Module-2

Chlor-Alkali Industries

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Pulp and Paper Industries

Chlor-Alkali Industries

This industry represents three major chemicals: a) Soda ash (Na_2CO_3), b) Caustic soda (NaOH), and c) Chlorine Cl_2.

Soda Ash (Sodium Carbonate-Na_2CO_3)

- M.W: 106.0, M.P: 851°C, B.P: Decomposes, soluble in water (8.9 g/100 g water at 20°C).
- Grades: 99% Na_2CO_3 (58% Na_2O) as light and dense grade of granular product.
- Washing soda ($Na_2CO_3.10H_2O$)
- Uses: In India, 40% Soap and detergent, 18% glass, 15% sodium silicate, 9% trade, 12% chemical industry, 6% Miscellaneous. In worldwide it is used in pulp and paper, desulfurization etc.
- The oldest process of manufacture of soda ash was ***LeBlanc process*** (1973). Salt cake (sodium sulfate) reacts with limestone to produce soda ash and troublesome product gypsum. This method is obsolete nowadays.
- $Na_2SO_4 + CaCO_3 \rightarrow Na_2CO_3 + CaSO_4$
- In 1864, ***Solvay*** process was invented (Ernest Solvay) that is ***ammonia-soda*** process.

- ***Trona ore*** or ***sodium sesquicarbonate*** $Na_2CO_3 \cdot NaHCO_3 \cdot 2H_2O$ (45% Na_2CO_3, 36% $NaHCO_3$, 15 % water, and impurities) is found 500 m below the surface. Heating this ores ***natural soda ash*** is produced hugely in U.S and it replaces Solvay process.
- Other method of production of soda ash is ***dual process*** (Na_2CO_3+NH_4Cl).

Solvay or ammonia-soda process

Chemical reactions

a) Overall reaction: $\mathrm{CaCO_3(s) + 2NaCl(aq) \rightarrow Na_2CO_3 + CaCl_2}$

This reaction takes place in a number of steps:

b) $\mathrm{CaCO_3(s) \rightarrow CaO(s) + CO_2(g)}$; $\Delta H = +43.4\ Kcal$

c) $\mathrm{C(s)} + O_2(g) \rightarrow \mathrm{CO_2(g)}$; $\Delta H = -96.5\ Kcal$

d) $\mathrm{CaO(s)} + H_2O(l) \rightarrow Ca(OH)_2(aq)$; $\Delta H = -15.9\ Kcal$

e) $NH_3\mathrm{(g)} + H_2O(l) \leftrightarrow NH_4^+OH^-$; $\Delta H = -22.1\ Kcal$

f) $\mathrm{CO_2(g)} + OH^- \leftrightarrow HCO_3^-$

g) $\mathrm{CO_2(g)} + H_2O(l) \leftrightarrow HCO_3^- + H^+$

h) $Na^+ + Cl^- + NH_4^+ + HCO_3^- \rightarrow NH_4^+Cl^-(aq) + NaH\mathrm{CO_3} \downarrow$

i) $2NaH\mathrm{CO_3(s)} \rightarrow \mathrm{Na_2CO_3}(s) + \mathrm{CO_2(g)} + H_2O\mathrm{(g)}$; $\Delta H = +30.7\ Kcal$

j) $2\mathrm{NH_4}Cl(aq) + Ca(OH)_2(s) \rightarrow 2NH_3\mathrm{(g)} + \mathrm{CaCl_2}(aq) + 2H_2O(l)$; $\Delta H = +10.7\ Kcal$

Raw materials: Major requirements are salt, coal, and limestone.

Basis: 1 ton of Na_2CO_3 (58% NaO) requires

Salt	**1.55 ton**
Limestone	1.2 ton
Coke	0.09 ton
High pressure steam	1.35 ton
Low pressure steam	1.60 ton
Ammonia make up	1.5 kg
Cooling water	40-60 ton
Electric power	210 kWH

Process description:

- The purified brine is pumped to the ammonia absorber tower where it dissolves NH_3 with liberation of heat (reaction (e)). Some CO_2 also dissolves in the tower.
- The ammoniated and partially carbonated brine is cooled to 30°C and pumped to the carbonating tower that is on cleaning duty. In order to accelerate the cleaning process, weak CO_2 gas is admitted at the bottom of the tower (made of cast iron, 22-25 m long, 1.8-2.5 m diameter). As the tower gradually becomes fouled by bicarbonate cake, the cleaning is required.

