 through small holes to bubble across the water column. In this way, water steam as well as lye drops are removed. Water is added to the washing tank 6 from the reservoir 13 of emergency and service water. Certain part of the water used goes to the first precipitator 16 $Al(OH)_3$. The washed hydrogen goes to separation of water to the separation tank 8.

The separation tank 8 is the tank 90% filled with Raschig rings where water from the washing tank 6 is precipitated and ran down on the rings with subsequent draining to the reservoir 13 of the emergency and service water. Relatively dry hydrogen continues to low-pressure hydrogen tank 3.

The low-pressure hydrogen tank 3 serves as temporary store for generated hydrogen and for separation of residual water with the use of freezing lamellas cooled down to temperature of – 20 °C. Freezing takes place with the use of the cooler 22. The lamellas must be defrosted regularly with the service water from the reservoir 35 of hot service water. Defrosted water is drained to the reservoir 13 of emergency and service water. Dried hydrogen is pumped from the low-pressure hydrogen tank 3 with the use of medium-pressure compressor 21′ to the medium-pressure reservoir 24 of service hydrogen from where it is used as H_2 rinse for rinsing (filling and air-displacing) of the reservoirs in the hydrogen zone. Pressure in low-pressure hydrogen tank 3 must be lower than operating pressure. Water contents in the finished hydrogen should not exceed 5 ppm.

Excessive hydrogen from the low-pressure hydrogen tank 3 is fed via high-pressure compressor 21 to high-pressure hydrogen tank 9 where it is stored under pressure of 230 at. Hydrogen is distributed from the high-pressure hydrogen tank 9 in the filling and distributing point 10 of hydrogen. The high-pressure hydrogen tank 9 is also fitted with draining of residual condensed water drained to the reservoir 13 of the emergency and service water.

The filling and distributing point 10 of the hydrogen may pose various methods of use and sale of purified product (depends on agreement with customers). For example, hydrogen may be filled in pressure cylinders or after repeated pressure reduction it may be used for electricity production when hydrogen is fed to the engine 45 that drives the alternator 46 producing electric energy.

Another important feature of the method and device according to the invention is treatment of the reaction liquid and production of aluminium hydroxide. From the reactor 1 the reacting liquid is drained to the tank 11 with solenoid that traps all particles that can be captured by magnet. It may particularly include iron with admixture of trace elements of other metals. Reaction liquid flows to the mechanical filter 12, which is the tank fitted with filters arranged in descending order from 1,000 micrometres to 4 micrometres. This filtration removes all mechanical particles larger than 4 micrometres. Purified reaction liquid flows for processing in the first 16 $Al(OH)_3$ precipitator.

For the device to operate in the hydrogen zone, accessory reservoirs are important, particularly the reservoir 13 of emergency and service water mainly used as reservoir of the emergency water for uncontrolled reaction of the reactor 1. It is furthermore used as reservoir for collection of all service treated and oxygen-free water as well as for preparation of the reprocessed reaction liquid.

The reservoir 13 of the emergency and operation water is connected to the deaeration and saturation reservoir 14 used for deaeration of newly feeding treated water from the reservoir 23 of the cooling water and to subsequent saturation with service hydrogen (H_2

rinse). Water treated in this way is pumped to the reservoir 13 of emergency and service water with the use of the medium-pressure service hydrogen (H_2 rinse). Another accessory tank is the first reservoir 15 of hydrochloric acid, which is the tank for deaerated HCl used partially for neutralization of the reaction liquid in the first 16 $Al(OH)_3$ precipitator.

The first precipitator 16 $Al(OH)_3$ is the reservoir where pH is partially reduced for the reaction liquid coming from the mechanical filter 12 with the use of HCl from the mentioned first reservoir 15 of hydrochloric acid to value pH = 12.95, whereas vast majority of dissolved aluminium hydroxide $Al(OH)_3$ is precipitated from the reaction liquid. The suspension is then fed to the filter 17 for removal of $Al(OH)_3$ from the reaction liquid. The filter 17 is the tank fitted with filters of size from 80 micrometres down to 20 micrometres in descending order. Filtered aluminium hydroxide is manually transferred to the second precipitator 29 $Al(OH)_3$ in the zone without hydrogen, clean reaction liquid is fed to the inter-reservoir 18 of the reaction liquid. Here, the reaction liquid is divided so that 80% of the liquid drains to the reservoir 19 for reprocessing of the reaction liquid and 20% of the reaction liquid feds to the neutralizing unit 25 where full neutralization is performed.

