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Innovative processes in the production of inorganic bases and derived salts of current interest

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Abstract:

Ammonia and sodium hydroxide are two important inorganic bases which served as the basis or precursors of other compounds with multiple uses. Some of their derived salts, i. e. ammonium nitrate, are of the paramount importance for daily life. Others salts, such as lithium carbonate, are gaining a primary role in the development of smart technologies, i. e. E-cars. This chapter described developments in the production of these useful compounds: ammonia, sodium and potassium hydroxides, related salts, i. e. ammonium nitrate, sodium and potassium carbonates, and finally, lithium carbonate.

Keywords: ammonia, chloralkali, lithium, potash, processing, salts

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1 Introduction

The production of inorganic bases (mainly ammonia and caustic soda) is nowadays an important industrial business. There are a miriade of practical uses of these bases and their derivatives.

However, the basis for the production of these two bases is more or less the same those years ago. Ammonia was first produced around 1909 by the Haber–Bosch process; in this process N_2 and H_2 reacts, under given conditions and in the presence of an iron-catalysts, forming NH_3 . Nowadays the process used more refined conditions but the same principle.

In the case of caustic soda (and potash), this chemical is really a sub-product in the production of chlorine gas, that was at the beginning and it is now; however, the technology had also been improved from the first processes and the use of mercury cells to the now more efficient membrane cells, and in a very lesser extent, diaphragm cells.

Salts derived from the above bases are normally produced by reacting the corresponding base with the corresponding chemical under known processes, and it is only in the last years that lithium carbonate enters the industrial scene due to the importance that e-cars have today, and being this salt an important component of the lithium-ion batteries associated with this new type of mobility.

This chapter reviews some of the most definitive advances in the production of these bases and their derived salts, including the production of lithium carbonate.

2 Ammonia [1–10]

Ammonia has many uses and in different industries, as summarized in Table 1.

Table 1: Uses of ammonia.

Uses	Examples
Fertilizer	Ammonium nitrate, urea, ammonium salts
Chemical synthesis	Nitric acid, sodium bicarbonate, hydrazine
Explosives	Ammonium nitrate

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Fibers and plastics	Nylon and other polyamides
Refrigeration	
Pharmaceuticals	Manufacturer of drugs (sulfonamide), anti-malarials, B vitamin
Pulp and paper	
Mining and metallurgy	Zinc, cobalt and nickel processing
Cleaning	

Approximately 85% goes to fertilizers for the food industry.

The largest producing countries of ammonia are China, India, Russia, USA, Trinidad-Tobago and Indonesia, whereas the global demand for regions is Asia-Pacific, Europe, North America, rest of world and Latin America.

As it is said in the Introduction, NH_3 is produced by the Haber or Haber–Bosch process. In this process, N_2 and H_2 react in presence of a catalyst (mainly based on Fe) forming NH_3 . H_2 is produced by reaction of natural gas and vapor at high temperatures, whereas N_2 addition is by the air. NH_3 production at the cheapest cost is of the foremost importance for the industry. Hydrocarbons are the usual compounds to provide energy and H_2 , though there are alternatives such as charcoal or electric power. Light hydrocarbons reforming is the most efficient route, summarizing more than 75% of world ammonia capacity based on gas as natural source. Thus, in actual vapor reforming plants, 40–50% of the overall energy consumption, related to NH_3 production, is in excess of the thermodynamic minimum. Losses due to compression are the responsible for more than half of this excess, whereas the useful minimum consumption is near 130% of the theoretical minimum.

Sizes of big single-train NH_3 plants are 1000–1500 t/day, though larger capacities are provided in new plants, i. e. 3000 t/day. Process efficiency in energy is reached by integrating it with the providing energy source. The ammonia plant can be alone or be integrated, as it can be seen latter, with other plants on the site, i. e.: urea or methanol plants.

Nowadays, large NH_3 plants have a great reliability with their equipment and related tools, whereas technical on-stream factors greater than 90% are the norm. Actually in Europe, ammonia is mainly produced by two types of processes:

- vapor reforming of natural gas or other light hydrocarbons,
- partial oxidation of heavy fuel oil.

Coal gasification and water electrolysis are not in use in the European NH_3 manufacture. Syn-ammonia synthesis process is non-dependent of the type of syn-gas gas manufacturing process: however, syn-gas quality has a marked influence on the circuit design and operating work.

2.1 Conventional steam reforming

The corresponding flow-sheet of the conventional vapor reforming operation is shown in Figure 1. More than 80% of world NH_3 production relies on vapor reforming.

Figure 1: Flowsheet for ammonia production using natural gas as feed.

2.1.1 Conversion

Using CH_4 as feed, the reaction is

Syn-gas production and purification work under 25–35 bar pressure, whereas the NH_3 synthesis used pressures between 100 and 250 bar.

2.1.2 Sulfur removal

The catalysts used in the process are sensitive to S and related compounds. Feed products usually contain up to $5 \text{ mg S}_x\text{N}/\text{m}^3$ as S-bearing compounds. Inlet gas is preheated until 350–400 °C, often in the primary reformer convection section, prior to its treatment in a de-sulfurization device. In this step, the sulfur compounds are hydrogenated to form H_2S , very often by means of a Co-Mo catalyst, and then adsorbed on pelletized ZnO:

resulting in a gas, containing a concentration not exceeding 0.1 mg/L sulfur, which feeds the system, whereas ZnS remained in the adsorption bed. The necessary H_2 , eq. (3), is recycled from the syn-site.

2.1.3 Prim-reforming site

A mixture of the sulfur-cleaned gas and process vapor, generated in a turbine, is heated until 500–600 °C in the convection site and prior to enter to the prim-reformer. In recent or revamped plants, the above mixture and before entering the prim-reformer, goes to an adiabatic pre-reformer and reheated operation is included in the convection section. In a number of plants, part of the process vapor comes by feed-gas saturation. The amount of process vapor is calculated by the S/C ratio (process vapor to carbon molar relationship), which needed to be lower than 3.0. Several parameters influenced this relationship, i. e. feed quality, purge gas recovery, prim-reformer capacity, shift operation, and the overall vapor balance.

The primary reformer is of a large number of high-Ni-Cr alloy tubes filled with Ni-catalyst. Being an endothermic reaction, addition of heat is needed to elevate the temperature to 780–830 °C at the reformer outlet. The gas exiting the primary reformer has a composition as follows:

with $\Delta H^\circ = 206 \text{ kJ/mol}$, and

this reaction being exothermic, with ΔH° of -41 kJ/mol . Natural gas and other fuels supplied the heat for the primary reforming process. The burned gas, after supplying the high level heat of the reforming process, exiting the radiant box with temperatures exceeding 900 °C. Approximately, a half of the heat value of the fuel is directly used into process. The waste heat of the flue-gas feeds the reformer convection unit. The energy requirement providing by fuel, in the ordinary reforming process, is 40–50% of the process feed-gas energy. Principal sites for emissions produced in the plant are generated by the flue-gas exiting the convection section at 100–200 °C. These consisted of CO_2 , NO_x , and minor quantities of SO_2 and CO.