During the precipitation cycle, the temperature gradient is maintained as 20-25°C at both ends and 45-55°C in the middle. The carbonated tower is periodically used as a make tower (3 days) and cleaning duty (12 hr). Various towers are alternatively used in series in the process. In the make tower reactions (f), (g) and (h) take place. In the tower, lean lime kiln gases are injected near the middle of the tower, and rich CO_2 gas from bicarbonate calciner is recompressed and pumped to the bottom of the tower. The tower is constructed with a series of cooling boxes and slopped baffles so that the precipitated bicarbonate settles to the bottom and is pumped to slurry or rotary filter.

- The solids from the rotary filter are calcined at about 200°C in calciner which is gas fired or steam-heated.
- The remaining process is ammonia recovery and recycle. The filtrate liquor from the rotary filter is sent to the pair of ammonia stills. In the first still, free ammonia from the solution is recovered by distillation. The bottom product of the still is fed to the lime still where the reaction (j) releases NH_3 gas and effluent liquor containing $CaCl_2$ is disposed.
- The product from the calciner is soda ash (light). To produce the dense grade, sufficient water is milled in to form monohydrate and mixture is recalcined.

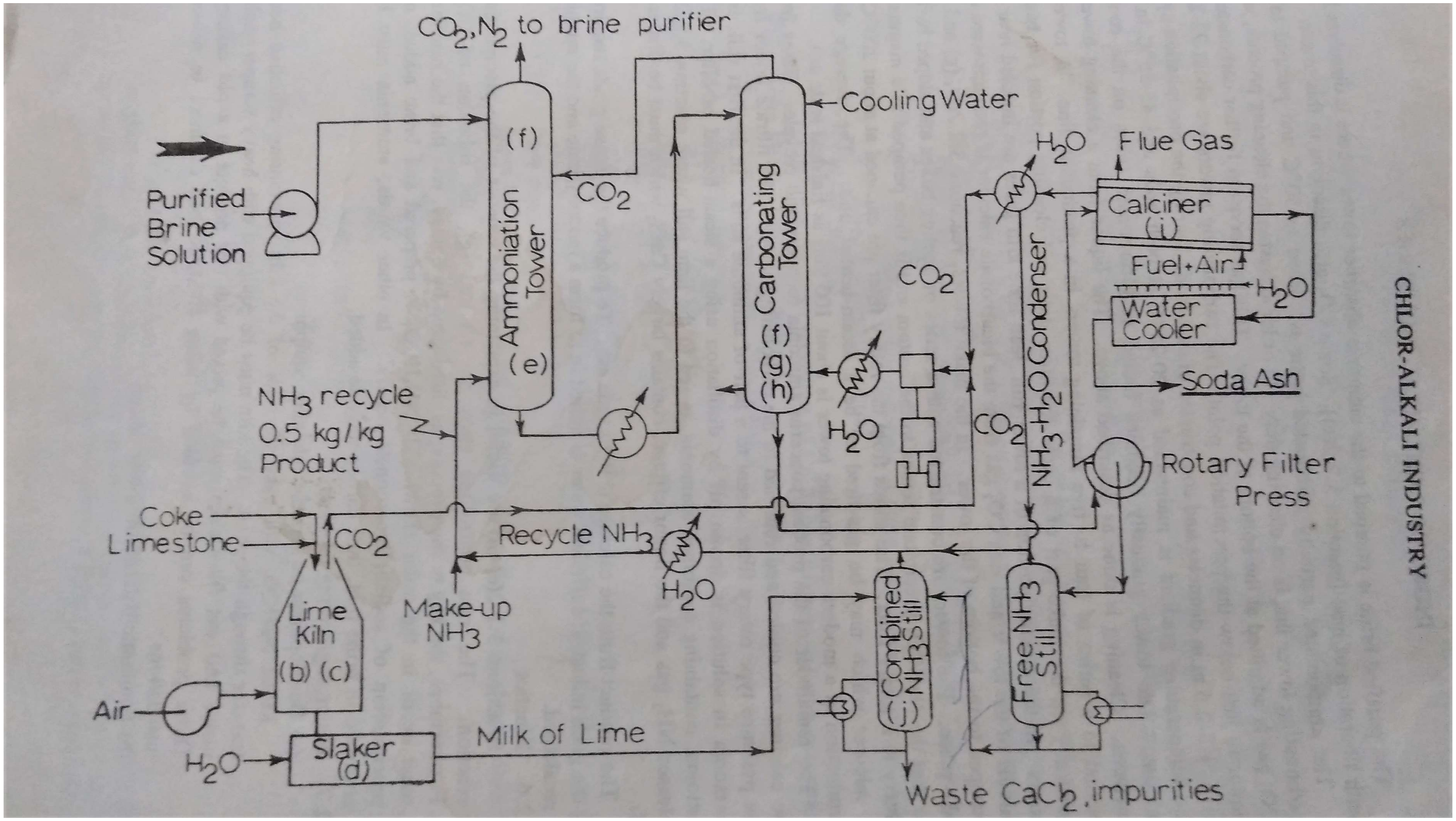


Fig. Manufacture of soda ash by Solvay process.

