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MASS AND ENERGY BALANCE OF AMMONIA RECOVERY
PLANT

Degree Programme in Chemical Engineering

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ABSTRACT

Subject of this thesis was to evaluate process design for ammonia recovery pilot plant at Norilsk Nickel Harjavalta Oy. The idea of the ammonia recovery plant is to recover ammonia from solution and use it again in the process. The main task of this thesis was to calculate mass and energy balance for the ammonia recovery process. Process behavior and operational conditions were studied by making laboratory experiments.

Mass and energy balances were calculated from reaction equations and initial process data received from Norilsk Nickel Harjavalta Oy. Laboratory experiments were carried out in two parts: first reactions of process chemicals were studied, then the neutralization reaction was tested. Rotating reactor with grinding bodies was the main part of testing equipment. In all experiments process solution (ammonium sulphate solution) from Norilsk Nickel Harjavalta Oy and calcium oxide were used.

Mass and energy balance gave useful information for becoming ammonia recovery pilot plant testing. Quantity of products received from mass balance calculations, and for example the necessity of process cooling water, can be estimated from the results.

Information of process chemicals behavior was gained from laboratory experiments and test results were suggestive for example increment of pH and temperature, and gypsum formation. In the experiments with the rotating reactor, ammonium content of solution was measured during the test, which gave information for the extent of reaction.

AINE- JA ENERGIATASE AMMONIAKIN TALTEENOTTOPROSESSILLE

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TIIVISTELMÄ

Tämän opinnäytetyön tavoitteena oli laatia aine- ja energiataseet Norilsk Nickel Harjavalta Oy:lle suunnitteilla olevalle ammoniakin talteenottoprosessille. Ammoniakin talteenottoprosessin tarkoituksena on ottaa talteen prosessiliuoksessa oleva ammoniakki ja käyttää se uudelleen. Lisäksi työssä tehtiin laboratoriokokeita, joiden tarkoituksena oli tutkia prosessissa käytettävien kemikaalien käyttäytymistä sekä prosessin toimivuutta.

Aine- ja energiataseet laskettiin reaktioyhtälöiden ja Norilsk Nickel Harjavalta Oy:lta saatujen lähtötietojen perusteella. Laboratoriokokeet tehtiin kahdessa osassa. Ensimmäisissä kokeissa tutkittiin prosessissa käytettävien kemikaalien reaktioita eri olosuhteissa. Jälkimmäisissä kokeissa testattiin prosessia jäljittelevää laitteistoa, jonka pääosana käytettiin pyörivää reaktoria jauhinkappaleineen. Kaikissa kokeissa käytettiin Norilsk Nickel Harjavalta Oy:lta saatua prosessiliuosta (ammoniumsulfaattiliuos) sekä kalsiumoksidia.

Aine- ja energiataseet antoivat hyödyllistä tietoa tulevaa prosessin koeajoa varten. Ainetaseen perusteella saatiin prosessituotteiden suuruusluokat selville ja energiataseen avulla pystytään arvioimaan esimerkiksi prosessin jäähdytysveden tarvetta.

Laboratoriokokeilla saatiin käsitys siitä, miten prosessikemikaalit käyttäytyvät kyseisissä olosuhteissa ja kokeiden tulokset antoivat suuntaa muun muassa pH:n ja lämpötilan muutoksille prosessissa sekä kipsin muodostumiselle. Kokeissa, joissa käytettiin pyörivää reaktoria, mitattiin liuoksen ammoniakki-pitoisuutta ajan funktiona, joka antoi viitteitä reaktion etenemisnopeudesta.

TABLE OF CONTENTS

SYMBOL LIST

ρ = density, [kg/m^3]

c = specific heat capacity, [kJ/kg˚C]

$\dot{E}$ = energy flow, [kW]

h = specific enthalpy, [kJ/kg]

H = molar enthalpy, [kJ/mol]

$\dot{m}$ = mass flow, [kg/h]

M = molar mass, [g/mol]

$\dot{n}$ = amount of substance, [mol/h]

$\dot{Q}$ = amount of heat, [kW]

t = temperature, [˚C]

$\dot{V}$ = volume flow, [l/h]

1 INTRODUCTION

The purpose of this thesis was to calculate mass and energy balance for ammonia recovery pilot plant and make laboratory experiments to study the behavior of the process at given conditions. Intention was to get useful information before testing the pilot plant.

Laboratory experiments were made in two parts: preliminary tests with the process materials and actual experiments made with process simulating equipment. Mass and energy balance were calculated in parts and were found realistic.

Ammonia is one of the basic chemicals in chemical industry and it's widely used, also in Norilsk Nickel Harjavalta Oy. So the ammonium recovery process is cost-effective and useful purchase for the company.

2 GENERAL

2.1 MMC Norilsk Nickel

MMC Norilsk Nickel is a nickel and palladium mining and smelting operator in northern Russia. The company is the world's leading producer of nickel and palladium, and one of the largest global producers of platinum and copper. MMC Norilsk Nickel also produces a variety of by-products, such as cobalt, rhodium, silver, cold, iridium, ruthenium, selenium, tellurium and sulphur. /1/

2.1.1 Norilsk Nickel Harjavalta

Norilsk Nickel Harjavalta processes nickel concentrates from the Norilsk Nickel Group's operations and nickel semi-products from third parties. Norilsk Nickel Harjavalta refinery has the capacity to produce 60 thousand tones per year nickel products. Harjavalta plant produces saleable nickel, including nickel cathodes, briquettes and salts, as well as semiproducts including copper cake compounds and cobalt salutation which are further processed by third parties. /2/

3 AMMONIA

Ammonia, NH_3, a colorless alkaline gas, is lighter than air and possesses a unique, penetrating odor. Table 1 lists the important physical properties of ammonia. Ammonia is an excellent solvent for salts, and has an exceptional capacity to ionize electrolytes. The alkali metals and alkaline earth metals are readily soluble in ammonia. /3/

Table 1 Physical properties of anhydrous ammonia.