The reservoir 19 for reprocessing of the reaction liquid is used for preparation of the reprocessed reaction liquid for further use in the reactor 1. Here, 80% of partially neutralized reaction liquid from the inter-reservoir 18 of the reaction liquid is combined with 20% of new lye from the first reservoir 20 of sodium hydroxide. The reaction liquid treated in this way flows back to the reactor 1 remaining 20% of the reaction liquid flows to the neutralizing unit 25. The first reservoir 20 of sodium hydroxide is the reservoir for clean new 50% sodium hydroxide added to the reaction liquid with 20% vol. share. The lye is deaerated, saturated with hydrogen and it is added to the reservoir 19 for regeneration of the reaction liquid.

In addition to the hydrogen zone, so-called zone without hydrogen is important for operation of the device according to the invention (depicted on figure 1 outside the hydrogen zone with dashed line). The first device in the zone without hydrogen is the reservoir of cooling water 23, which is a tank used as reservoir of cooling water for reactor 1 as well as reservoir of treated service water. Water for the reservoir 23 is obtained from the water treatment plant 44 from water pipeline or from other source, then also from the recrystallizing unit 27 for NaCl or condensate is fed from the condenser 28. Water from the reservoir 23 of cooling water is fed to the reactor 1, washing tank 6, deaeration and saturation reservoir 14, to the neutralizing unit 25 and to the reservoir 31 for washing of $Al(OH)_3$ as mentioned below.

Vast majority of the devices arranged in the zone without hydrogen is used for purification of aluminium hydroxide and for refining of its properties for subsequent sale; in addition this device is used for production of sodium chloride and distribution of hot service water.

The reaction liquid flowing from the inter-reservoir 18 in the hydrogen zone is fed to the neutralizing unit 25 in the zone without hydrogen. The neutralizing unit 25 is the tank used for complete neutralization of the reaction liquid by dilution with cooling water from the reservoir 23 of the cooling water in proportion 2 : 1, and then with 37% HCl from the second reservoir 36 of hydrochloric acid. Acidity of the reaction liquid is treated to value pH = 7.0 and all aluminium hydroxide contained in the reaction liquid is precipitated. Then, the suspension drains to filtration in the first filter 26 $Al(OH)_3$. The first filter 26 $Al(OH)_3$ is the tank fitted with filters in descending mesh size from 80 micrometres to 20 micrometres where the precipitated aluminium hydroxide is captured. After saturation, it is transported to the second precipitator 29 $Al(OH)_3$. The solution of sodium chloride flows from the first filter 26 to the crystallizing unit 27 for NaCl crystallization. The crystallizing unit 27 consists of three tubs of volume 10 m3 to which aqueous solution is drained from the first filter 26 $Al(OH)_3$ and the third filter 32 $Al(OH)_3$. Here, salt solution is evaporated using hot service water from the reservoir 35 of hot service water. At temperature of 85 °C salt crystallizes and manually transported to the NaCl dryer 34. Water steams from salt solutions are fed to the condenser 28, cooled service water is drained to the reservoir of cooling water 23. The condenser 28 serves to condensation of water steams coming from the NaCl crystallizing unit 27. Condensed water is drained from the condenser 28 to the reservoir of cooling water 23.

In NaCl dryer 34, the crystallized sodium chloride from the crystallizing unit 27 is dried in the tubs, also with the use of hot service water from the reservoir 35 of that service water, and subsequently it is manually transferred to NaCl store 38 NaCl for dispatch. Salt steams from drying are drained to atmosphere.