Kinetics: The rate controlling steps are (f) and (g) reactions, the solvation of CO_2. If brine is added after the absorption of NH_3 and CO_2, the NH_4HCO_3 precipitates instead of $NaHCO_3$. So, ammonia is absorbed in brine, then CO_2 is absorbed.

Major engineering problems:

a) Development of suitable calcining equipment: Moist $NaHCO_3$ will cake on the side of the kiln, preventing effective heat transfer through shell in heating. It must be equipped with heavy scrapper chain inside and wet filter cake is mixed with dry product to avoid caking. This problem can be overcome with the installation of fluidized bed calciner.

b) Economic tower design: Tower height, pressure and temperature are optimized to give 75% yield of $NaHCO_3$.

c) Ammonia recovery: NH_3 inventory cost is 4-5 times that of Na_2CO_3 inventory, so losses must be kept low by using proper equipment with better design and maintenance.

d) Plant modernization: Three old plant in India (prior to 1947) had to be modernized by better material of construction and automatic control.

Advantages of Solvay process:

- Can utilize low grade brine.
- Less electric power.
- Less corrosion problems.
- No co-product to dispose off.
- Does nor require NH_3 plant investment.

Disadvantages of Solvay process:

- Higher salt consumption.
- Higher investment in NH_3 recovery units versus crystallization units for NH_4Cl.
- Waste disposal of $CaCl_2$-brine stream.
- More steam consumption.
- Higher capacity plant for economic break-even operation.
- With current fertilizer shortages, all of the NH_4Cl will be used as a mixed chemical fertilizer ingredients in dual process (Na_2CO_3+NH_4Cl). No waste disposal is required.

References

1. Dryden's Outlines of Chemical Technology, M. Gopala Rao, M. Sittig, 3rd Edition, East West Press.

Pulp

- Pulp is a commercial cellulose($(C_6H_9O_4OH)_n$ derived from bamboo, bagasse, wood, etc., by mechanical and chemical method.
- **Mechanical method:** Debarked wood is mechanically shredded to form fibers for the production of newsprint, toweling, toilet tissue, cheap paperback book where strength and bleaching are not major requirements.
- **Chemical:** Lignin and other non-cellulosic fractions of the wood are removed from cellulosic fraction by reacting with chemicals like, ***sulfate*** (***Kraft process***), ***sulfite*** of alkali metal. The yield is half of the mechanically groundwood process (40-65%). The pulp obtained by chemical process is suitable for chemical grade cellulose (rayon and cellulose derivatives), paper of high strength and fine texture.
- **Semi-chemical:** Wood chips are gone through mild chemical treatment with dilute mixture of sulfate, sulfite and soda ash reagents, by which the wood is softened to allow mechanical separation of fiber with lesser power than that of mechanical process only. A higher yield of 65-90% is obtained with better quality of pulp make this process popular over other process.

Characteristics	Sulfate pulp	Sulfite pulp
Trade name	Kraft	Sulfite; Magnifite; Neutral
Reagents	60% NaOH; 25% Na_2S, 15% Na_2CO_3 in 10-15% aqueous solution	**Magnifite:** $Mg(HSO_3)_2$+ free SO_2 in acid media **Neutral sulfite:** Na_2SO_3, Na_2CO_3, $NaHCO_3$ **Acid sulfite:** $NaHSO_3$, Na_2SO_3
Digestor condition	T=170-180°C; P=10 atm. Time: 2-5 hr for wood-base material;5-6 min for bagasse; longer time for chemical cellulosic pulp.	T=120-150°C; P=4-6 atm. Time: 6-10 hr for wood, 20-40 min for bagasse.
Chemical recovery	92-98% of Na and S	92-98% of Na and S
MOC	Mild steel, alloy (caustic liquor compatible); Inconel tube for external heat exchanger.	Digestor lining of acid-proof brick; metal parts - 316-SS, bronze, lead for acid magnifite process. Neutral process can use same as Kraft process.

Characteristics	Sulfate pulp	Sulfite pulp
Types of pulp	Brown color; removed colors using chlorine bleaching; unbleached fibers are very strong.	Dull white color; easily bleached; fibers are weaker than that produced by Kraft process.
Paper products	Strong brown bag; brown paper wrapping; paperboard boxes; strong white paper through bleaching.	White grade paper; book paper; sanitary tissue.