2.1.4 Sec-reforming

Due to the nature of the operational conditions and the related Chemistry, a mere 30–40% of the hydrocarbons feeding the operation is treated in the primary reformer. The above implies that temperature must be increased

to increase conversion. This operation is performed in the sec-reformer by internal combustion of part of the gas with the process air, at the same time N_2 is provided for the syn-gas production. Often, the grade of primary reforming is adjusted in the form that the air supplied to the sec-reformer meets both the heat balance and the stoichiometric synthesis gas need. The process air is compressed to the reforming pressure and heated further in the primary reformer convection section to near 600°C . The process gas is mixed with air and passed through a Ni-bearing catalyst. At the exit, temperature is almost of 1000°C , and near 99% of the hydrocarbon feed (exiting the primary reformer) is converted, with a residual CH_4 content of 0.2–0.3% (based on dry gas) in the gas exiting the sec-reformer. The exiting gas is then conveniently cooled at $350\text{--}400^\circ\text{C}$.

2.1.5 Shift conversion

The gas produced in the secondary reformer contained 12–15% CO (based on dry gas), with the CO converted in the shift section (eq. (6)). In the High Temperature Shift (HTS) conversion, the gas goes to a bed of iron-chromium oxides catalyst at around 400°C , here, the CO content decreased to near 3% (based on dry gas), limited by the shift equilibrium of the operational temperature. Conversion can be improved by the use of Cu-bearing catalyst. Exiting gas, from the HTS, is cooled and goes across the Low Temperature Shift (LTS) converter. This converter contained a Cu-Zn oxides-based catalyst and works at near $200\text{--}220^\circ\text{C}$. The CO content in the con-gas is in the 0.2–0.4% range (based on dry gas). The process efficiency increases as the residual CO content decreases.

2.1.6 Removing CO_2

The gas exiting the low temperature shift converter contains hydrogen, nitrogen and CO_2 together with vapor. This gas is cooled, and most of the excess vapor is condensed prior it enters the CO_2 removal system. This gas often contains 1500–2000 mg/L ammonia and 800–1200 mg/L of methanol. Amines, formic acid and acetic acid may be found in the condensate. All these compounds needed to be stripped, from the condensate, and/or recycled. The heat produced during cooling/condensation has various uses, i. e. the regeneration of the CO_2 scrubbing solution, with CO_2 removal by a chemical or a physical absorption process. The chemicals used in chemical absorption are, principally, aqueous amine solutions such as, mono ethanolamine (MEA), thought is not labeled as the best available technology, activated methyl diethanolamine (aMDEA) or hot potassium carbonate solutions. Physical solvents are glycol dimethylethers (Selexol), propylene carbonate and others. In new ammonia plants the following CO_2 removal processes can be considered as usefulness technologies:

- i. aMDEA standard 2-steps operation,
- ii. Benfield process (HiPure, LoHeat),
- iii. Selexol or related physical absorption processes.

Variations of the above concepts must be also considered, whereas Swing Adsorption (PSA) conception is the best available technology in a series of new plants; consideration of this option also assumed that the PSA unit is not the single function of the CO_2 removal. Overall range of heat consumption, in new chemical absorption process, is $30\text{--}60\text{ MJ k/mol } CO_2$. The physical absorption operations are designed for zero heat consumption, but if compared with the chemical processes, the mechanical energy requirements need to be considered.

2.1.7 Methanation

The amounts of CO and CO_2 , which are found in the syn-gas, are toxics to the syn-ammonia catalyst and need to be eliminated, as methane, in the methanator:

The synthesis showed in eqs. (7) and (8) occurred at near 300°C in reactors containing a Ni-based catalyst. The reactions product is an inert gas, however, H_2O needed to be removed prior to enter to the converter. The operation is performed in two sequential steps, (i) cooling and condensation downstream of the methanator, and (ii) condensation and absorption in the produced NH_3 a convenient drying unit.

2.1.8 Syn-gas compression and NH_3 synthesis

Recent NH_3 operations use centrifugal compressors to perform the syn-gas compression, this is carried out by vapor steam turbines, using the vapor produced in the NH_3 plant. The condensation of NH_3 is performed in a compressor which used a vapor turbine. NH_3 is synthesized on Fe-catalysts using pressures in the range 100–250 bar range, and temperatures of 350–550 °C, in a reaction given by eq. (2) with $\Delta H^\circ (298 \text{ K}) = -92.4 \text{ kJ/mol}$. At each single operation about 20–30% reacts, being this attributable to the non-favorable equilibrium conditions. The separation of the as-formed NH_3 from the gas is done by cooling/condensation, loop pressure is maintained by substitution of the gas with fresh gas. Much heat exchange is needed due to the exothermic reaction, together with the large temperature range found in the loop. The apparition of recent Ru-catalyst is promising since they have a greater activity per unit of volume, with the possibility of increase conversion and lower operating pressures. As recently as 2018, it was published about the properties of a new ruthenium catalyst which is formed by calcium amide with a small amount of added barium, $\text{Ba-Ca}(\text{NH}_2)_2$, together with Ru nanoparticles immobilized onto it. Results presented in Table 2 indicated that with the use of this new catalyst, and working at temperatures below 300 °C, the efficiency of ammonia synthesis is about 100 times greater that of the obtained with conventional Ru catalysts.

Table 2: Comparison of ammonia synthesis activity using three types of catalysts.

Catalysts	Ammonia synthesis rate, mmol/g h
Conventional Ru (Cs-Ru/MgO)	0.072
Industrial Fe	2.2
Ru-Ba-Ca(NH_2) ₂	7.5

Temperature: 260 °C. Pressure: 9 atm.

Also, it can be observed that its performance is more than three times greater than the corresponding of industrial Fe catalyst.

Reforming with methanation, as the final purification step, produces a syn-gas, which contained CH_4 and Ar and in un-dissolved amounts in the condensed NH_3 . An important amount of these inert compounds is eliminated by a purge stream from the loop, resulting in the lowering of inert to 10–15%. Water is used to eliminate NH_3 from the gas prior to its use as fuel or prior to be used as H_2 . Condensation operation on NH_3 is not achieved completely if the operation utilized water or air, and it is dependent on loop pressure and the temperature of the cooling agent. NH_3 in gaseous form is the coolant agent in an important number of NH_3 producing plants. NH_3 vapor is liquated in a coolant compressor.

2.1.9 Vapor and power system

Vapor reforming NH_3 plants produced a great level of excess heat, being used for vapor production in the reforming, shift conversion, and syn-sections, also in the convection section of the prim-reformer. Most of this excess heat is utilized for high pressure vapor production, being useable in turbines to drive compressors and pumps, and as process vapor exiting the turbine system. Recent vapor reforming NH_3 plants may work as self-sufficient from an energy point of view, but often, a small vapor export and electricity import are the norm.

Some processes reduced prim-reforming using part of the second-reformer facilities, being this attributable to the *marginal* low efficiency of the prim-reformer.

