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TECHNICAL LECTURE SERIES

50 Years' Development of the Bayer Process and Outlines of the Future

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Something about the Presenter

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Chem. Eng. (MSc.,1972), Patent Attorney (1992),

George has 50 years hands on experience of processing bauxites of different types and grades using the low or high temperature digestion processes, process modelling, material and energy conservation of the alumina production. His specialties cover the valorisation of bauxite residue (red mud) and co-ordination of R&D projects. He is the principal inventor and driver of the Improved Low Temperature Digestion (ILTD) Process which makes possible to process virtually all the gibbsitic bauxites in a viable and sustainable way. (Co-)author of 42 publications.

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What is Bayer process? (1of2)

- **Bayer process was invented by Karl Joseph Bayer Austrian-born chemist in 1887 (precipitation) and 1892 (digestion).**
- **The Bayer process is based on the discovery: the caustic liquor is able to keep the dissolved sodium aluminate in solution at relatively high temperatures, typically 140-270 ^oC, depending on the mineralogy of bauxite, while significant amount of the dissolved alumina crystallizes as aluminium hydroxide at relatively low temperatures, 60-70 ^oC, (and lower concentrations than those of the digestion).**
- **The aluminium hydroxide is then calcined at about 1000 ^oC so that it be converted to technically pure aluminium oxide (Al_2O_3), also known as alumina as per the reaction equation:**

$$2Al(OH)_3 \rightarrow Al_2O_3 + 3H_2O$$

What is Bayer process? (2of2)

Principal variants

- **Low temperature digestion (typically 140-150^{o}C) for gibbsitic bauxites**
- **High temperature digestion (typically 240-270^{o}C) for boehmitic/diasporic bauxites**

Substantial progresses have been experienced over the last 130 years, such as capacity of the alumina plants, energy conservation (heat recovery), quality of the product (floury vs sandy, purity), automation, settling/washing, dewatering and disposal of bauxite residue, prevention and removal of scalings, calcination. Nevertheless, the basic principles have not been altered.

The most important features of the chemical reactions

- Reaction equations, stochiometry
- Equilibrium solubilities
- Kinetics (how the reactions proceed in the function of time, preferably along with rate equations)
- Reaction mechanism

Basic reactions of the Bayer process

- **Dissolution reactions of gibbsite and boehmite (digestion)**

$$Al(OH)_3 + OH^- \rightarrow [Al(OH)_4]^- \qquad \text{gibbsite} \quad (1)$$

$$AlO(OH) + H_2O + OH^- \rightarrow [Al(OH)_4]^- \qquad \text{boehmite} \quad (2)$$

- **Dissolution reaction of kaolinite (most important side-reaction)**

$$Al_4(OH)_8(Si_4O_{10}) + 12OH^- + 2H_2O \rightarrow 4[SiO_2(OH)_2]^{2-} + 4[Al(OH)_4]^- \qquad (3)$$

- **DSP (desilication product) formation**

$$6[SiO_2(OH)_2]^{2-} + 6[Al(OH)_4]^- + 20Na^+ + X^{2-} \rightleftharpoons [Na_2O.Al_2O_3.2SiO_2.(1+k)H_2O]_3.Na_2X + 12OH^- + 12Na^+ + (9-3k)H_2O \qquad (4)$$

$X = 2OH^-$, CO_3^{2-}, SO_4^{2-}, $2Cl^-$, $2[Al(OH)_4]^-$, etc. at temperatures 140-160^{o}C, $k = 0 – 1$