Regarding purification of aluminium hydroxide, the zone without hydrogen is fitted with the second precipitator 29 $Al(OH)_3$, which is a tank where aluminium hydroxide is from the filter 17 for removal of $Al(OH)_3$ in the hydrogen zone and from the first filter 26 $Al(OH)_3$ in the zone without hydrogen, is combined after adding of new clean lye from the second reservoir 37 of sodium hydroxide and after heating up to temperature of 85 °C hydroxide is dissolved again and after adding of relevant dose of 37% HCl from the second reservoir 36 of hydrochloric acid, pH of the solution is modified to pH = 7.0 and drained for filtration to the second filter 30 $Al(OH)_3$. The second filter 30 is also fitted with the filters of descending mesh size from 80 micrometres to 20 micrometres. Here, the precipitated hydroxide is separated and then manually transferred to the reservoir 31 for washing of $Al(OH)_3$. Liquor is pumped for hydrogen treatment to the reservoir 42 for deaeration and saturation and lye saturation with hydrogen in the hydrogen zone. In the reservoir 31 for washing of $Al(OH)_3$ the filtered hydroxide from the second filter 30 is mixed with clean water from the reservoir of cooling water 23 and NaCl present in the suspension is dissolved under constant stirring. Then the suspension is let to sediment, flow off drains the salt solution to the third filter 32 $Al(OH)_3$, clean water is filled again and the sediment is mixed after NaCl presence analysis. If the analysis result is NG, the suspension is drained to the third filter 32 $Al(OH)_3$. If NaCl is still present after second washing, washing repeats again up to quality requested. Identically to previous cases, the third filter 32 of aluminium hydroxide consists of the tank fitted with filters of 80 micrometres to 20 micrometres in descending order. In this tank, already clean and washed aluminium hydroxide is filtered and manually transferred to drying in the dryer 39, the water phase is drained to the NaCl crystallizing unit 27. The aluminium hydroxide dryer 39 contains tub heated with service water from the hot service water reservoir 35. After drying, aluminium hydroxide continues to dispatch to packing and distribution point 33 $Al(OH)_3$, water steams are exhausted to atmosphere. The packing and distribution point 33 consists of a hall for warehousing of dried aluminium hydroxide intended for sale in the form requested by customer.

The zone without hydrogen contains accessory devices such as hot service water reservoir 35. This is the reservoir for hot water coming from cooling of the reactor 1. Hot water is distributed to the operation, excessive water may be then used for other purposes such as drying of wood etc. The second reservoir 36 of hydrochloric acid is the tank for 37% hydrochloric acid used for neutralization of lye in the first precipitator 16 $Al(OH)_3$, neutralizing unit 25 and the second precipitator 29 $Al(OH)_3$, and for refilling of the first reservoir 15 of hydrochloric acid in the hydrogen zone. The second reservoir 37 of sodium hydroxide is the reservoir used for storing of operation lye (purchased) used for neutralization in the first precipitator 16 $Al(OH)_3$, neutralizing unit 25 and the second precipitator 29 $Al(OH)_3$, and for refilling of the first reservoir 20 of sodium hydroxide in the hydrogen zone.

Industrial applicability

The method and device according to the invention can be used for the industrial production of hydrogen and other products from waste aluminium materials in various forms, whereas the hydrogen and other products are purified to a condition suitable for subsequent industrial use.

Overview of relation figures used in the drawing

1	reactor
2	hot water heat exchanger of the reactor
3	low-pressure hydrogen tank
4	vacuum pump
5	chimney
6	washing tank
7	filling and dosing device
8	separation tank
9	high-pressure hydrogen tank
10	filling and distribution point of hydrogen
11	tank with solenoid
12	mechanical filter
13	reservoir for emergency and service water
14	deaeration and saturation reservoir
15	first reservoir of hydrochloric acid
16	first precipitator of $Al(OH)_3$
17	filter for removal of $Al(OH)_3$
18	inter-reservoir of reaction liquid
19	tank for reprocessing of reaction liquid
20	first reservoir of sodium hydroxide
21	high-pressure compressor
21'	medium-pressure compressor
22	cooler
23	cooling water reservoir
24	medium-pressure reservoir of service hydrogen
25	neutralizing unit
26	first filter of $Al(OH)_3$
27	crystallizing unit of NaCl
28	condenser
29	second precipitator of $Al(OH)_3$
30	second filter of $Al(OH)_3$
31	reservoir for washing