Features diverging from the ordinary concept are summarized as follows:

- Decreased firing in the prim-reformer.
- Increased process air flow to the second-reform operation.
- Methanation followed of cryogenic purification.
- Decreasing the level of inerts of the make-up syn-gas.

2.2 Partial oxidation of heavy oils

If heavy compounds than nafta are feeding, partial oxidation with oxygen is carried out in the syn-gas manufacture. A scheme of a partial oxidation process is shown in Figure 2.

Figure 2: Flowsheet for ammonia manufacture using heavy oils as feed.

2.2.1 The process

The partial oxidation operation is used to gasify heavy feeds, i. e. residual oils and coal. High viscosity hydrocarbons and plastic wastes are used as fractions of such feed. The partial oxidation process can be considered as an alternative for future uses of these wastes. O_2 is provided by a partial oxidation step carried out in an in the regulation of temperature. The reaction is as follows:

By-products are CO_2 , CH_4 and soot. Chemicals containing S are converted to H_2S , whereas mineral compounds, present also in the feed, evolved into ashes. Waste heat recovery is followed by the elimination of solids from the process gas, being the soot is recycled-back to the feed. Ashes are eliminated with the condensate, and/or together with a part of the soot. In some European plants, the soot is separated from soot water in a filtration step, which avoided ash build-up in the air separation unit, whereas N_2 addition is carrying out in the liquid N_2 nitrogen wash, with the objectives of the removal of impurities present in the syn-gas, and to obtain the correct H_2/N_2 relationship in it. This oxidation is a not-catalytic driven and occurs at pressures exceeding 50 bar, and temperatures in the 1400 °C range. Some vapor is needed downstream gasification cycle. Heavy metals, such as V, Ni and Fe are recovered. H_2S presented in the gas is separated, in a selective absorption step, and reprocessed, in a Claus unit, to zero valent sulfur. The shift conversion used two high temperature shift catalyst beds with intermediate cooling. Vapor used in the shift conversion is supplied by a cooler-saturator, and by vapor injection. CO_2 is eliminated by the use of an absorption compound which resembled that used in the S elimination stage. Traces of the absorption compound and CO_2 are eliminated from the process gas, prior to the last purification operation, using liquid N_2 washing. In this step, most of the impurities are removed and N_2 is added to reach the H_2 to N_2 stoichiometric ratios. NH_3 synthesis resembled the operation in vapor reforming plants, however, in the case of NH_3 , the operation is easier to perform and more efficient, due to the high purity of the syn-gas coming from the liquid N_2 wash units and the syn-loop without purges.

2.2.2 Vapor and power system

A vapor-feeding compressor needed auxiliary boilers. The flue-gas generated in these power plants is the principal source of emissions containing SO_2 , NO_x and CO_2 . Special compressors, i. e. electric driven, decreased the site emissions.

2.3 Modern conventional flow-sheets

In general terms, the principal process stages are the same for every plants, being the major differences between them related to the design of various equipment and refinements of the various process steps. Hydrogen recovery is used in most modern plants.

2.3.1 Haldor Topsoe ammonia production

The features of the technology offered included:

- i. side fired reformer,
- ii. radial flow converters,
- iii. S-series of converters.

Some of the offered processes are:

– IMAP Ammonia+™

This process (Figure 3) employs an “in-line” ammonia-methanol concept. The production of methanol is a once-through process carried out at high pressure to reach maximum conversion and efficiency. This process can be complemented by a flexible skid-mounted UFC85 urea formaldehyde unit to create a fully integrated solution at fertilizer complexes. With this process design, ammonia is the main product and methanol is the by-product (up to 35%).

Figure 3: Haldor Topsoe IMAP Ammonia+™ process.

The design can be used for grassroots plants and revamps of existing plants, especially where there is local demand for small amounts of methanol, or when methanol prices are comparatively favorable, if no methanol is needed, this part of the process can be bypassed. According with the company, the process benefits are: shared reforming section, in-line design and once-through process, high conversion and efficiency, very flexible solution.

– SynCOR Ammonia™

This is a new process for grassroots plants (Figure 4), offering, among other benefits, greater economies of scale. The process appeared to be a technological must in NH₃ manufacture.

Figure 4: Haldor Topsoe SynCOR Ammonia™ process.

As we aware, every NH_3 plants rely on ordinary two-step reforming, which are based on tubular vapor methane reforming and an air-burned secondary reformer, whereas SynCOR Ammonia™ used the unique Topsoe SynCOR™ solution. This is an idea based on oxygen-burned autothermal reforming, which eliminates the use of the two reformers. This differentiated well the process against conventional ammonia plants (Table 3).

Table 3: Variations between conventional ammonia plants and SynCOR Ammonia™.

Step	Conventional plant	SynCOR Ammonia™
Desulfuration	standard	standard
S/C ratio	3.0	0.6
Reforming	tubular steam reformer and air blown secondary reformer	Pre-reformer and oxygen blown SynCOR™
Shift	high temperature and low temperature shifts	two high temperature shifts in series
CO_2 removal	standard	standard
Syn-gas cleaning	methanation	N_2 wash with purge and N_2 addition
Syn-ammonia	syn-ammonia circuit with purge	inert free synthesis circuit with no purge
Purge gas treatment	NH_3 wash followed by H_2 recovery	no treatment required

In addition, the conventional plant relative energy consumption of 100 is reduced to 97, and the relative make-up water of 100 is reduced to 40–50.

– Haldor Topsoe low energy ammonia process

This process, having practically the same scheme of Figure 1, uses steam and air reforming and is applicable for both small and large scale capacities up to 3500 t/day of ammonia.

– Green ammonia: the Haldor Topsoe concept of solid oxide electrolyzer cell

The next generation of ammonia plants developed by Haldor Topsoe uses a solid oxide electrolysis cell (SOEC) to fabricated syn-gas, which I used to feed the proprietary company existing technology of ammonia synthesis sites. Thus, NH_3 was fabricated using air, water and renewable electricity. A small industrial scale green- NH_3 plant is expected to build by 2025, and commercially available by 2030. The new project was awarded funds from the Danish Energy Agency, allowing Haldor Topsoe to demonstrate the system with its academic partners (University of Aarhus, Denmark).

This new concept is an advanced integration of electrolyzer and Haber–Bosch unit, reducing the capital operational expenditure and the operational expenses in relation to other electrolyzer technologies but similar to conventional NH_3 plants using natural gas. In its operation, the necessity of an air separation unit is avoided, fulfilling one of the economical concepts mentioned before. Large scale green ammonia plants will be benefit for the above, whereas small scale plants are expected to improve their economics if the reduction of the inversion is combined with the electrolyzers scaling-up. Relative to the expenses, often influenced by energy costs, the new plant concept will produce green NH_3 an energy consumption of near 26GJ which compared very well with the value of 36 GJ which is the overall standard today. The technology is claimed to be carbon-free.

Another difference between the new technology and the conventional ones using alkali electrolytic cells (AEC) is the Chemistry involved in the process. Figure 5 and Figure 6 showed schemes of the steps which feed the ammonia synthesis step:

Figure 5: SOEC and air separation unit feeding the ammonia synthesis step. **Figure 6:** SOEC unit feeding the ammonia synthesis step.