- **Crystallization of aluminium hydroxide (precipitation)**

$$[Al(OH)_4]^- \rightarrow Al(OH)_3 + OH^- \qquad (5)$$

Equilibrium solubilities and A/C cycles

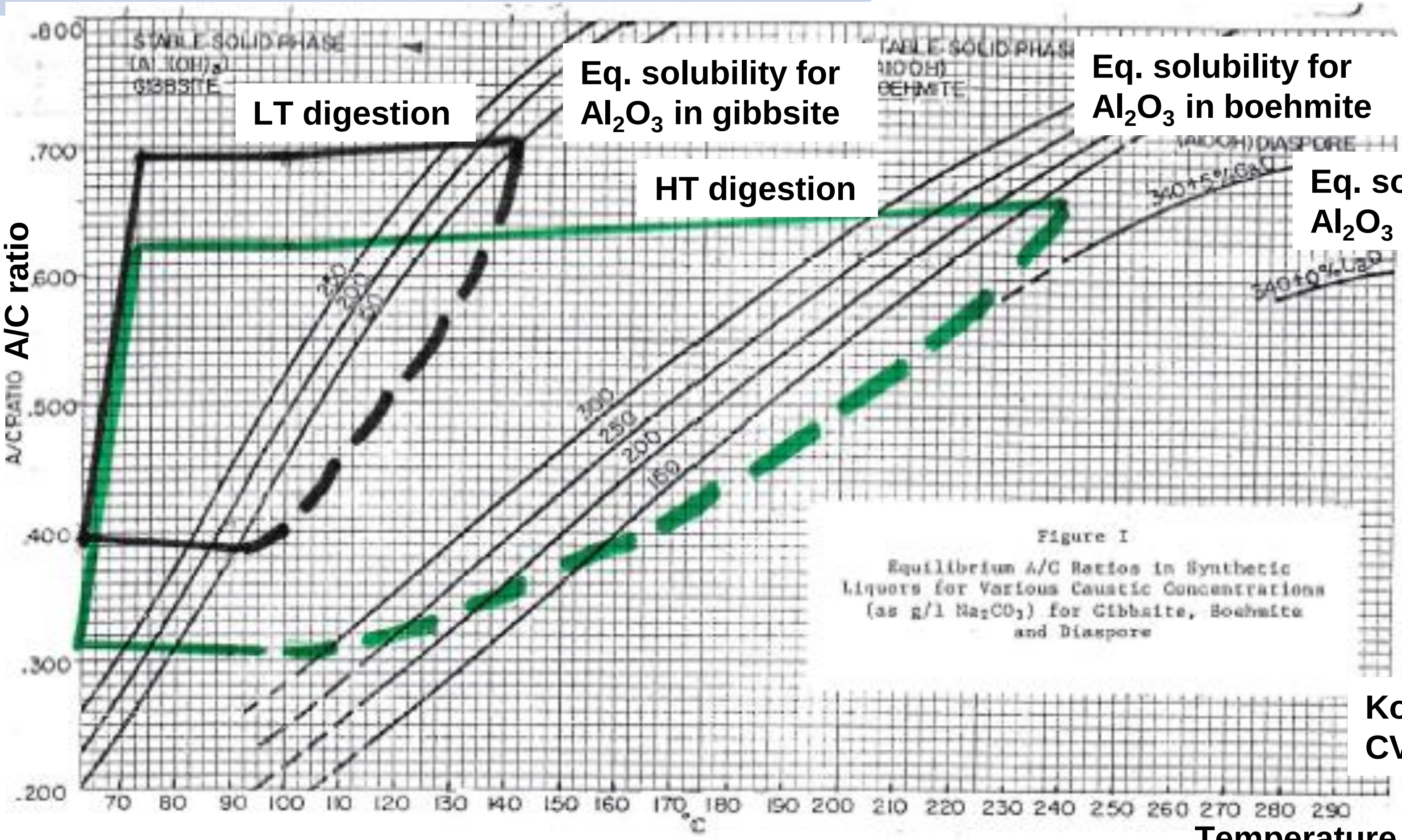


Figure I

Equilibrium A/C Ratios in Synthetic Liquors for Various Caustic Concentrations (as g/l Na_2CO_3) for Gibbsite, Boehmite and Diaspore