Sulfate (Kraft) pulp process

- **Chemical reaction:**
- **Digestion: Hydrolysis and solubilization of lignin**

$$\mathbf{R - R' + NaOH \rightarrow R''COONa}$$

$$\mathbf{R - R' + NaOH \rightarrow ROH}$$

$$\mathbf{R - R' + Na_2S \rightarrow R''SH\ (Mercaptans)}$$

- **Chemical recovery from wood digestion black liquor**
  - **Smelting furnace:**

$$\mathbf{2NaR\ (Lignin\ salt) + air \rightarrow Na_2CO_3 + CO_2}$$

$$\mathbf{Na_2SO_4 + 2C\ (from\ R) \rightarrow Na_2S + 2CO_2}$$

  - **Causticizing**

$$\mathbf{Na_2CO_3(aq) + Ca(OH)_2\ (s) \rightarrow 2NaOH\ (aq) + CaCO_3(s)}$$

$$\mathbf{CaCO_3(s) \rightarrow CaO + CO_2}$$

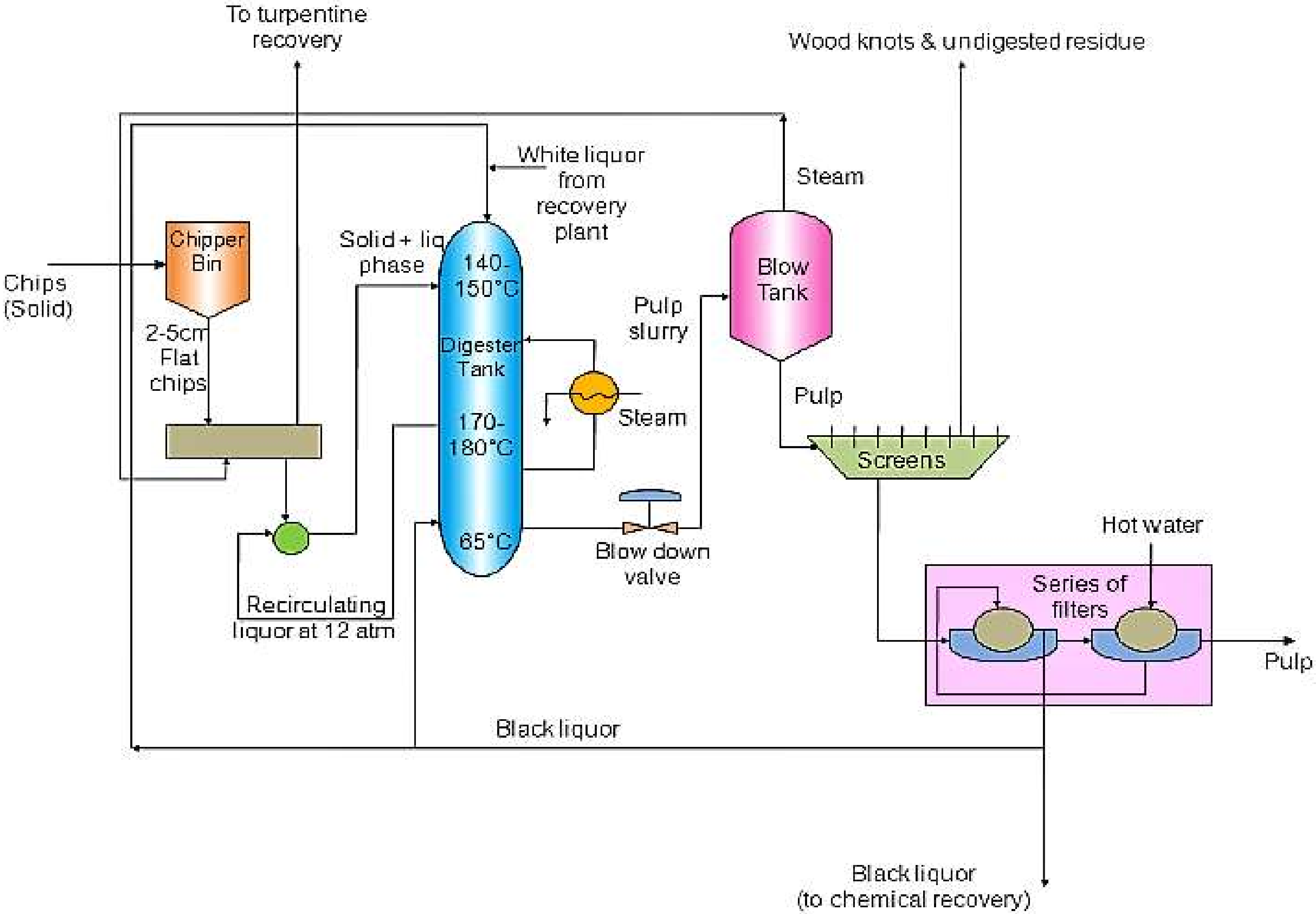
$$\mathbf{CaO + H_2O \rightarrow Ca(OH)_2}$$