Whereas the SOEC step transfers O^{2-} through its membrane, the AEC step transfer OH^- ions, this difference makes the new technology to be an important cost saving change in the design of a green NH_3 plant, which evidently is to avoid of the air separation unit. In the Haldor Topsoe integrated technology, the SOEC produces the requirements of H_2 and N_2 needed in the HB unit. In the SOEC step, N_2 is generated from the air input by burning H_2 produced in the electrolyzer, here, O_2 is removed from air generating vapor. Accordingly, the electrolyzer produced H_2 in excess to the requirements of the syn- NH_3 sites, and the process becomes more efficient in energy terms.

Other difference, between SOEC and AEC, is that SOEC consumes power in the form of electricity or heat. The vapor generated by burning H_2 may be partially recycled to the system, which provided water input and heat energy to the electrolyzer. The new process operates at a lower voltage. In conclusion, SOEC presented high energy efficiency and the process eliminated the air separation unit.

With the built of 60 ammonia plants since 2000 year, some recent projects participating of Haldor Topsoe technology are shown in Table 4.

Table 4: Recent ammonia plants using Haldor Topsoe technology.

Plant	Country	NH_3 production, t/day	Year
Turkmenhimiya	Turkmenistan	2000	2018
United Chemical Co.	Russia	370	2018
Shchekinoazot			
Tatarstan	Russia	1964	2016

2.3.2 ThyssenKrupp industrial solutions AG ammonia production

Recent plants built by the corporation are summarized in Table 5.

Table 5: Recent ammonia plants built by ThyssenKrupp industrial solutions AG.

Plant	Country	NH_3 production, t/day	Year
SAFCO	Saudi Arabia	3300 + 11%	2017
Ma'aden	Saudi Arabia	3300	2016
CF Industries	USA	2200	2016
SASOL	South Africa	930	2016
CF Industries	USA	3300	2015
CF Industries	Canada	1300 + 11	2015
QAFCO 4	Qatar	2300	2013

– Uhde ammonia process

With basically the same scheme than that shown in Figure 1, this process has a number of significant features such as:

- a top-burned prim-reformer with a cold exit manifold,
- sec-reformer containing a circumferential vortex burner, and

iii. a magnetite-based three-bed radial heat exchange synthesis containing one or two synthesis converters.

Depending of plant location and special requirements, the total plant consumption is in the order of 27.6–30.1 GJ.

Besides the above, there are other 11 plants built since 2000 year.

– Uhde dual-pressure ammonia process

This process was developed in collaboration with Johnson Matthey-Catalysts. The most important innovation of this process is the addition of medium pressure once through syn-NH₃ connected in series with a conventional high pressure syn-NH₃ circuit. Some of the highlights of the process can be summarized as:

- i. more energetically efficient (4%) than the conventional Uhde process,
- ii. process characteristics, allowing the reduction of piping sizes in the high pressure loop,
- iii. considering plants in the order of 3000 t/day of ammonia production, the syngas compressor is of the same size that those used in lower capacity, i. e. 2200 t/day, plants,
- iv. one third of H₂, recovered from the purge gas, is converted to NH₃ in the once through step,
- v. the operation utilizes magnetite-based catalysts in all the stages.

2.3.3 Others flowsheet

– Braun

The Braun process used a primary reformer with exiting temperature of 700 °C, and excess air addition to the secondary reformer. Methane slip is in the 2–2.5 mol% range. Excess N₂ and CH₄ are cryogenically removed down the methanator, whereas H₂O is removed from the ammonia synthesis step due to its poisoning characteristics against catalysts. The S/C ratio can reduce to 2.7–3.0.

– ICI AMV (Ammonia V) process

The main features are summarized as: using excess air. Excess nitrogen goes to the circuit. This operates at pressures of 80–110 bar. Usage of ICI LP catalyst (KATALCO™ 74–1). Saturation of feed gas. S/C ratios of 2.8.

– ICI LCA (Leading Concept Ammonia) process

The process is defined for plants of near 500 t/day, in which the excess air is used to close the heat balance and a PSA system to eliminate CO₂ and excess N₂.

– Linde Ammonia Concept (LAC)TM process

In this offering, no secondary reformer is present in the process, and N₂ is cryogenically produced and added after a PSA unit. The process uses an isothermal shift and the methanation step is not considered. Inert free-ammonia syngas generation was produced with the correct H₂ to N₂ ratio, adjustable and CO₂/NH₃ product relationships. Design feedstock flexibility from light hydrocarbon feedstocks (LAC.L) to heavy hydrocarbon feedstocks (LAC.H). One example of this type of processing is the ammonia plant of Sadara Complex (Saudi Arabia), with a capacity of 650 t/d and starting at 2016. A scheme of the Linde Concept is shown in Figure 7.

Figure 7: The Linde ammonia concept.

– Casale

Under this label, two processes for ammonia synthesis are offered. First, is the STANDARD process, designed for plant capacities of 2500–3000 t/day ammonia production. This process, which used natural gas as feed, is based on the chemical reforming route (with hydrogen recovery).

The second process, named MEGAMMONIA[®], developed in conjunction with Lurgi, was designed for plant capacities higher than 3000 t/day ammonia. The sequential of the main steps of the process is: air separation unit, desulfurization, autothermal reforming, high temperature shift, CO₂ removal, nitrogen wash, compression and ammonia synthesis. Using natural gas as feed the process used an autothermal reforming to generate the syngas at a higher pressure than the standards. A physical process for the CO₂ removal (Rectisol[®]) is used, the step which works at a higher pressure is more efficient than standard chemical processes, and a shift ammonia synthesis converters, which in combination with a nitrogen wash unit, allowed to keep the size of these converters (and of the entire synthesis loop) at standard sizes. Either the autothermal reforming or the CO-shift unit used Casale technology. The CO-shift unit consisted of two axial-radial beds of conventional high temperature catalyst in series. The CO₂ is removed by absorption in cold methanol (Rectisol[®] process). Syn-ammonia unit is of Casale axial-radial design, having the ammonia converter three beds configuration with two interchanges. The overall consumption may be around 27.6 GJ.

– KBR purifier and KAAPTM

The technology uses a purifier (cryogenic syngas PurifierTM) which is located after the methane dryer stage; however, the process can be operated without this purifier. KAAPTM is located after the compression unit, the recycle purge is added to the methane dryer step. KAAPTM uses a ruthenium catalyst, which apparently is more active than traditional iron catalysts, thus, the technology allows lower synthesis loop pressure and the use of a single-barrel syngas compressor.

The KRESTM (KBR Reforming Exchanger System) has been developed to replace the traditional primary reformer. This system operates with air instead of oxygen, because downstream purifier needed excess nitrogen, Within the KRESTM system there is no necessity of an air separation unit.

Recent KBR ammonia plants are summarized in Table 6.

Table 6: Recent KBR ammonia plants.