Property	Value
molecular weight	17.03
boiling point, °C	−33.35
freezing point, °C	−77.7
critical temp, °C	133.0
critical pressure, kPa^a	11,425
specific heat, J/(kg·K)^b	
0°C	2097.2
100°C	2226.2
200°C	2105.6
heat of formation of gas, ΔH_f, kJ/mol^b	
0 K	−39,222
298 K	−46,222
solubility in water, wt %	
0°C	42.8
20°C	33.1
40°C	23.4
60°C	14.1
specific gravity	
−40°C	0.690
0°C	0.639
40°C	0.580

Ammonia is comparatively stable at ordinary temperatures, but decomposes into hydrogen and nitrogen at elevated temperatures. Ammonia reacts readily with a large variety of substances. Oxidation at a high temperature is one of the more important reactions, giving nitrogen and water. /3/

3.1 Ammonium sulphate

Ammonium sulphate, $(NH_4)_2SO_4$, is a white, soluble, crystalline salt, having a formula weight of 132. The solubility of ammonium sulphate in 100g of water is 71g at 0˚C and 104g in 100˚C. $(NH_4)_2SO_4$ is moderately toxic by several routes. When heated to decomposition, it emits very toxic fumes. /4/

Ammonium sulphate is produced from the direct neutralization of sulfuric acid with ammonia. $(NH_4)_2SO_4$ is also recovered as a by-product in large amounts during the coking of coal, nickel refining, and organic monomer synthesis. Almost all $(NH_4)_2SO_4$ is used as a fertilizer; for this purpose it's valued both for its nitrogen content and for its readily available sulfur content. /4/

4 AMMONIA RECOVERY PROCESS

Ammonia recovery process separates ammonia out from the acidic ammonium sulphate solution. Process includes the following steps: combining ammonium sulphate solution and quicklime in a vibrating reactor to provide a reaction slurry, running the milling means whereby the milling action thereof acts to break up any gypsum precipitate as it forms in the reaction slurry or milling means so as to liberate ammonia and transferring the reaction slurry containing liberated ammonia from the vibrating reactor to a stripping column for ammonia recovery. /5/

4.1 Chemical Reactions

Ammonia is recovered from acidic solution of ammonium sulphate by adjusting the pH up to alkaline level with hydrated lime ($Ca(OH)_2$). Ammonium ions in solution react to ammonia (NH_3 (aq)), which is water soluble. The hydrated lime is typically produced by reacting quicklime with water. The reaction is represented by Equation 1. Reaction is exothermic. See below. /5/

$$CaO(s) + H_2O(l) \rightarrow Ca(OH)_2(aq) \tag{1}$$

The lime must be hydrated prior to addition to the stirred tank as gypsum is formed during the process. The gypsum thus formed coats the quicklime and consequently there is very poor utilization of quicklime in the process. Gypsum formation reaction is represented by Equation 2. /5/

$$Ca(OH)_2(aq) + H_2SO_4(aq) \rightarrow CaSO_4 \cdot 2H_2O(s) \tag{2}$$
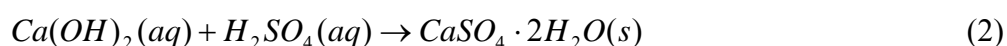
When ammonia sulphate reacts with the milk of lime, ammonia is liberated by the reaction of the ammonium ion with the hydroxide ions in the milk of lime. The reaction is presented by Equation 3. /5/

$$NH_4^+(aq) + OH^- \leftrightarrow NH_3(aq) + H_2O(l) \tag{3}$$

The ammonia is stripped off from the slurry by heating it to about 90˚C to 100˚C by the addition of steam. The stripping process is presented by Equation 4. /5/

$$NH_3(aq) \rightarrow NH_3(g) \tag{4}$$

The ammonia is able to be recovered in a relatively pure form as a solution of ammonia in water by cooling the off-gases from the process. The overall reaction formula for the liberation and stripping process is shown by Equation 5. /5/

$$2NH_4^+(aq) + SO_4^{2-}(aq) + Ca(OH)_2(aq) \rightarrow 2NH_3(g) + CaSO_4 \cdot 2H_2O(s) \tag{5}$$

4.2 Process Equipment

Process equipment is described in figure 1. Reaction occurs in vibrating reactor producing ammonia NH_3 (aq) and gypsum slurry. Milling action breaks up gypsum precipitate. The reaction slurry is transferred with a pump to a stripping column, where the ammonia is stripped off the slurry by the addition of steam. The off-gases are cooled down with heat exchangers and ammonia water is received as a product. Bottom product is transferred with a pump to further processing. /5/

Figure 1 Ammonia recovery process.

5 MASS BALANCE

Mass balance is evaluated in the process seen in figure 2.

Figure 2 Mass balance for ammonia recovery process.

5.1 Mass Balance over Reactor

$$\dot{m}_{AS,RIN} + \dot{m}_{CaO,RIN} = \dot{m}_{G,ROUT} + \dot{m}_{SOL,ROUT} \qquad (6)$$

where $\dot{m}_{AS,RIN}$ ammonium sulphate mass flow into the reactor

            $\dot{m}_{CaO,RIN}$ calcium oxide mass flow into the reactor

            $\dot{m}_{G,ROUT}$ gypsum mass flow out of the reactor

            $\dot{m}_{SOL,ROUT}$ solution mass flow out of the reactor

Mass flow of ammonium sulphate solution can be calculated with equation (7). Ammonium sulphate solution's volume flow in was 500 l/h and density was measured 1300 kg/m^3 so mass flow in is:

$$\dot{m}_{AS,RIN} = \rho_{AS}\dot{V}_{AS} \tag{7}$$

$$\dot{m}_{AS,RIN} = 650 kg/h$$

where ρ_{AS} ammonium sulphate solution's density, [kg/m^3]

$\dot{V}_{AS}$ ammonium sulphate solution's volum flow, [m^3/h]

Ammonium sulphate solution consists 500 g/l ammonium sulphate and 50 g/l natrium sulphate. Ammonium sulphate's amount of substance can be calculated with equation (8).

500 g/l $(NH_4)_2SO_4 \rightarrow$ 250 kg/h

50 g/l $Na_2SO_4 \rightarrow$ 25 kg/h

$$\dot{n}_{(NH_4)_2SO_4} = \frac{\dot{m}_{(NH_4)_2SO_4}}{M_{(NH_4)_2SO_4}} \tag{8}$$

$$\dot{n}_{(NH_4)_2SO_4} = 1894 mol$$

where $\dot{m}_{(NH_4)_2SO_4}$ ammonium sulphate solution's mass flow, [kg/h]

$M_{(NH_4)_2SO_4}$ ammonium sulphate solution's molar mass, [g/mol]

Amount of substance of ammonia is calculated by equation (9).

$$\dot{n}_{NH3} = 2 \cdot \dot{n}_{(NH_4)_2SO_4} \tag{9}$$

$$\dot{n}_{NH3} = 3788 mol/h$$

Amount of quicklime (CaO) required is 110% of theoretical need, see reaction formula (1) and (5). Mass flow of CaO is calculated with equations (12) and (13).