32	third filter of $Al(OH)_3$
33	packing and distribution point of $Al(OH)_3$
34	NaCl dryer
35	hot service water reservoir
36	second reservoir of hydrochloric acid
37	second reservoir of sodium hydroxide
38	NaCl store for dispatch
39	dryer of $Al(OH)_3$
40	aluminium sorting and crushing line
41	crushed aluminium storage
42	reservoir for deaeration and saturation and lye saturation with hydrogen
43	collection and gathering place of aluminium
44	water treatment plant from water pipeline
45	engine
46	alternator
47	flange
48	aluminium supply
49	safety valve
50	hydrogen output
51	rinsing output
52	agitating device

K – collection pipeline for each device output in hydrogen zone, fed via the safety valves to chimney 5

VP – collection pipeline for inputs from each device in hydrogen zone to vacuum pump 4

H_2 RINSE – rinsing distribution of rinsing hydrogen from medium-pressure reservoir of service hydrogen 24 to each tank in hydrogen zone.

PATENT CLAIMS

1. A method for the production of hydrogen and other products from waste aluminium by a reaction of aluminium with water in reactor (1) in the presence of sodium hydroxide or potassium hydroxide as a catalyst and in the formation of $Al(OH)_3$ and heat **characterized by that** the gas is successively removed with the use of a vacuum pump (4) to a minimum pressure of 0.5 kPa from the reactor (1) and/or other accessory devices before the reaction itself, the reactor and devices are then filled with hydrogen of a minimum purity of 99.5%, the gas is pumped away again followed by a repeated filling with hydrogen of a minimum purity of 99.5% to a positive pressure at least 0.1 MPa, whereas gas removed from the reactor (1) and/or accessory equipment with the use of the vacuum pump (4) is exhausted to chimney (5) and dispersed into the atmosphere.

2. The method for the production of hydrogen according to claim 1 **characterized by that** the hydrogen produced in the reactor (1) is washed in washing tank (6) in treated service deaerated water and saturated with hydrogen.

3. The method for the production of hydrogen according to claim 2 **characterized by that** hydrogen is fed from the washing tank (6) for separation of residual water in the separation tank (8) fitted with Raschig rings and is subsequently collected in a low-pressure hydrogen tank (3) where the last residual water is frozen using the freezing lamellas connected to the cooler (22).

4. The method for the production of hydrogen according to claim 3 **characterized by that** hydrogen taken from the low-pressure hydrogen tank (3) is compressed to a medium-pressure reservoir (24) of service hydrogen (H2 RINSE) used to rinse the reactor (1) and other accessory devices and for saturating the service water with hydrogen.

5. The method for the production of hydrogen according to claim 1 **characterized by that** the reaction liquid used from the reactor (1), containing H2O, NaOH, and Al particles, is fed to the input of a tank with a solenoid (11), where ferromagnetic

admixtures are separated, then it is fed to the input of a mechanical filter (12) where mechanical admixtures are separated, from where it is fed to the input of the first precipitate (16) $Al(OH)_3$, where aluminium hydroxide is precipitated with the use of hydrochloric acid, then the suspension formed is filtered in filter (17) for $Al(OH)_3$ removal, and the purified reaction liquid is collected and reprocessed by the addition of new sodium hydroxide, and the reprocessed reaction liquid is reused for hydrogen production in the reactor (1).