Plant	Country	NH ₃ production, t/day	Year
BASF group, Yara Int.	USA	2200	2018
Dyno Nobel	USA	2300	2016
PT Pupuk Sriwidjaja	Indonesia	2200	2016
Pupuk Kaltim	Indonesia	2700	2015
Petrobras	Brazil	2200	2015
Moron	Venezuela	1800	2014
Turkmenhimiya	Turkmenistan	1200	2014
China Coal	China	1630	2014

Recently (published date 24 January 2018), the company had been awarded with a contract, by Indorama, for an ammonia plant to be built in Nigeria.

2.4 The future

Broadly speaking, in NH₃ manufacture not a unique process can be considered as best available technology. However, there are some points to take into account, thus, ammonia synthesis needed processes which considered:

- Reduction of power consumption.
- Improvement of stack losses.
- Cut-off energy consumptions for CO₂ removal.
- Low S/C ratios.
- More efficient and cheaper catalysts.

- H₂ recovery is a necessity.
- Improvement in the environmental emissions.
- Electrochemical membrane reactors; photochemical routes to feedstocks; ionic liquid reaction media

The treatment of natural gas with vapor and air is the easiness operation of NH₃ syn-gas production. The comparative consumptions of natural gas reforming, heavy oil and coal gasification are showed in Table 7.

Table 7: Comparative consumptions of ammonia synthesis gas production using various feeds and standard procedures.

	Natural gas	Heavy oil	Coal
Energy consumption	1.0	1.3	1.7
Investment cost	1.0	1.4	2.4
Production cost	1.0	1.2	1.7

In the basis of actual resources of fossil raw materials, it is expected that natural gas still continues being the feed for ammonia in future years. Thought future is unpredictable, at the half of the present century, and based on world reserves and consumption rate, coal will take place as feed material instead of natural gas. Heavy oil may be considered due to its feed flexibility and under determined environmental concerns i. e. unavailability of natural gas, and if the partial oxidation operation solves the waste problem of heavy residues and plastics recycle.

It is expected that the actual 175,000,000 t/year of ammonia production will increase in 1–2% during years.

3 Sodium hydroxide [11–14]

Sodium hydroxide (caustic soda) is the by-product yielded from the Cl₂ generation. Chemically speaking, this hydroxide is alkaline and of pure ionic character (formed by Na⁺ and OH[−] ions), thus, it is easily soluble in water. NaOH is a very useful product as precursor of sodium chemicals, being the key component in many important chemical processes. Some chemicals are: sodium formate, cyanide, chloroacetate, stannate, picramate, metasilicate, orthosilicate, phenolate, propionate, sulfite, molybdate, formaldehyde sulfoxylate, fluoroacetate, oleate, naphenate, lauryl sulfate, stearate and monosodium glutamate. Its uses in processes including: aluminum ore, cobalt hydroxide, xylenesulfonic acid, chemical wood pulp, polycarbonate, hydrazine, vanillin, epoxy resin, water treatment, disinfection, effluent treatment, galvanization, rubber reclamation, regeneration of ion exchange resins and fruit and vegetable products.

The key ingredients needed to make chlorine and sodium hydroxide are: salt, water and electricity. Industrially it is produced by different processes namely:

3.1 Membrane cell process (the most widely used)

Figure 8 showed a scheme of a membrane cell for the production of Cl₂ and NaOH. In the device, the anode and the cathode are separated by an ion-exchange membrane. The membrane role is to allow Na⁺ ions (and water) to go across the membrane and reached the cathode. In the anode

Figure 8: Membrane cell. 1 – Saturated brine, 2 – Depleted brine, 3 – Non-permeable ion exchange membrane, 4 – Pure water, 5–30% NaOH, 6 – 33% NaOH.

whereas on the cathode, H_2 splitted, collecting the bubbles conveniently:

The remained NaOH phase leaves the cell at near 30% concentration prior to a second concentration step, until 50%.

In the anode, Cl_2 exits and the “spent” brine is re-saturated with more “rich” salt prior to its purification using ion-exchange technology. Gaseous Cl_2 can be contaminated with O_2 , and in this case must be purified by liquefaction and evaporation. In this process, energy consumption is the lowest of the three processes (membrane, diaphragm and mercury), and the amount of vapor needed to concentrate the soda solution is also low (less than one ton per ton of soda).

3.2 Diaphragm cell process

In this operation, a permeable diaphragm separates the anode and the cathode (Figure 9). The entering brine material goes to the anode compartment flowing across the diaphragm toward the cathode compartment. The chemical reactions involved in the anode and the cathode are exactly the same as those described in eqs. (10) and (11), respectively.

Figure 9: 1 – Saturated brine, 2 – Diluted brine, 3 – Permeable diaphragm, 4 – Diluted caustic soda and diluted brine.

Diluted caustic brine exits the device. If necessary, soda can be concentrated until 50%. Normally, this is done by evaporation at the cost of three ton of vapor per ton of soda. Salt by-product is reusable to saturate dilute brine. If Cl_2 contains some O_2 , the purification step occurred in the same manner that in the membrane cell process.

3.3 Mercury cell process

This operational mode for the production of Cl_2 -NaOH is phased out and it is not in operation in Europe.

By 2017, near 80% of the industrial capacity of chlorine and sodium hydroxide manufacturing process is claimed to membrane process, 12% to diaphragm, near 6% to mercury and less than 5% to others technologies.

A new process for the production of NaOH from seawater desalination brine had been recently proposed [11]. The new process included the new steps of nanofiltration, electrodialysis, evaporation, chemical softening and ion exchange prior to enter the membrane electrolyzer (Figure 10).

Figure 10: Brine to membrane cell for NaOH production.

In the nanofiltration step, the brine was purified from sulfate and a fraction of the accompanying calcium and magnesium. The resulting permeate is concentrated *via* the electrodialysis and evaporation steps. In the exiting solution, remaining calcium and magnesium are completely removed by the chemical softening, using sodium carbonate or sodium hydroxide, and ion exchange, using a cationic resin, steps. On the partial pure and concentrated brine HCl is added prior entering the membrane cell to yield sodium hydroxide, chlorine and hydrogen. Accordingly to the authors, the process presented advantages as follows:

- i. decreasing of effluent generated in the reverse osmosis step,
- ii. reusing the electrodialysis eluate,
- iii. avoid the concentration-dilution cycle,
- iv. it has a potential revenue from side products, and
- v. it reduces the transportation costs.

Global caustic soda capacity by world region distributed as: Asia-Pacific (55%), Europe (20%), North America (20%), Middle East, Africa and Latin America (5%). Asia-Pacific provides more than half of global caustic soda production, with the market expecting to grow at 3% per year. This market, together with these of Latin America and Middle East are expected to increase with decrease of the Europe and North America markets.

Future: Concentrated caustic soda could be used to efficiently store heat in homes for later release when it gets cold at night.

4 Potassium hydroxide

The manufacture of potassium hydroxide used potassium chloride instead of sodium chloride in the very same electrolysis process. Thus, the reactions involved in the process are the very same as described in eqs. (10) and (11) for the anode and the cathode, respectively.