$$\dot{n}_{NH_4^+} = \dot{n}_{NH_3} \tag{10}$$

$$\dot{n}_{CaO} = \frac{1}{2}\dot{n}_{NH_4^+} \tag{11}$$

$$\dot{m}_{CaO} = \dot{n}_{CaO}M_{CaO} \tag{12}$$

$$\dot{m}_{CaO,RIN} = 1,1 \cdot \dot{m}_{CaO} \tag{13}$$

$$\dot{m}_{CaO,RIN} = 117 kg / h$$

Gypsum is formed according to the reaction formula (1) and (2). Mass flow of gypsum is calculated with equation (16).

$$\dot{n}_{CaO} = \frac{\dot{m}_{CaO}}{M_{CaO}} \tag{14}$$

$$\dot{n}_{CaSO_4 \cdot 2H_2O} = \dot{n}_{CaO} \tag{15}$$

$$\dot{m}_{G,ROUT} = \dot{n}_{CaSO_4 \cdot 2H_2O}M_{CaSO_4 \cdot 2H_2O} \tag{16}$$

$$\dot{m}_{G,ROUT} = 359 kg / h$$

Mass flow of solution, which consist of water, ammonia and Na_2SO_4, is:

$$\dot{m}_{SOL,ROUT} = \dot{m}_{TOT,RIN} - \dot{m}_{G,ROUT} \tag{17}$$

$$\dot{m}_{SOL,ROUT} = 408 kg / h$$

where $\dot{m}_{SOL,ROUT}$ corresponds the "solution feed" into the stripper ($\dot{m}_{SOL,SIN}$)

5.2 Mass Balance over Ammonia Stripper

$$\dot{m}_{G,SIN} + \dot{m}_{SOL,SIN} + \dot{m}_{S,SIN}$$
$$= \dot{m}_{NH_3,SOUT} + \dot{m}_{S,SOUT} + \dot{m}_{G,SOUT} + \dot{m}_{H_2O,SOUT} + \dot{m}_{Na_2SO_4,SOUT} \tag{18}$$

where $\dot{m}_{G,SIN}$ gypsum mass flow into the stripper

$\dot{m}_{SOL,SIN}$ solution mass flow into the stripper

$\dot{m}_{S,SIN}$ steam mass flow into the stripper

$\dot{m}_{NH_3,SOUT}$ ammonia mass flow out of the stripper

$\dot{m}_{G,SOUT}$ gypsum mass flow out of the stripper

$\dot{m}_{S,SOUT}$ steam mass flow out of the stripper

$\dot{m}_{H_2O,SOUT}$ water mass flow out of the stripper

$\dot{m}_{Na_2SO_4,SOUT}$ Na_2SO_4 mass flow out

The following values have been determined above:

$$\dot{m}_{G,SIN} = 359 kg/h$$

$$\dot{m}_{S,SIN} = 150 kg/h$$

$$\dot{m}_{SOL,SIN} = 408 kg/h$$

Ammonia mass flow out of the stripper can be calculated with equation (19).

$$\dot{n}_{NH_3} = 3788 mol/h \text{ (assumed 100\% conversion)}$$

$$\dot{m}_{NH_3} = \dot{n}_{NH_3} M_{NH_3} \qquad (19)$$

$$\dot{m}_{NH_3} = 64 kg/h$$

Steam input is 150 kg/h and it vaporizes the same amount of water.

$$\dot{m}_{S,SIN} = \dot{m}_{S,SOUT} \qquad (20)$$

Ammonia water to the product tank will be 214 kg/h, see equation (21).

$$\dot{m}_{NH_3} + \dot{m}_{S,OUT} = 214 kg/h \qquad (21)$$

Percentage of ammonia can be calculated with equation (22).

$$\frac{\dot{m}_{NH_3}}{\dot{m}_{NH_3} + \dot{m}_{S,OUT}} \cdot 100\% = 30 weight-\% \tag{22}$$

(solubility of ammonia is 32weight-% at 25°C)

Na_2SO_4 does not react in the process, therefore we can write:

$$\dot{m}_{Na_2SO_4,IN} = \dot{m}_{Na_2SO_4,OUT} = 25 kg/h \tag{23}$$

Water mass flow out of the stripper can be calculated with equation (24).

$$\dot{m}_{H_2O,SOUT} = \dot{m}_{SOL,SIN} - (\dot{m}_{NH_3,SOUT} + \dot{m}_{Na_2SO_4,SOUT}) \tag{24}$$

$$\dot{m}_{H_2O,SOUT} = 319 kg/h$$

5.3 Total Mass Balance

Definition of stationary state is:

$$\dot{m}_{TOT,IN} = \dot{m}_{TOT,OUT} \tag{25}$$

where $\dot{m}_{TOT,IN}$ total mass flow in

$\dot{m}_{TOT,OUT}$ total mass flow out

$$\dot{m}_{AS,IN} + \dot{m}_{CaO,IN} + \dot{m}_{S,IN}$$

$$= \dot{m}_{NH_3,OUT} + \dot{m}_{S,OUT} + \dot{m}_{G,OUT} + \dot{m}_{H_2O,OUT} + \dot{m}_{Na_2SO_4,OUT} \quad \therefore \tag{26}$$

6 ENERGY BALANCE

Energy balance is evaluated in the process seen in Figure 2. Calculations are based on the assumption that no dilution of ammonium sulphate is used.

Figure 3 Energy balance for ammonia recovery process.

Stationary State Conditions:

$$\dot{E}_{IN} = \dot{E}_{OUT} + \Delta\dot{Q} \qquad (27)$$

where

$\dot{E}_{IN}$ energy flow in, [kW]

$\dot{E}_{OUT}$ energy flow out, [kW]

$\Delta\dot{Q}$ heat of reaction plus physical phase changes, [kW]

and see reaction figure (11).