6. The method for the production of hydrogen according to claim 5 **characterized by that** part of the clean reaction liquid, favourably 20% vol., and part of the reprocessed reaction liquid, favourably 20% vol., are fed to a neutralising unit (25) where the liquid is diluted with water in proportion of 2:1 and the pH is brought to 7.0 using hydrochloric acid, whereas aluminium hydroxide is precipitated and filtered out using the first $Al(OH)_3$ (26) filter, fed to the second $Al(OH)_3$(29) precipitator where the previously obtained aluminium hydroxide is fed from the filter for $Al(OH)_3$ removal (17), new lye is added, the mixture is heated to 85 °C, HCl is added to bring the pH value to 7.0, and the suspension is then filtered in the second $Al(OH)_3$ (30) filter, whereas the filtered lye is fed to the tank (42) for deaeration and saturation with hydrogen and fed to the inter-tank (18) of the reaction liquid where the used reaction liquid is collected.

7. The method for the production of hydrogen according to claim 6 **characterized by that** the aluminium hydroxide from the second filter $Al(OH)_3$ (30) mixes with water in the washing tank $Al(OH)_3$ (31) and NaCl contained in the suspension is dissolved under constant stirring, the suspension is then let to sediment, the salt solution is fed to the third $Al(OH)_3$ (32) filter, the tank (31) is again filled with water and the sediment is mixed after an analysis for the presence of NaCl; the washing process is then either repeated or the suspension is fed to the third $Al(OH)_3$ filter (32).

8. The method for the production of hydrogen according to claim 7 characterized by that aluminium hydroxide filtered from the third filter (32) is dried in the dryer (39) and transferred to the $Al(OH)_3$ packing and distribution point (33).

9. The method for the production of hydrogen according to claim 7 or 8 **characterized by that** the salt aqueous solution from the third filter $Al(OH)_3$(32) is fed to the crystallizing unit (27) where sodium chloride is let to crystallize at a temperature of 85 °C, dried in the dryer for NaCl drying (34) and transferred to the NaCl store (38) for dispatching.

10. The method for the production of hydrogen according to at least one of the claims 1 to 9 **characterized by that** the second precipitator (29) $Al(OH)_3$, NaCl crystallizing unit (27) and NaCl drying device (34) are connected to hot water distribution from the hot service water reservoir (35) to which hot water is fed from the hot water heat exchanger (2) of the reactor.

11. The device for production of hydrogen from waste aluminium by its reaction with water under the presence of sodium hydroxide or potassium hydroxide as a catalyst, during the formation of $Al(OH)_3$ and heat, including a reactor (1) with water heat exchanger (2) and at least one low-pressure hydrogen tank (3), **characterized by that** it contains at least one service tank for the treatment of reaction liquid or reaction products, whereas the inner space of the reactor (1), the low-pressure hydrogen tank (3) and service tank is connected to a vacuum pump (4) and its output is fed to a chimney (5) while at the same time the reactor (1), the low-pressure hydrogen tank (3) and the service tank are independently connected to the chimney (5) via safety valves.

12. The device according to claim 11 **characterized by that** the hydrogen output from the reactor (1) is connected to the washing tank (6) input for separation of steam and captured lye drops, and the output from the washing tank (6) is fed to the separation tank (8) with Raschig rings for the separation of residual water, from where hydrogen is fed to the low-pressure hydrogen tank (3) and the precipitated water is fed to the reservoir (13) of emergency and operation water.

13. The device according to claim 12 characterized in that the low-pressure hydrogen tank (3) is connected with the cooler (22) for cooling hydrogen in a low-pressure hydrogen tank (3).

14. The device according to claim 12 or 13 **characterized by that** the low-pressure hydrogen tank (3) is connected to the medium-pressure service hydrogen tank (24) via the medium-pressure compressor (21) of service hydrogen (H2 RINSE), intended for washing the reactor and operation tanks for the production and treatment of hydrogen and other products and for treatment of the reaction liquid.

15. The device according to at least one of the claims 12 to 14 **characterized by that** the low-pressure hydrogen tank (3) is connected via high-pressure compressor (21) to the high-pressure hydrogen tank (9) from which the compressed hydrogen is fed to the hydrogen filling and distribution point (10).