KOH is used as electrolyte in batteries, the manufacturing of soaps, chemicals and fertilizer production, petroleum refining and in de-icing and cleaning solutions. Its uses also included the pH balance.

5 Salts [15–24]

5.1 Ammonium nitrate (AN) and calcium ammonium nitrate (CAN)

AN is amply utilized as a fertilizer containing N_2 , basically due to the high percentage of nitrogen (33.7%) presented in its molecule. This salt is only manufactured by reaction of NH_3 gas and HNO_3 solutions. The resulting AN solution has various uses, depending of its application:

- i. storage as a solution and then used in downstream plants or sold as such,
- ii. transformation into solid AN by prilling or granulation, and
- iii. forming a mixture with a solid filler.

Calcium carbonate is often used as filler. This salt can be found as ground limestone, dolomite or as a secondary product of nitrophosphate processing. When mixed with AN a product named calcium ammonium nitrate (CAN) is formed, this product can be prilled or granulated. Granular products with AN and NH_3 or $CaSO_4$ are found.

One of the parameters to consider in the manufacture of AN is the strength of the HNO_3 feed, this strength varies from 50% to 70%. Often AN is synthesized using the HNO_3 fraction coming from the own site, though purchasing it can be another option.

The end product can leave the production site both, as loose bulk or in various pack sizes.

Product must conforms to current European Union specifications, including (i) decreasing the sensitivity of AN to heat or detonation with non-addition of external compounds, (ii) the oil retention must pass a specified test, (iii) the combustible material must be less than 0.2% for product containing more than 31.5% N and less than 0.4% for product between 28% and 31.5% N, (iv) the pH value of a 10% solution must be greater than 4.5, (v) less than 5% of product must be smaller than 1 mm and less than 3% smaller than 0.5 mm, (vi) chlorine content tolerances less than 0.02% by weight, (vii) heavy metals must not be added and traces incidental to the process should not exceed the limit fixed by the regulations.

AN declared as EU Fertilizer may only be supplied to the final user in packages, however, the legislation of the AN receiving country must be consulted for the precise details of particular requirements. The production process (Figure 11) consisted of three operations:

- i. neutralization,
- ii. evaporation,
- iii. solidification (prilling and granulation).

Figure 11: Steps for AN production.

In the case of AN manufacturing no single route can be identified as best available technology; several reasons for the above include: (i) the selected solidification process depended of certain commercial considerations, (ii) the goal of the operational units is the prevention or emissions, but it may be under the terms for the vendor to render the emission harmless by end-of-pipe treatment.

5.1.1 Neutralization or production of AN solution

The reaction of NH_3 , in gaseous form, and HNO_3 produced AN and steam, this reaction is of exothermic nature.

Gaseous NH_3 may contain minimum quantities of inert impurities such as H_2 , N_2 and CH_4 . These impurities needed to be vented from the neutralizer system at levels depending of the given process.

HNO_3 can be pre-heated using equipment with corrosion resistance, especially if the concentration of nitric acid is near the lower limit of 50%. Pre-heating operation is carried out by the use of steam or hot condensate from the AN processing. The amount of pre-heat can be estimated from the concentration of HNO_3 and the required concentration of the resultant AN solution by means of the enthalpy balance. The formation of AN can be carried out in one or two stages. In this second option, the first neutralizer operates at a low pH value, that is, in acidic conditions, whereas in the second stage the conditions are of a neutral pH value. Whereas the equipment operated at different pressures and temperatures, in most neutralizers, these operational variables, including concentration, are in closed relationship of the boiling point of AN solutions.

Neutralizers, as used in Europe, have different configurations, i. e. circulating systems, pipe reactors, etc. There are several environmental factors which influence the choice of neutralizer: (i) a single-stage neutralizer is simpler and cheaper (ii) a two-stage neutralizer produced most of the boil-off steam in the first stage and most of the NH_3 emission from the second stage, decreasing the total emission of ammonia, (iii) neutralization, at an elevated pressure, produced steam at a higher temperature (and AN at a higher concentration), thus, favoring the use of such steam in downstream processes, i. e. evaporation and drying, (iv) the control of the neutralizer is a critical parameter. The pH and the temperature must both be strictly controlled to limit the losses from the equipment, consequently, all neutralizers unit must included pH and temperature controls to avoid any environmental issue, (v) impurities must be controlled, within the operating temperature of the neutralizer, impurity control is of the foremost importance also to avoid control safety and associated environmental issues. This is because some plants do not recycle AN screenings to the neutralizer. Recycling is especially risky if there are contamination by an organic anticaking additive. In general terms, an AN acidic solution is less stable than an alkaline one.

In neutralizers unit, best available technologies may consider: (i) in the event of water addition to the unit, this water should be used to the safe recycling of AN solution, (ii) impurities should be rigorously excluded, though some recycling may be practicable, (iii) the steam formed within the neutralizer contained both ammonia and AN in concentrations of a few thousand mg/L of each. The careful design of the neutralizer equipment can ten-fold reduced them.

The steam, by-product of AN fabrication, exiting the neutralizer needed to be purified, or it can be condensed and then purified. The steam is used, in the evaporator (see below), or it may be used to preheat and evaporate NH_3 or be used to preheat HNO_3 . The next operations have been used commercially for the purification of the steam: (i) drop separation methodologies (knitted wire mesh demister pads, wave plate separators, fiber pad separators), and (ii) scrubbing units (packed columns, venturi scrubbers, irrigated sieve plates).

The formation of AN in the neutralizers is a removal challenge since the particles are very fine. Often, a combination of drop separators and scrubbers are used for the above. In the scrubbers, it is required the addition of acid, often nitric acid, to neutralize any free ammonia and optimization of its removal.

The condensate must be cleaned using various technologies, including ion exchange resins; however, safety concerns with the use of this technology may be considered. The recycle of organic resins to the AN process may be avoid, and the resin may not be nitrated. The choice of the cleaning methodology is dependent on the necessity of nitrate elimination, and this is dependent on the receiving water. The final condensate exiting the neutralizer, can be differently discharged: (i) to drain, (ii) to a HNO_3 plant to be used as absorption water, if nitric acid fulfill all the requirements, (iii) to other uses on the site, i. e. in the manufacture of solution fertilizers, (iv) to boiler water feed, i. e. after further purification, (v) to an aquatic environment for control/analysis purposes or for subsequent evaporation by the heat of natural sources or for disposal to land, though neither of these is practicable in many countries in Europe because of the climate or the amount of land required.

Biological treatment is an alternative for the removal of N_2 from fertilizer site effluents, however, this is not the used norm on a commercial basis in Europe, except in the case of an existing public utility or on a large integrated chemical site.

The final product, from the neutralizer, is AN solutions, with concentrations depending of the feed materials and the operational uses. It is stored without further processing, but, if it is to be used in the manufacture of solid AN, CAN or NPK fertilizer, it is normally concentrated by evaporation. NPK is a three component fertilizers providing nitrogen, phosphorous and potassium.