Reference level is 25˚C (energy level is zero at 25°C)

6.1 Energy Balance over Reactor

$$\dot{m}_{AS} h_{AS} + \dot{m}_{CaO} h_{CaO} = \dot{m}_{SOL} h_{SOL} + \Delta \dot{Q} \qquad (28)$$

Specific enthalpy (h) can be calculated from the following equation:

$$h = c \cdot \Delta t \qquad (29)$$

where $\qquad \Delta t = t - t_{ref} = t - 25°C$
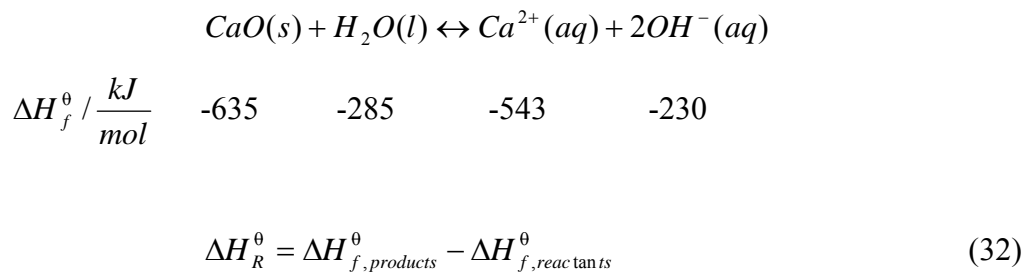
$$h_{AS} = c_{AS} \Delta t \qquad (30)$$

$$h_{AS} = 105 kJ / kg \qquad \text{(assumption } t_{AS,0} = 60°C\text{)}$$

$$h_{CaO} = 0 \text{ (assumption } t_{CaO,0} = 25°C \rightarrow \Delta t = 0\text{)}$$
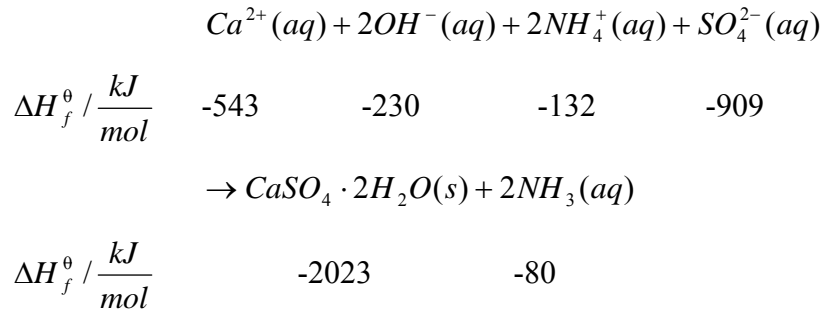
$$h_{SOL} = c_{SOL} \Delta t \qquad (31)$$

Molar enthalpy of hydrolysis of CaO is calculated with equation (32).

$$CaO(s) + H_2O(l) \leftrightarrow Ca^{2+}(aq) + 2OH^-(aq)$$

| $\Delta H_f^{\theta} / \dfrac{kJ}{mol}$ | -635 | -285 | -543 | -230 |

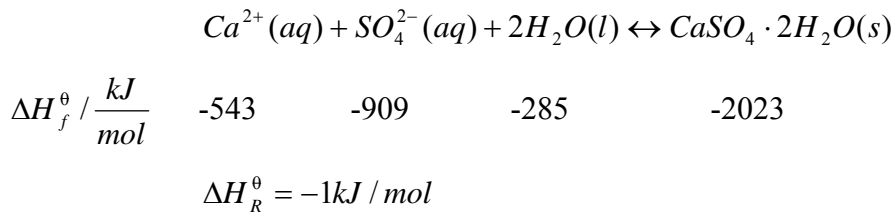$$\Delta H_R^{\theta} = \Delta H_{f,products}^{\theta} - \Delta H_{f,reac\tan ts}^{\theta} \qquad (32)$$

$$\Delta H_R^{\theta} = 2 \cdot (-230) + (-543) - (-285) - (-635) = -83 kJ / mol$$

Molar enthalpy of gypsum formation is also calculated with equation (32):

$$Ca^{2+}(aq) + 2OH^-(aq) + 2NH_4^+(aq) + SO_4^{2-}(aq)$$

$$\Delta H_f^\theta / \frac{kJ}{mol} \qquad -543 \qquad -230 \qquad -132 \qquad -909$$

$$\rightarrow CaSO_4 \cdot 2H_2O(s) + 2NH_3(aq)$$

$$\Delta H_f^\theta / \frac{kJ}{mol} \qquad\qquad -2023 \qquad\qquad -80$$

$$\Delta H_R^\theta = -7kJ / mol$$

$$Ca^{2+}(aq) + SO_4^{2-}(aq) + 2H_2O(l) \leftrightarrow CaSO_4 \cdot 2H_2O(s)$$

$$\Delta H_f^\theta / \frac{kJ}{mol} \qquad -543 \qquad -909 \qquad -285 \qquad -2023$$

$$\Delta H_R^\theta = -1kJ / mol$$

$$\Delta H_{R,TOT} = -91kJ / mol \quad (\text{1 mol CaO reacts} \rightarrow \text{91kJ heat liberates})$$

Total generated heart is calculated with equation (33):

$$\Delta \dot{Q}_R = \dot{n}_{CaO} \cdot \Delta H_{R,TOT} \tag{33}$$

$$\Delta \dot{Q}_R = -48kW$$

Amount of heat generated is 48 kW.

Temperature of output solution can be calculated from the following equations:

$$h_{SOL} = \frac{\dot{m}_{AS}h_{AS} + \dot{m}_{CaO}h_{CaO} - \Delta \dot{Q}_R}{\dot{m}_{SOL}} \tag{34}$$

$$h_{SOL} = 319kJ / kg$$

$$h_{SOL} = c_{SOL}\Delta t \tag{35}$$

$$\Delta t = \frac{h_{SOL}}{c_{SOL}} \tag{36}$$

Temperature rises $106\,^{\circ}C \rightarrow t_{SOL} \approx 130\,^{\circ}C$

The real temperature increase depends on the dilution factor of the basic ammonium sulphate solution. For example, if dilution 1:1 is used, the temperature difference will be about 50°C.

6.2 Energy Balance over Stripper

Suspension in contains energy 48 kW:

$$\Delta \dot{Q}_R = 48kW$$

Quantity of energy of steam into the stripper:

$$\Delta \dot{Q}_{S,IN} = \Delta H_f^{\theta} \cdot \dot{m}_S \tag{37}$$

$\Delta \dot{Q}_{S,IN} = 110kW \qquad$ It is assumed that pressure of the steam is 4 bar (abs).