16. The device according to claim 11 **characterized by that** the output of the used reaction liquid from the reactor (1) is fed to the input of the container (11) with solenoid for the separation of ferromagnetic admixtures, the output of which is fed to the input of the mechanical filter (12) for separation of mechanical admixtures, the output of which is fed to the input of the first $Al(OH)_3$ precipitator (16) for the precipitation of aluminium hydroxide, which is connected with the first container of hydrochloric acid (15), the output of which is connected to the filter (17) input for the removal of $Al(OH)_3$ and the clean reaction liquid output is fed to the reaction liquid inter-tank (18), and the output of the filtered out aluminium hydroxide is transferred for further processing.

17. The device according to claim 16 **characterized by that** the output of the clean reaction liquid is connected to the input of the tank for reprocessing the reaction liquid (19) from the reaction liquid inter-tank (18), whereas the tank (19) is connected with the first reservoir (20) of sodium hydroxide and output of the reprocessed reaction liquid is fed back to the reactor (1) from the tank (19).

18. The device according to at least one of the claims 12 to 17 **characterized by that** the reservoir for emergency and service water (13) is connected with the reactor (1), the washing tank (6) and the deaeration and saturation reservoir (14) for deaeration of service water and saturation with hydrogen.

19. The device according to at least one of the claims 11 to 18 **characterized by that** it includes the reservoir of cooling water (23) which is connected to the hot water heat exchanger (2) of the reactor (1), washing tank (6) and deaeration and saturation reservoir (14).

20. The device according to claim 17 **characterized by that** the output of the reaction liquid from the inter-tank (18) of the reaction liquid and reprocessed reaction liquid from the tank (19) of the reprocessed reaction liquid is fed to the neutralizing unit (25) connected with the second hydrochloric acid tank (36) and the output of the neutralized suspension from the neutralizing unit (25) is fed to the input of the first $Al(OH)_3$ (26) filter, the output of which is connected to the input of the second $Al(OH)_3$ (29) precipitator, the output of which is connected to the input of the second $Al(OH)_3$ (30) filter, the output of which is fed to the input of the washing tank $Al(OH)_3$ (31), the output of which is fed to the input of the third filter $Al(OH)_3$ (32) and the output of the separated aluminium hydroxide is fed from the third filter $Al(OH)_3$ (32) via the dryer (39) to the packing and distributing point (33) for the sale of $Al(OH)_3$.

21. The device according to claim 20 **characterized by that** the second precipitator (29) of $Al(OH)_3$ is connected to the hot service water reservoir (35) to which the hot water output from the hot water heat exchanger (2) of the reactor (1) is fed.

22. The device according to claim 20 or 21 **characterized by that** the second precipitator (29) $Al(OH)_3$ is connected to the second reservoir of hydrochloric acid (36).

23. The device according to claim 20, 21 or 22 **characterized by that** the second precipitator (29) $Al(OH)_3$ is connected to the second reservoir of sodium hydroxide (37).

24. the device according to claim 20 **characterized by that** the solution of sodium chloride from the first filter (26) $Al(OH)_3$ is fed to the input of the NaCl crystallizing unit (27), from where the output of crystallized sodium chloride is fed via the NaCl dryer (34) to the NaCl store (38) for dispatch.