LT digestion

Eq. solubility for Al_2O_3 in gibbsite

Eq. solubility for Al_2O_3 in boehmite

HT digestion

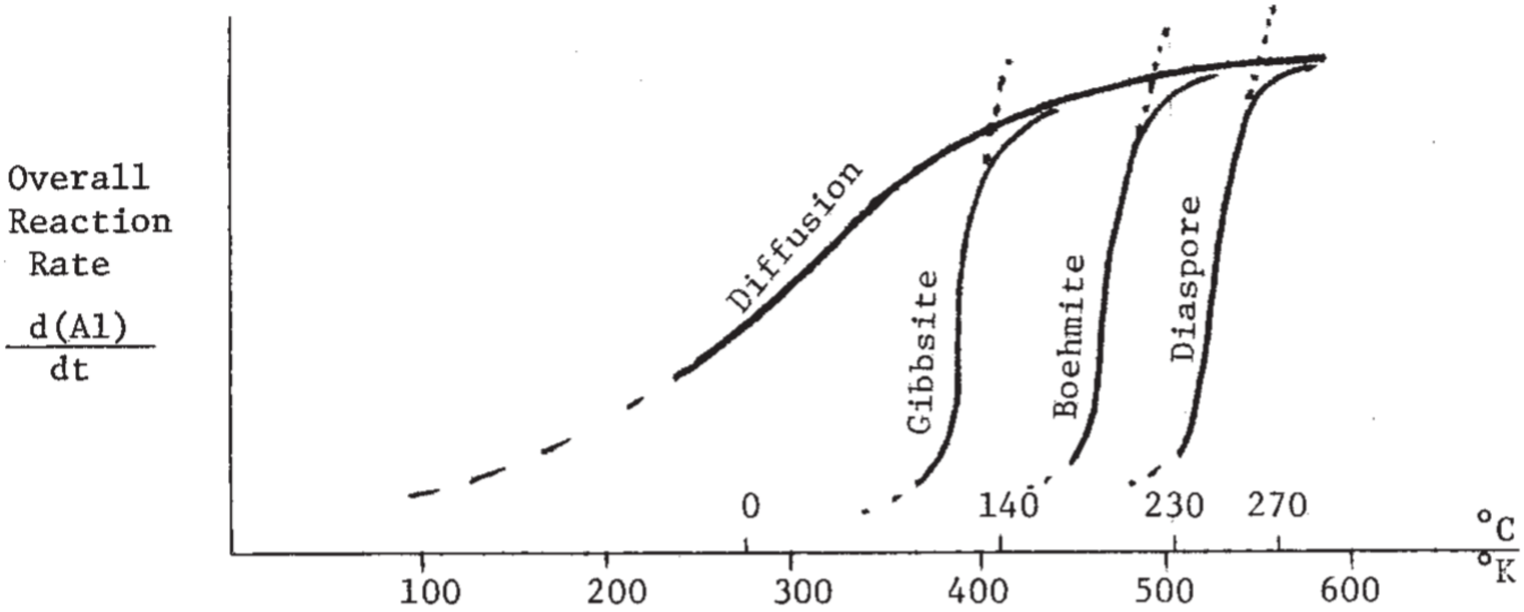
Eq. solubility for Al_2O_3 in diaspore

A/C ratio

Temperature, °C

Kotte, LM 1981,
CVG 1997, Ajka 1990

Dissolution kinetics of gibbsite, boehmite and diaspore



Kotte, LM 1981

Formation of (pseudo-)boehmite

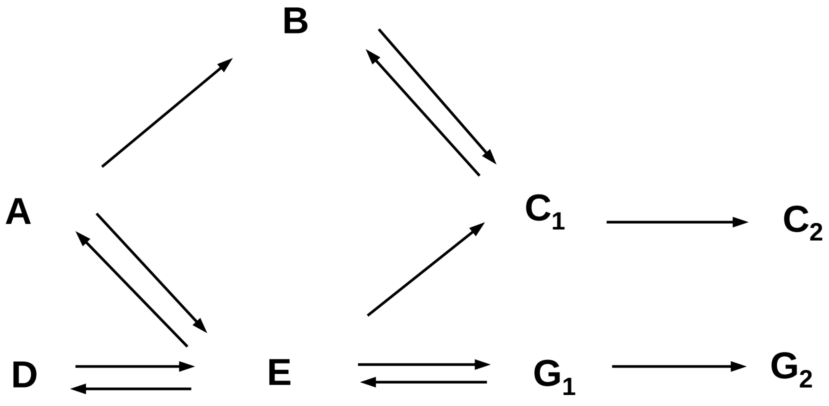
Formation of amorphous boehmite (pseudo-boehmite)