Steam out is the same than steam in:

$$\Delta \dot{Q}_{S,OUT} = \Delta \dot{Q}_{S,IN} \tag{38}$$

Quantity of energy of ammonia out of the stripper can be calculated from the following equations:

$$\Delta H_f^{\theta} = c_p^{\theta} \Delta t \tag{39}$$

$$\Delta \dot{Q}_{NH_3} = \Delta H_f^{\theta} \cdot \dot{n}_{NH_3} \tag{40}$$

$$\Delta \dot{Q}_{NH_3} = 2{,}7kW$$

Bottom product out contains energy 44 kW:

$$h_{SOL} = c_{SOL} \Delta t \tag{41}$$

$$\Delta \dot{Q}_{SOL,OUT} = h_{SOL} \cdot \dot{m}_{SOL} \tag{42}$$

$$\Delta \dot{Q}_{SOL,OUT} = 44 kW$$

6.3 Cooling Requirement

Cooling requirement consists of following parts:

1. Condensation of steam:

$$\Delta \dot{Q}_{C,1} = \Delta H_{vap} \cdot \dot{m}_S \tag{43}$$

$$\Delta \dot{Q}_{C,1} = -94 kW$$

2. Cooling of water:

$$\Delta \dot{Q}_{C,2} = c \cdot \dot{m}_{H_2O} \cdot \Delta t \tag{44}$$

$$\Delta \dot{Q}_{C,2} = -13 kW$$

3. Cooling of ammonia gas:

$$\Delta \dot{Q}_{C,3} = c_p^\theta \cdot n_{NH_3} \cdot \Delta t \tag{45}$$

$$\Delta \dot{Q}_{C,3} = -3 kW$$

4. Heat of dissolution:

$$NH_3(g) \leftrightarrow NH_3(aq) \qquad \Delta H_f^\theta = -34 kJ/mol$$

$$\Delta \dot{Q}_{C,4} = \Delta H_f^{\theta} \cdot \dot{n}_{NH_3} \cdot \dot{m}_{NH_3} \qquad (46)$$

$$\Delta \dot{Q}_{C,4} = -36 kW$$

$$\Delta \dot{Q}_{C,TOT} = -146 kW$$

Total cooling requirement is ca. 150 kW.

7 LABORATORY EXPERIMENTS

Purpose of the laboratory tests was to study the behavior of the process at given conditions. Ammonium sulphate solution received from Norilsk Nickel Harjavalta Oy was used in laboratory tests. Both burnt lime (CaO) and calcium hydroxide (Ca(OH)$_2$) were used as pH adjusting agent.

7.1 Neutralization of Ammonium Sulphate Solution

Test series was made with ammonium sulphate solution and calcium oxide (CaO). CaO was mixed in decanting glass with ammonium sulphate solution until pH didn't increase any more.

CaO was added gradually and pH, temperature and ammonia formation were followed. Ammonia formation was followed with smell. At the end, suspension was filtered and cake was dried and weighed after filtering. Test was repeated.

Test results were documented in the field book (Appendix 1). Ammonium sulphate solution and CaO were at room temperature when started the tests. Liberalization of ammonia started immediately after CaO was added. So reaction between CaO and ammonium sulphate is fast. However, dissolution of CaO was incomplete at room temperature, which may occur lack of heating and not enough powerful mixing. Fil-

tered cake weighted half as much as increment CaO, that is due to formation of gypsum.

7.2 Heat of Neutralization

Purpose of the test was to examine how much ammonium sulphate solution temperature rises after CaO addition, in other words, how much heat is generated in reaction.

Test was made in thermos bottle. Ammonium sulphate solution was mixed with required amount of CaO and bottle was sealed. Suspension was shaken and temperature was followed with thermometer as long as temperature was stabilized. Test was repeated.

Test results were documented in the field book (Appendix 2). Temperature rose at best 50°C during the test, but delay time was very long. Highest temperature was attained within 40-60 minutes.

7.3 Neutralization of Ammonium Sulphate Solution at Elevated Temperature

Test series was repeated at elevated (100°C) temperature. However, in this case $Ca(OH)_2$ was used. Ammonium sulphate solution was heated up to 100°C in decanting glass and $Ca(OH)_2$ was mixed in by using magnetic stirrer. $Ca(OH)_2$ was added gradually and pH, temperature and ammonia formation were followed. Ammonia formation was followed with smell.

Test results were documented in the field book (Appendix 3). Liberalization of ammonia started immediately afterwards calcium hydroxide was added, so reaction was fast. Calcium hydroxide didn't dissolve very well in ammonium sulphate concentrate and formation of gypsum was clearly noticed, which may occur because of insufficient mixing. Level of pH didn't rise very high, which may be due to heating, which led very rapid ammonia emission out of the solution.

7.4 Dilution Series

The following ammonium sulphate solution dilution series were made: 1:3, 1:2, 1:1 and 2:1, where the first number resembles the ammonium sulphate solution and the second one water. The purpose was to find out how concentrated suspension can be used in the process. In the test series was measured viscosity and used also visual estimate, temperature was followed. Testing arrangement is represented in figure 4. Test equipment consisted on: steel decanter, heater, mixer, thermometer, pH meter and glass tube for aeration. Solution's density was measured, solution was heated up to 60˚C and required amount of calcium oxide was added in the solution. After that the viscosity was measured with rotation viscosimeter, see figure 5. At the end, solution was heated up at the same level where it rose after adding CaO and to the solution was piped air to liberalizate ammonia. Air was piped until ammonia smell was disappeared. Solution was filtered and filtrate was sent to Norilsk Nickel Harjavalta Oy for ammonia analysis.