5.1.2 Evaporation

This step (Figure 11) is necessary to eliminate water, normally found, in the AN solution. The acceptable water content is dependent on each given process, but it is below 1% for a prilling product, however, amounts up to 8% is needed on some granulation processes. Evaporation is always performed using vapor usually coming from the neutralizers or from a vapor raising facility located within the plant location.

Undesirable AN decomposition is avoided by the use of saturated vapor heated at a given temperature. This step can be carried out at atmospheric pressure or under vacuum; in this second case, allowed the reuse of neutralizer vapor at the cost of more capital investments. In the step, some NH_3 is lost from the AN dissolution, and this needed to be replaced in advance to the next step. The vapor, boiling off, is contaminated with NH_3 , this chemical needed to be removed, whereas some AN, in the form of drops, are also found.

Evaporators used in practice included circulatory systems, shell and tube heat exchangers and falling film types (which presented some features such as: decreasing of the working volume and a shorter residence times). These equipment produced contaminated vapor, which needed to be decontaminated previously to its discharge to the environment. Methodologies used in the purification included: (i) drop separators, (ii) scrubbers and (iii) condensation of the vapor.

The evaporator produced AN solutions of the adequate concentration, and at a temperature which eliminated the risk of crystallization. Sometimes, the solution is cooled to decrease effluents emissions from downstream equipment.

5.1.3 Prilling and granulation

Prilling is the formation of granules by means of the solidification of drops of fertilizer materials. Granulation refers to methodologies which used agglomeration, accretion or crushing, to produce a granular fertilizer.

The prilling operation technique is used in a number of plants producing AN or even CAN. Granulation of AN is carried out in a plants used only to perform this task, or in CAN producing plants. As in the case of AN, there are plants which only granulated CAN, whereas this product can be produced in plants producing NPK fertilizers.

The feed of AN to a prilling plant needed to be almost anhydrous. Drops of the product are formed, falling to a prill tower. Air is allowed to flow upstream, and the drops cool and become solid. Drops are generated by (i) a rotating perforated bucket, or (ii) a static system of fixed orifices. If CAN is manufactured, ground CaCO_3 is added previously to the generation of the drops.

Several effluents resulted from the loss of NH_3 , AN and CaCO_3 (the latter in CAN production) to the air stream. Decreasing the melting temperature reduced emissions, whereas NH_3 is often eliminated neutralizing it in a wet scrubber.

Tiny AN particles are finding within the air, they are eliminated by the use of dedicated equipment. However, AN fume is lost from the prills surfaces, and being in the sub-micron sizes, it is non-easy eliminated. Its presence is determined by a persistent blue haze, which it is seen at larger distances from the plant. This problem is avoided by the use of irrigated candle filters (with candles incorporating fine glass fiber), but at millionaire (Euros) cost. In CAN prilling towers, candles are not used for the elimination of the effluent, because, insoluble CaCO_3 fouled the surface of the filter in an undesirable time. Similar situation is found if insoluble materials are added to the AN. Other scrubbing equipment did not improve the elimination of the effluent.

Granulation is a more difficult operation than prilling, and a variety of equipment is used in the industry, including: rotating pans and drums, fluidized beds and other more specialized equipment. From an environmental point of view and having effluent of the same nature, that in prilling processing, the advantage of granulation is that the amount of air to be treated is smaller, and the related equipment is cheaper and easier to install, being also lower the energy consumption. If the AN feeding the granulator has elevated moisture contents, the emission contained only coarser particles, against the presence of fumes, and consequently, the scrubbing operation is performed using cheaper equipment in comparison to candle filters. Granular products are made in a wider range of particle size than prills.

A number of granulation processes used AN containing up to 8% water, being this water eliminated within the process, and at a lower temperature.

In AN/CAN sites, granulators include: rotary pans and drums, spherodisers, pugmills and fluidized beds. If CAN is manufacture, the filler are added to the process before the granulator, and AN is added in the granulator spraying a hot concentrated solution, and no further drying of the granules are required. This product is screened, and the fines and crushed oversize are back to the granulator.

CAN and CAN/NPK granulators included drums and pugmills. The filler is mixed with AN solution prior to granulation or even in the granulator. Granules from this process are drying in a fluidized bed or rotary

drier; being an autothermal process, additional heat is not necessary in this drying step. Gases coming from the granulator and from the drier are cleaned by a combination of dry cyclones or bag filters and wet scrubbers. Candle, venturi and cyclon devices are frequently used for the latter. Candle filters are suitable if the emission contains a large proportion of sub-micron particles, but they can not be used in CAN plants.

NH₃ and AN emissions into air and generated in the prilling and granulation sections of AN and CAN plants can be decreased by a range of suitable equipment. The resultant emissions are dependent upon two principal factors: (i) the efficiency of the equipment used in the operation, and (ii) the volume to be treated.

For the fine particles produced in the prill tower, candle filters are normally required, these decrease particulate emissions to 15 mg/m³ of air. For coarser materials, as in granulation plants, dry equipment, i. e. bag filters or dry cyclones are better options.

Modern plants used lower air volumes; however, the reduction in air volume on an existing plant tends to be expensive.

Prill and granulator towers very often produce a product which requires further cooling, this step is done using rotary or fluid bed coolers, being the air cleaned by high efficiency cyclones, bag filters or wet scrubbers.

AN and CAN tend to caking during storage and need to be conditioned to prevent it. Anticaking agents are internal to the finished particle or applied, as a coating, to the outside; in addition, these additives are also useful to prevent dust formation and moisture pick-up during storage. Their characteristics vary according to the necessities of individual plants.

Losses to the atmosphere are a general problem but particular to any plants, some examples are: loss of AN to drain in a number of locations, losses from pump seals, leaks from flanges and valves, etc. The proper plant design and maintenance must be a necessity to avoid these different losses and to help to decrease waste products generated for the plant.

Packs of solid AN are stored in warehouses approved by specific authorities of each country, for AN duty. Since both, bulk AN and CAN, are hygroscopic, they needed to be protected from moisture.

AN solutions are stored prior to use in downstream plants or prior to sale. This storage is done at a temperature above the crystallization point of the solution. NH₃ gas is often added in quantities which maintained the solution at the correct pH value, because AN solutions tend to lost NH₃ during storage.

5.2 Sodium carbonate

Sodium carbonate or soda ash is a key product in many industries: glasses, soap, paper making, bleaching products, etc. Though sodium carbonate can be found naturally, it is often fabricated by the Solvay process (Figure 12), which uses purified brine and ammonia as starting reagents.

Figure 12: Production of sodium carbonate from purified brine.

The reactions occurring in the tower are

A final and key step is the recovery of ammonia:

5.3 Potassium carbonate

This salt is used as a pH buffer, fire suppressant, glass, welding and as a source of potassium intake of animal farms. It is prepared by electrolysis of KCl. On as-produced KOH, the carbonated salt is formed:

Asia-Pacific region accounted for more than a half of global potassium hydroxide precursor demand, followed by North America and Europe.