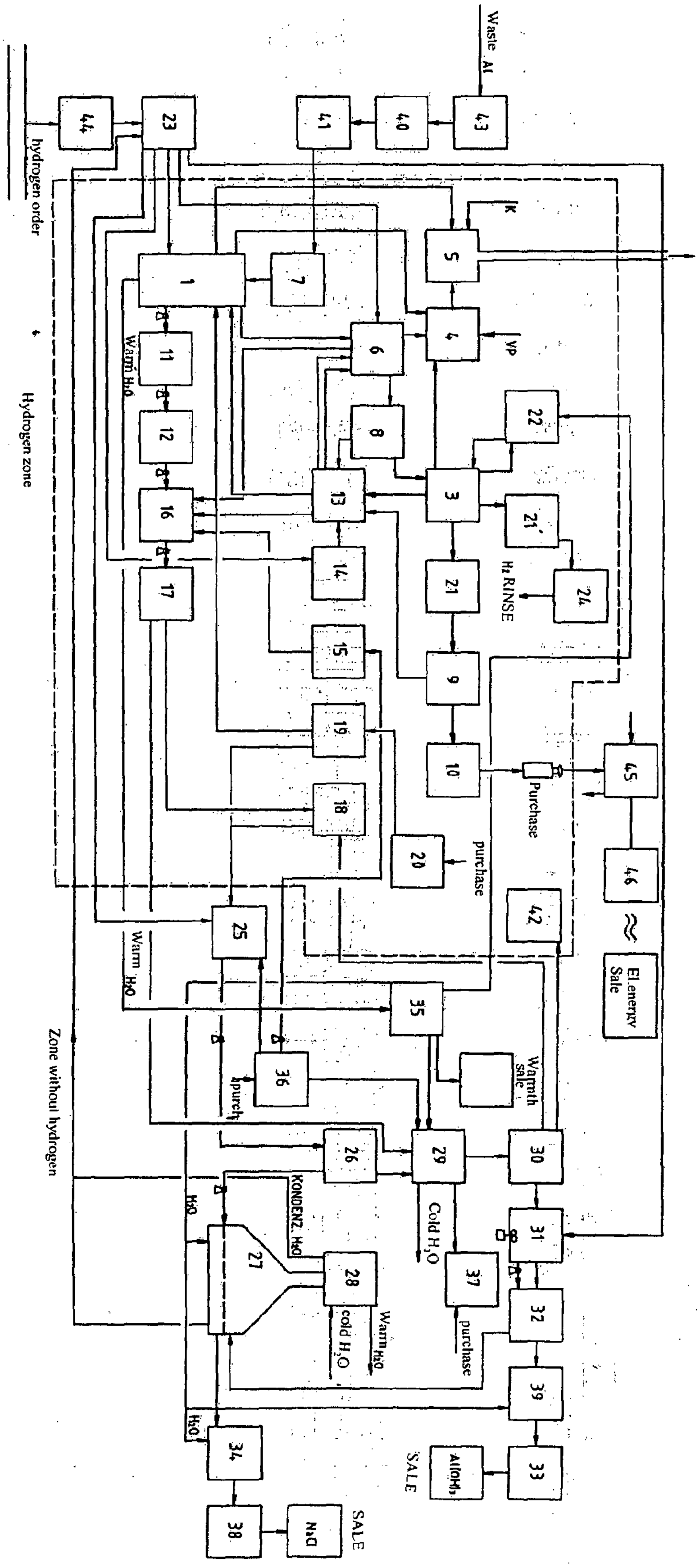
25. The device according to claim 24 **characterized by that** the NaCl crystallizing unit (27) is formed by at least from one tub with a hot service water feed from the hot service water tank (35), fitted with a skimmer of salt steams terminating in a condenser (28).

26. The device according to claim 25 **characterized by that** the liquid phase from the third filter (32) $Al(OH)_3$ inputs to the NaCl crystallizing unit (27).

27. The device according to at least one of the claims 24 to 26 **characterized by that** the NaCl dryer (34) is connected to the output of the hot service water from the hot service water reservoir (35).

28. The device according to at least one of the claims 11 to 27 **characterized by that** it contains a reservoir of cooling water (23) to which the input from the water treatment plant (44) is terminated while the water output from the NaCl crystallizing unit (27) and condensate (28) and the cooling water from the reservoir (23) is fed to the reactor (1), to the washing tank (6), to the deaeration and saturation reservoir (14), to the neutralizing unit (25) and to the reservoir for washing (31) of $Al(OH)_3$.

29. The device according to at least one of the claims 11 to 28 **characterized by that** the reactor (1) is fitted with an agitating device (52).