Test results were documented in the field book (Appendix 4). Viscosity measurement was a little unreliable, because solution contained quite much solids. After first dilution, solution was decanted before measuring of the viscosity. Viscosity couldn't be measured for the most concentrated sample. All the dilutions seemed to be so viscous that they should not cause any transfer problems in the process. All samples contained quite much ammonia, which reveals that mixing was not powerful enough and part of the calcium oxide did not react because gypsum coats it.
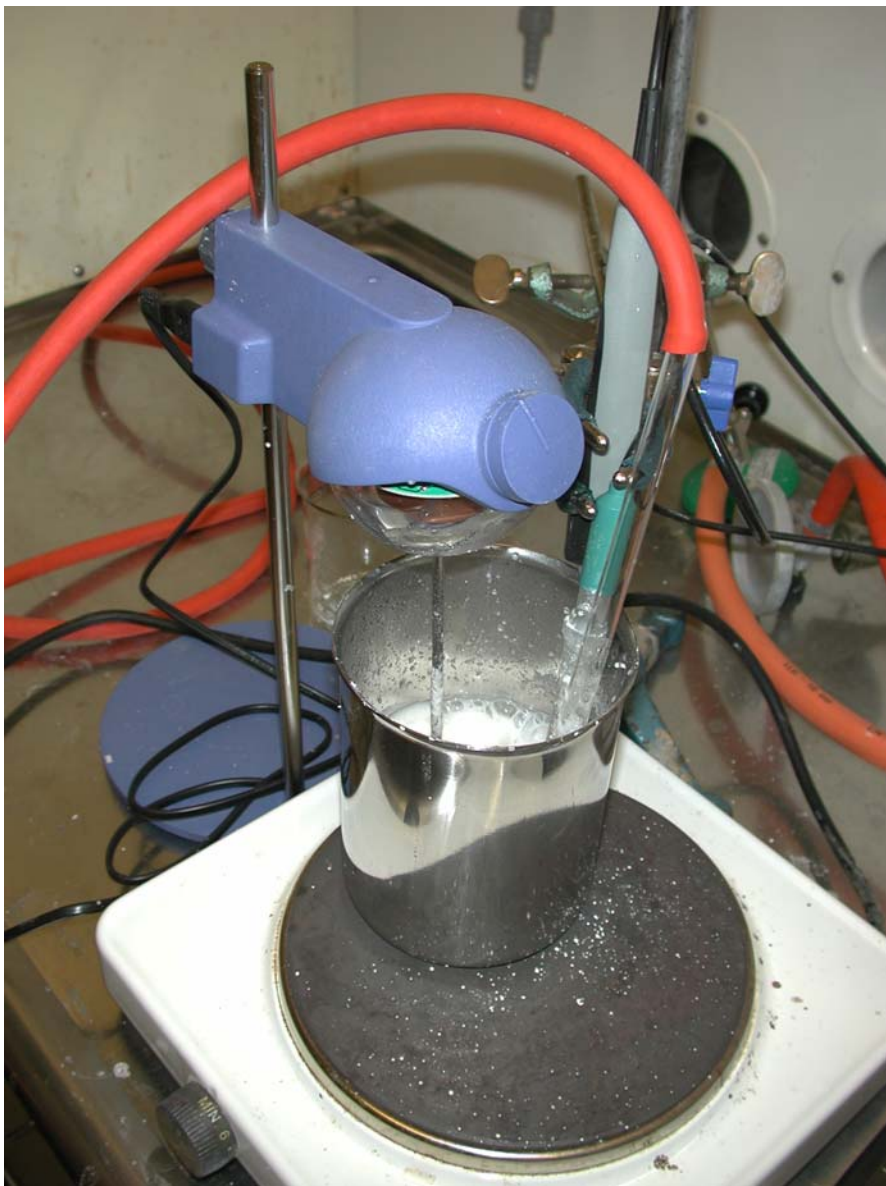
Figure 4 Neutralization of ammonium sulphate solution with CaO.

Figure 5 Viscosimeter.

7.5 Experiments with Rotating Reactor

Test series (12 experiments) were made with rotating rector, see figure 6. The reactor was rotated with a barreling engine and steel balls were used as grinding bodies. In the experiments was used ammonium sulphate solution, which ammonium content was 136 g/l. These experiments were made in Norilsk Nickel Harjavalta Oy research laboratory.

Figure 6 Reactor and grinding bodies.

7.5.1 Experiment 1

Steel balls and CaO were added in the reactor and the reactor started to rotate. Dilution 1:1 of water and ammonium sulphate solution were heated to 60°C and added in the reactor. Released ammonia gas was led with a vacuum pump to the gas washing bottle wherein was sulphuric acid (H_2SO_4). The reactor was rotated about half an hour and after that a sample of sludge was taken and pH was measured. Sample were filtered and of the filtration and dried cake were analyzed NH_4-percentage. H_2SO_4 were analyzed in order to find out how much acid was consumed. Experimental arrangement is presented by figure 7.

Test results were documented in the field book (Appendix 5). According the results, ammonia didn't release from the solution very well. Maybe ammonia gas stays in the reactor or testing conditions are not right.
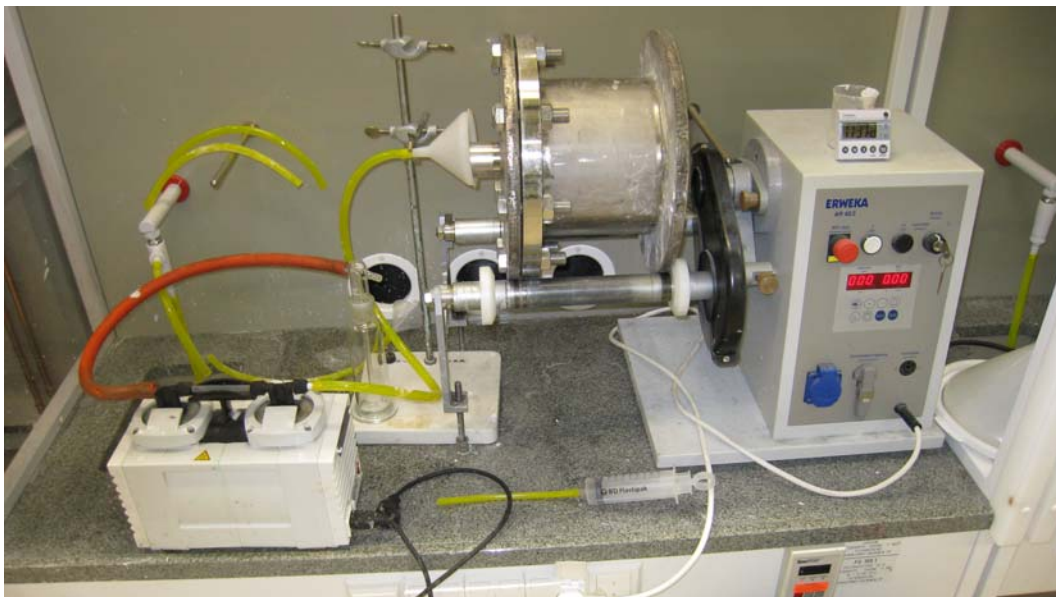
Figure 7 Testing arrangement of experiment 1.

7.5.2 Experiment 2

The previous test was repeated, but the difference was that ammonium gas were led to decanting glass where was 1 mol/l H_2SO_4. Purpose of the test was that pH of sulphuric acid can be followed during the test and this way liberalization of ammonia can be observed.

Test results were documented in field book (Appendix 5). H_2SO_4's pH didn't rise almost at all, which tells that ammonia don't release from the solution or acid was too strong to indicate pH chancing.

7.5.3 Experiments 3, 4 and 5

The following ammonium sulphate solution dilution series were made: 1:1, 1:2 and 1:3, where the first number resembles the water and the second one the ammonium sulphate solution. CaO addition was 110% of theoretical amount.

CaO was added with steel balls into the reactor and started to rotate. Solution was heated up to 60°C and added to the reactor, at the same time stopwatch was started.

Samples were taken from the reactor regularly. Concentration of ammonia and pH were analyzed. Testing arrangement is presented in figure 8.