- **Basis:** 1 ton of pulp
- Bamboo or wood: 2.2-2.5 ton; Lime make-up: 18 kg; Salt cake make up: 50 kg; Sulfur: 8 kg
- Most popularly used process. This is an alkaline process. Na_2SO_4 is added to the cooking liquor. So its common name is sulfate process. The presence of sodium sulfide makes bleaching of pulp easier and the paper produced has better strength.

- Process: $\mathbf{Na_2S + H_2O \rightarrow NaOH + NaSH}$

$$\mathbf{NaOH + NaSH + wood \rightarrow Sodium\ compound + sulfer\ compound}$$

- Wood contains cellulose (40-45%), hemi-cellulose, Lignin (18-32%), fats, and resins. In the Kraft process, wood pulp contains 70-75% cellulose and lignin 2-5%. During the cooking process, alkali is reacting with (1) lignin, (2) different organic acids (original wood acids or produced by hydrolysis) (3) resins in the wood. Alkali dissolves carbohydrates and adsorb by the fibers. The 60-70% of alkali is consumed by neutralizing the organic acids; 20-30% of alkali is consumed by the lignin.
- In the cooking reaction fat, resin are converted into soaps from black liquor. The hazardous gases are produced CH_3SH, CH_3SCH_3, $CH_3S_2CH_3$ etc. The turpentine and methanol are the byproducts.



Picture: NPTEL – Chemical – Chemical Technology II, Lecture 26: Preparation of wood pulp by sulfate (kraft) process.

- **Chipper bin:**
  - Chips are fed in this device.
  - Cut logs are conveyed to the chipper where rotary disks with heavy knives reduce the wood to size 2-5cm flat chips.
  - Size reduction is done to maximize penetration of process chemicals.
- **Digester tower:-**
  - Continuous digester tower is 25 – 30m tall.
  - Chips are preheated with volatilizing turpentine and non-condensable gases.
  - For controlling digestion temperature, cooking liquor is withdrawn as side streams and circulated through heat exchanger.
  - Digestion is done to free lignin and other non-cellulosic content.
  - Cooking time is about one and a half hours at 170°C.
  - To avoid mechanical weakening of fibres, digested chips are cooled with recycled black liquor.
  - Temperature is maintained at 140-180°C and pressure at about 10 atm.
  - Bottom temperature is maintained at 65°C
- **Blow down valve:**
  - This valve reduces the pressure of the stream from 80atm to 1atm before entering blow tank.

- **Blow tank:-**
  - When hot pulp slurry is passed to the blow tank, heat is recovered in the form of steam.
  - The chips are preheated with this recovered steam.
  - The blow tank has high concentration of pulp and low concentration of water.
- **(e) Screens**
  - Pulp is screened so as to remove wood knots and undigested residues.
- **(f) Series of filters**
  - Pulp is filtered to separate black liquor for chemical recovery plant.
  - Black liquor is also recycled back to digester for cooling the digested chips.
  - Hot water is added to second filter for better filtration.

- **Turpentine recovery:**
- Sulfate turpentine is an economically important by-product which can be recovered from the Kraft pulping of resinous woods. Relief gases from the digester pass through a fiber separator into the turpentine condenser. Condensate from the condenser is then decanted to separate the turpentine. Turpentine then overflows to turpentine storage while the water underflow is removed for treatment as effluent.
- **Bleaching of pulp:**
- To produce white paper, the pulp is bleached. The chemicals used to bleach pulp must be environment friendly. Bleaching with chlorine produces dioxins and other undesirable products. So, nowadays pulp is bleached with hydrogen peroxide, ozone, chlorine dioxide, oxygen etc. The objective of bleaching is to remove small fractions of lignin that remains after digestion.
- Reference

- Dryden C. E., Outlines of Chemical Technology, East-West Press, 2000.
- NPTEL – Chemical – Chemical Technology II, Lecture 26: Preparation of wood pulp by sulfate (kraft) process.
- http://www.pulppapermill.com/the-chemical-reactions-in-kraft-pulping-process/
- A.H. Lundberg, Inc., Everett, WA.