Waste Al
43
40
41
44
23
hydrogen order
K
5
7
1
4
vp
6
11
Warm H2O
8
22
12
Hydrogen zone
13
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21'
16
14
21
H2 RINSE
24
17
15
9
19
10
Purchase
45
18
20
purchase
46
42
El.energy Sale
25
Warm H2O
35
36
purch
Warmth sale
Zone without hydrogen
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29
30
KONDENZ. H2O
Cold H2O
31
H2O
27
28
37
32
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33
Al(OH)3
SALE
38
N2O
SALE

FIG.1

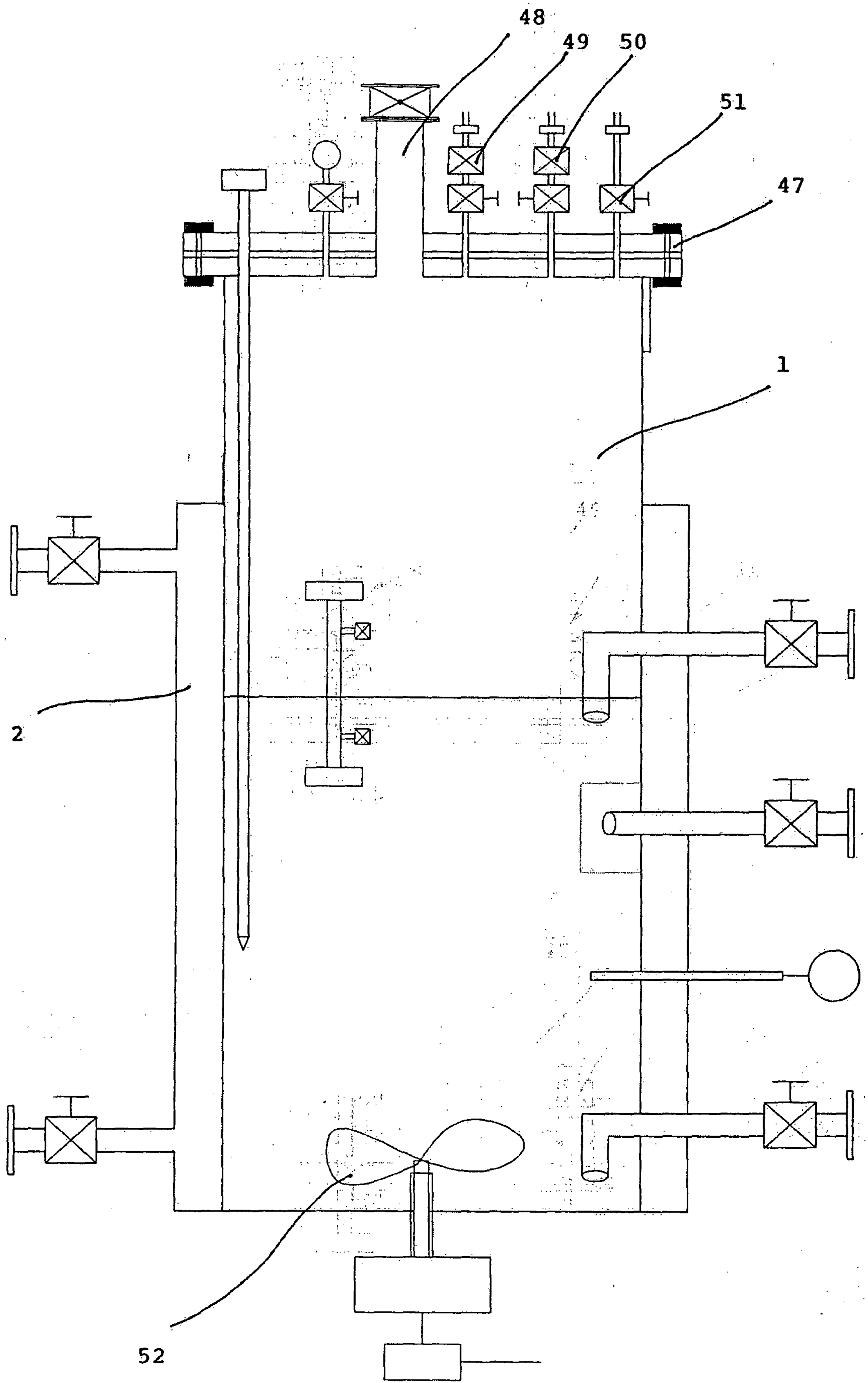

FIG.2