Test results were documented in field book (Appendix 5). According to results ammonia do not be liberated from the solution very well or ammonia gas stays inside the reactor. That may ensue of insufficient ventilation in reactor. The solution doesn't stay warm in the reactor, which may also have an effect to extent of reaction.

Figure 8 Testing arrangement with rotating reactor.

7.5.4 Experiment 6

Testing conditions were same as a previous tests but air inlet was made to the reactor bottom. Suction was associated on the other end with a vacuum pump. Purpose was to get ammonia out of the reactor more effective. In the test was used dilution 1:1 of water and ammonium sulphate solution and CaO addition was 110% of theoretical amount.

Test results were documented in field book (Appendix 5). According the test results (pH, content of ammonia in solution), ammonia still stays in the reactor. Probably the suction is not powerful enough.

7.5.5 Experiment 7

Test was made the same way as experiment 2, but compressed air blast was added to get ammonia out of the reactor better. In the test was used dilution 1:1 of water and ammonium sulphate solution and CaO addition was 110% of theoretical amount.

Test results were documented in field book (Appendix 5). Acid's pH didn't change in this test either, but content of ammonia in solution got lower. That tells that ammonium gas stays in the reactor and with powerful ventilation it comes out.

7.5.6 Experiments 8, 9 and 10

Test series were repeated in same conditions as in experiments 3-5, but now with compressed air blast. Dilution 1:1 were used in experiments 8 and 10 and dilution 3:1 (water : ammonium sulphate solution) was used in experiment 9. In experiments 9 and 10 were used remarkable excess of CaO. At the last experiment CaO were added after solution. Testing arrangement is presented in figure 9.

Test results were documented in field book (Appendix 5). In these tests ammonia content of solution got remarkable down during the test, especially with excess of CaO. So the success of the reaction requires enough CaO and sufficient ventilation. Sequence of the addition of CaO and ammonium sulphate solution didn't seem to affect.

Figure 9 Rotating reactor with compressed air blast.

7.5.7 Experiments 11, 12 and 13

These tests were made in the higher temperature by heating the reactor with warm-air heater. Amount of steel balls in the reactor was bigger than in previous experiments. After the test sludge were heated again in decanter glass (only in the first test) to imitate stripping unit and get all the ammonia out of the solution. Dilutions 1:1 and 3:1 (water : ammonium sulphate solution) were used. Used CaO addition was, 110% in experiments 11 and 13 and 120% in experiment 12, of theoretical amount.

Test results were documented in field book (Appendix 5). These experiments gave the best results of getting the ammonia out of the solution. Significant factors in these tests were the temperature and the amount of grinding bodies. Higher temperature clearly helps extent of the reaction and powerful enough grinding helps too. Gypsum formation became remarkable less in these tests than in previous ones.

8 RESULTS

Mass balance was calculated with given process data and reaction equations. Calculations were checked and found correct. Energy balance was calculated by mass balance and those results were realiable, too.

At the first laboratory experiments were studied how the process chemicals behave in different conditions and found out that reaction with ammonium sulphate solution and CaO icreases temperature and pH of solution, and ammonia liberazation starts immediately. Gypsum formation was remarkable in these tests.

Experiments with the rotating reactor gave more exact information. Ammonia liberated almost completely from the solution in last experiments. The problem was that the delay time was quite long. In chart 1 is presented how ammonium content changed during the experiments.
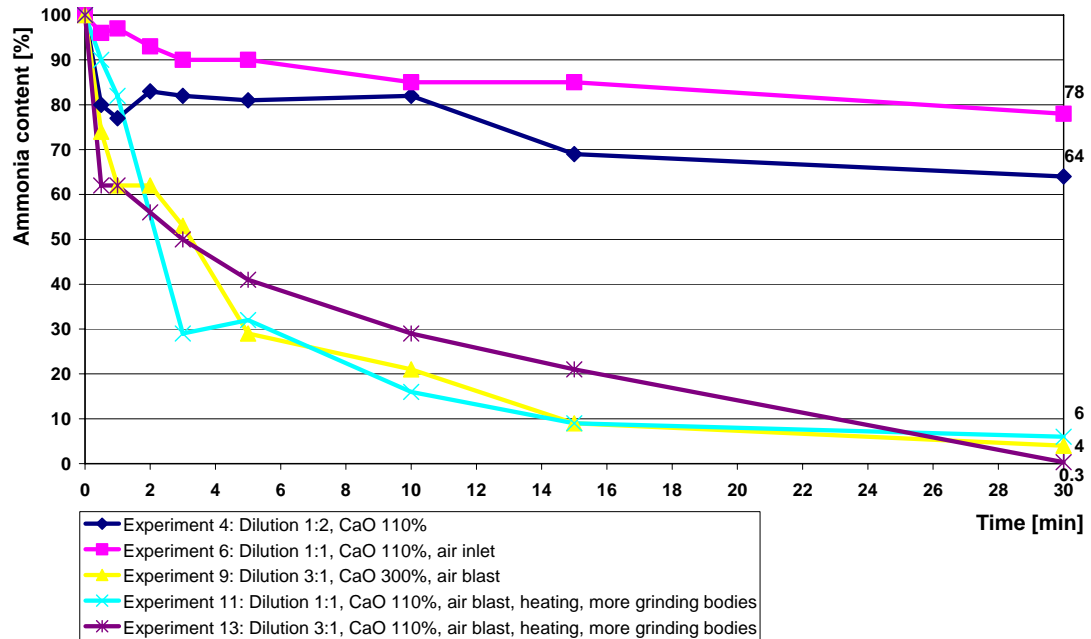
Chart 1 Ammonium percentage during the experiments with rotating reactor.

In chart 1 were selected experiments with different conditions in order to make results clearer. As in chart 1 can be seen, the best results were got in experiments where was used air blast, heating and also sufficient grinding gave better results.

9 CONCLUSIONS

Mass and energy balance gave useful information for running of the process in the future. Quantity of products and reactants is known and for example the necessity of process cooling water is easy to estimate by calculations.

Laboratory experiments gave useful information of the process, inter alia how process chemicals behave and got suggestive data of pH and temperature changes. Also gypsum formation was one of the questions and it was noticed that sufficient grinding removes the problem. Experiments with a rotating reactor were carried out at close to the real process conditions. The results of these tests were quite reliable. It came out that process works at the real conditions. The most important process fac-

tors were: sufficiently high temperature, grinding and ventilation to get ammonia out from the reactor.