5.4 Lithium carbonate

Actually, 35% of the lithium production goes towards battery production, other industries which used lithium compounds are ceramics, glass, greases, etc. Lithium consumption for batteries is being increasing due to the use of rechargeable Li batteries, electric tools and especially in e-cars and hybrid cars. One of the most important derivatives of lithium is lithium carbonate.

Besides several uses, including the treatment of bipolar disorder (lithium carbonate is included in the WHO list of essential medicines), this salt is a key component in the manufacture of lithium-ion batteries, since it serves as precursor of lithium cobalt oxide (LiCoO_2) which formed the cathode in a number of these batteries. The preparation of the oxide consisted in the reaction of the stoichiometric concentrations of lithium carbonate and cobalt (II,III) oxide (Co_3O_4), or even zero valent cobalt, at temperatures in the 600–800 °C range, and further annealing of the product at 900 °C under oxygen atmosphere.

Lithium carbonate is basically produced by three general routes: the treatment of brines, the treatment of certain ores/clays and the recycle of batteries or electrolytes.

In the case of brines, the top producers' countries are Australia, Chile and China. Lithium carbonate is produced by a general scheme of steps as it is shown in Figure 13. The recovery time is about 18–24 months, since solar evaporation is a slow process.

Figure 13: Production of lithium carbonate from brines.

Other possibilities about the lithium recovery from seawater brines are by membranes or solvent extraction technologies.

In the case of geothermal brines, CMI (USA), had developed the CIM Lithium Project, in which lithium is extracted from the brines, purified, concentrated and converted along the next steps (Figure 14).

Figure 14: Basic steps for lithium processing from geothermal brines.

Various types of adsorbents/ion exchangers are proposed to purified Li from these geothermal brines:

- i. spinel type lithium manganese oxide (Li-Mn-O), which is a cation exchanger,
- ii. spinel type lithium titanium oxide (Li-Ti-O), also a cation exchanger, and
- iii. lithium aluminum layered double hydroxide chloride (LDH) with $\text{LiCl} \cdot 2\text{Al}(\text{OH})_3$ stoichiometry, though stoichiometries as $[\text{LiAl}_2(\text{OH})_6]^+ \text{X}^- \cdot n\text{H}_2\text{O}$ where $\text{X} = \text{Cl}^-$ or Br^- also applied, and adsorbent.

The production of battery-grade lithium compounds directly from brines was investigated in a laboratory-scale process by the use of ion exchange and chemical precipitation. Thus, brine, without impurities, can be used in an industrial membrane electrolysis process. Various sequences and conditions were investigated to purify lithium-concentrated brines, principal impurities found in the natural brines were Ca^{2+} , Mg^{2+} and sulfate, being all of these remove under the operational conditions used. In the chemical precipitation process, lithium-concentrated brine reacted with the precipitating agents at different steps. Then, the pulp obtained, and after sedimentation, it was filtered, allowing the removal or decreasing the presence of impurities in the lithium brine. Removal efficiencies for Ca^{2+} , Mg^{2+} and SO_4^{2-} were of 98.93%, 99.93%, and 97.14%, respectively. Further, ion-exchange technology decreased the concentration of Ca^{2+} and Mg^{2+} to values less than 0.001 g/L.

The treatment of brines and seawater can be also accomplished by precipitation, solvent extraction, membrane technologies, ion exchangers and adsorbents. Green solvents, as ionic liquids seemed to be, are suitable to recover Li from these natural compounds.

In the case of ores/clays, two mixed pyro-hydrometallurgical process had been proposed to recover Li from a Li-rich ore. One used roasting and leaching, whereas the other used chlorination and leaching steps, in both cases the end product is lithium carbonate. In the case of spodumene ($\text{LiO}_2 \cdot \text{Al}_2\text{O}_3 \cdot 4\text{SiO}_2$), either pressure leaching or bioleaching had been proposed as a method to dissolve this lithium material.

Li-ion based batteries are another resource for lithium production. The recycling of these batteries can be also done by pyrometallurgical, hydrometallurgical (including bioleaching step) and hybrid pyro-hydrometallurgical processing.

No less than 13 pyrometallurgical processes had been proposed by different companies for the treatment of batteries, and particularly 3 of them are specifically developed to lithium batteries. The pyrometallurgical processing includes the mechanical and thermal steps, whereas the thermal steps can be approached calcination, roasting, reduction or chlorine processing.

It was described, a process for the recycling of Li-ion batteries and the production of lithium carbonate. The steps are: nitration, selective roasting, water leaching and Li_2CO_3 preparation. In the process, metal-bearing materials in Li-ion battery waste are transformed into their nitrates salts, roasted to transform them to their non-soluble oxides, and solubilization of LiNO_3 in water. The best conditions for the above steps are: nitration (70 °C, 5 h, acid-to-scrap ratio of 30 mmol/g), selective roasting (250 °C, 1 h) and 4-stage cross-current water leaching (25 °C, liquid-to-solid ratio of 2:1). Li solubilizes up to 93%, whereas extraction of Co, Ni and Cu is less than 0.1%. On the as-obtained Li solution (34.1 g/L Li), a carbonation step at 95 °C for 30 min, is carried out, resulting in the formation of the Li-carbonate salt, having a richness up to 99.95%, which is above the usual minimum requirements for battery grade Li_2CO_3 .

In general terms, the hydrometallurgical recycling of Li-ion batteries comprises various steps including:

- i. pretreatment of the spent battery: dismantling the cells, thermal treatment and mechanochemical process. It can be pointed out that some of the battery components are flammable and toxic,
- ii. leaching of metals from the cathode material, and
- iii. separation of lithium and accompanying metals via a suitable process and depending of the metal concentrations in the solution obtained in (ii), i. e. solvent extraction, liquid membranes or impregnated exchange resins and adsorbents, all the above with or without the use of ionic liquids, chemical precipitation, electrochemically ion exchangers and adsorbents.

A process to prepare Li_2CO_3 from a Li-rich electrolyte generated in the aluminum industry was described elsewhere. The described process involved the next steps: H_2SO_4 leaching, elimination of impurities and precipitation of Li_2CO_3 . Near 98% Li leaching efficiency was obtained in 1 h using 6% sulfuric acid at 80 °C, and with a liquid-to-solid 2:1 relationship. The leaching solution, containing lithium sulfate, was treated with NaOH, until pH 11, and further by 3 g/L EDTA (ethylenediaminetetraacetic acid). Lithium carbonate (99.5% purity) was yielded by precipitation with 290 g/L sodium carbonate at 95 °C and 50 min reaction time.

In one European patented process, which simplified flow-sheet is showed in Figure 15, lithium carbonate is yielded from the treatment of lithium-bearing solutions.

Figure 15: Process to yield lithium carbonate from lithium-bearing solutions.

Accordingly with this flow-sheet, the lithium-bearing solution is purified from accompanying divalent metals, and from the resulting solution, first lithium hydroxide and secondly lithium carbonate is yielded as end product. The purification of the lithium solution, from divalent cations, is carried out by bipolar electrodyalisis, which also converted lithium to lithium hydroxide. This product is converted to the carbonate salt by a further carbonation step.

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