Laboratory experiments with the rotating reactor are recommended to be continued by these basics. Connecting the stripping unit to the testing equipment could be useful and it might give more accurate information of the process behavior.

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APPENDIXES

Test results of neutralization of ammonium sulphate solution

CaO addition: 27% of ammonium
sulphate solution's mass

CaO addition g	pH	Temperature ˚C
0	3	19
1	7.2	23
2	8.1	25
3	8.4	25
4	8.4	26
5	8.6	27
7	8.7	28
10	8.9	29
12	9	28
15	9.1	28
20	9.2	28
30	9.5	29
45	9.6	33
60	9.6	34
70	9.7	37

CaO addition: 31% of ammonium
sulphate solution's mass

CaO addition g	pH	Temperature ˚C
2	8.2	24
4	8.6	25
7	8.9	25
10	9	26
15	9.2	26
20	9.3	27
25	9.5	26
30	9.6	28
40	9.6	28
50	9.7	28
60	9.8	30

Test results of heat of neutralization

CaO addition: 29% of ammonium
sulphate solution's mass

Time min	Temperature ˚C	pH
0	24	2.9
10	46	
20	71	
30	76	
40	75	
50	74	
60	73	
70	72	
90	68	9.4

CaO addition: 24% of ammonium
sulphate solution's mass

Time min	Temperature ˚C	pH
0	23	2.3
10	43	
20	47	
30	53	
40	59	
50	62	
60	70	
70	66	
90	63	9.7

Test results of neutralization of ammonium sulphate solution at elevated temperature

Ca(OH)$_2$ addition: 17% of ammonium sulphate solution's mass

Ca(OH)2 g	pH	Temperature °C
0	2.9	22
1	6	94
2	6.4	97
3	6.5	96
5	6.7	96
7	6.8	96
10	7	92
15	7.1	89
20	7.2	86
25	7.4	84
30	7.5	85
35	7.5	85
40	7.5	85
45	7.5	81
55	7.7	79
60	7.8	80
65	8	72

Ca(OH)$_2$ addition: 18% of ammonium sulphate solution's mass

Ca(OH)2 g	pH	Temperature °C
0	3.5	85
1	6	95
3	6.6	98
5	6.8	95
10	7.2	94
15	7.4	91
20	7.5	89
25	7.7	87
30	7.8	85
40	8	81
50	8.2	79
60	8.4	76
70	8.4	76

Test results of dilution series

1 part ammonium sulphate solution + 3 parts water
ρ=1,065 g/cm³
CaO addition 110% of theoretical amount

pH	Δt ˚C	η mPas	Content of NH3 g/l
8.1	10.3	56	19

1 part ammonium sulphate solution + 2 parts water
ρ=1,098 g/cm³
CaO addition 110% of theoretical amount

pH	Δt ˚C	η mPas	Content of NH3 g/l
8.2	11	60	29

1 part ammonium sulphate solution + 1 part water
ρ=1,146 g/cm³
CaO addition 110% of theoretical amount

pH	Δt ˚C	η mPas	Content of NH3 g/l
8.2	12	66	25

2 parts ammonium sulphate solution + 1 part water
ρ=1,192 g/cm³
CaO addition 110% of theoretical amount

pH	Δt ˚C	η mPas	Content of NH3 g/l
8.2	20	?	11

Test results of experiments with rotating reactor

Test 1
Dilution 1:1, CaO addition 110%

Compo-nent	pH	NH4-content	H2SO4
Sludge	10.3		
Filtrate		68 g/l	
Cake		0.48 %	
H2SO4			1930 g/l

Test 2
Dilution 1:1, CaO addition 110%

Compo-nent	pH	NH4-content	H2SO4
Sludge	10.2		
Filtrate		61 g/l	
Cake		0.20 %	
H2SO4			143 g/l

Time min	pH (H2SO4)
2	0.16
3	0.17
4	0.16
5	0.17
10	0.18
15	0.18
20	0.19

Test 3
Dilution 1:1, CaO addition 110%

Time min	pH	NH4-content g/l
0.5	10	65
1	10.2	65.4
2	10.5	61.4
3	10.4	64.8
5	10.6	62.7
10	10.6	63.2
15	10.6	60.3

Test 4
Dilution 1:2, CaO addition 110%

Time min	pH	NH4-content g/l
0.5	10.6	72.1
1	10.7	68.5
2	10.6	74.6
3	10.7	73.8
5	10.7	73
10	10.8	73.6
15	10.9	61.8
30	11	57.9

Test 5
Dilution 1:3, CaO addition 110%

Time min	pH	NH4-content g/l
0.5	10.1	92.9
1	10.2	99.7
2		99.1
3		95.9
5	10.2	85.7
10	10.5	91.1
30		64.9

Test 6
Dilution 1:1, CaO addition 110%

Time min	pH	NH4-content g/l
0.5	10.1	92.9
1	10.2	99.7
2		99.1
3		95.9
5	10.2	85.7
10	10.5	91.1
15		81.5
30		64.9

Test results of experiments with rotating reactor

Test 7
Dilution 1:1, CaO addition 110%

Time	pH
2	0.14
3	0.13
4	0.12
5	0.12
10	0.13
15	0.13
20	0.13

Test 8
Dilution 1:1, CaO addition 110%

Time	pH	NH4-content
0.5	9.4	64.4
1		63.3
2	10.3	60
3		55.2
5		49.6
10		39.4
15	10	27.3

Test 9
Dilution 3:1 CaO addition 300%

Time min	pH	NH4-content g/l
0.5		25.1
1		21.3
2		21.3
3	13	17.7
5		10
10		7
15	13.1	3.2
30	13.1	1.4

Test 10
Dilution 1:1 CaO addition 150%

Time min	pH	NH4-content g/l
0.5	9.7	51.4
1		51.7
2	10.7	45.8
3	10.7	42.8
5		28.9
10	12.1	20
15	13.1	12.6
30	13.1	7.3

Test 11
Dilution 1:1 CaO addition 110%

Time min	pH	NH4-content g/l
0.5	10.3	61
1	10.3	56
3	11.2	20
5		22
10		11
15	13	6
30		4
Reheating		
5		1.4
10		0.6

Test 12
Dilution 1:1 CaO addition 120%

Time min	pH	NH4-content g/l
0.5	10.2	62.5
1	10.3	57.4
2	10.3	49.8
30	13.2	1

Test 13
Dilution 3:1 CaO addition 110%

Time min	pH	NH4-content g/l
0.5	10.1	21.1
1		21.8
2	10.1	18.8
3		16.8
5		14.2
10		9.7
15		6.8
30	13	0.1