$$[Al(OH)_4]^- \rightleftharpoons AlO(OH)_{(am)} + H_2O + OH^-$$

Transformation of amorphous boehmite (pseudo-boehmite) to crystalline

$$AlO(OH)_{(am)} \rightarrow AlO(OH)_{(cr)}$$

A comprehensive reaction mechanism for dissolution of gibbsite, formation of DSPs and (pseudo-)boehmite



Where

A - SiO_2 in kaolinite

B - SiO_2 in Na-silicate

C_1 - SiO_2 in DSP_1 (sodalite)

C_2 - SiO_2 in DSP_2 (cancrinite)

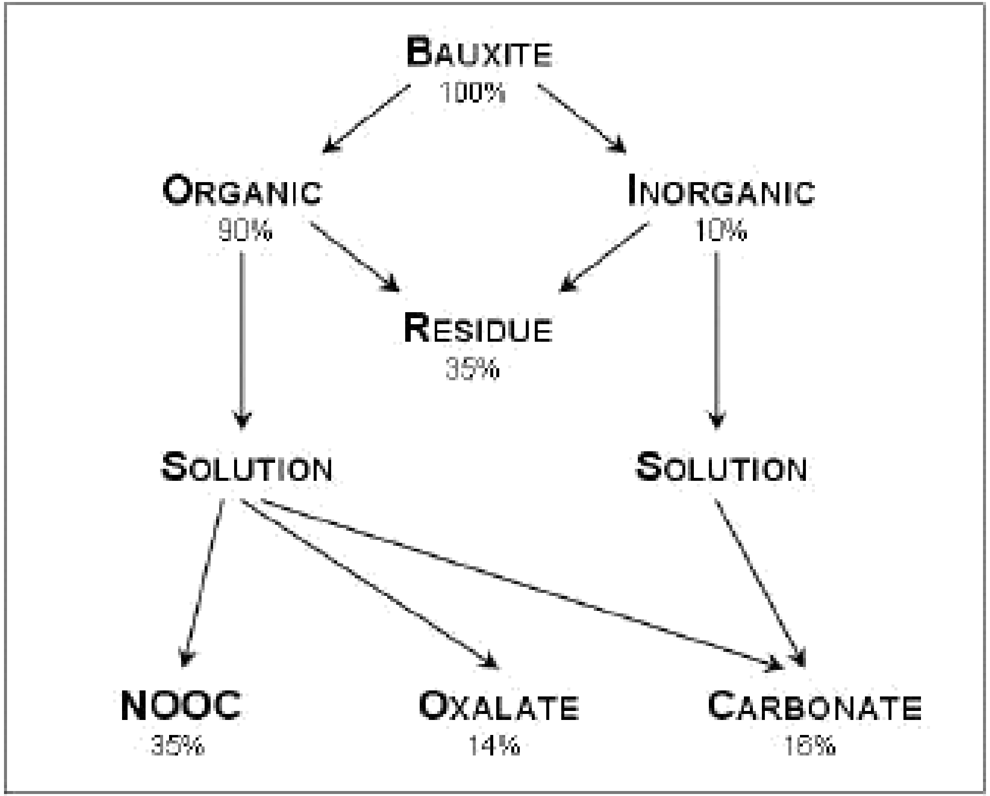
D – Al_2O_3 in gibbsite

E - Al_2O_3 in Na-aluminate

G_1 - Al_2O_3 in (pseudo-)boehmite

G_2 - Al_2O_3 in boehmite

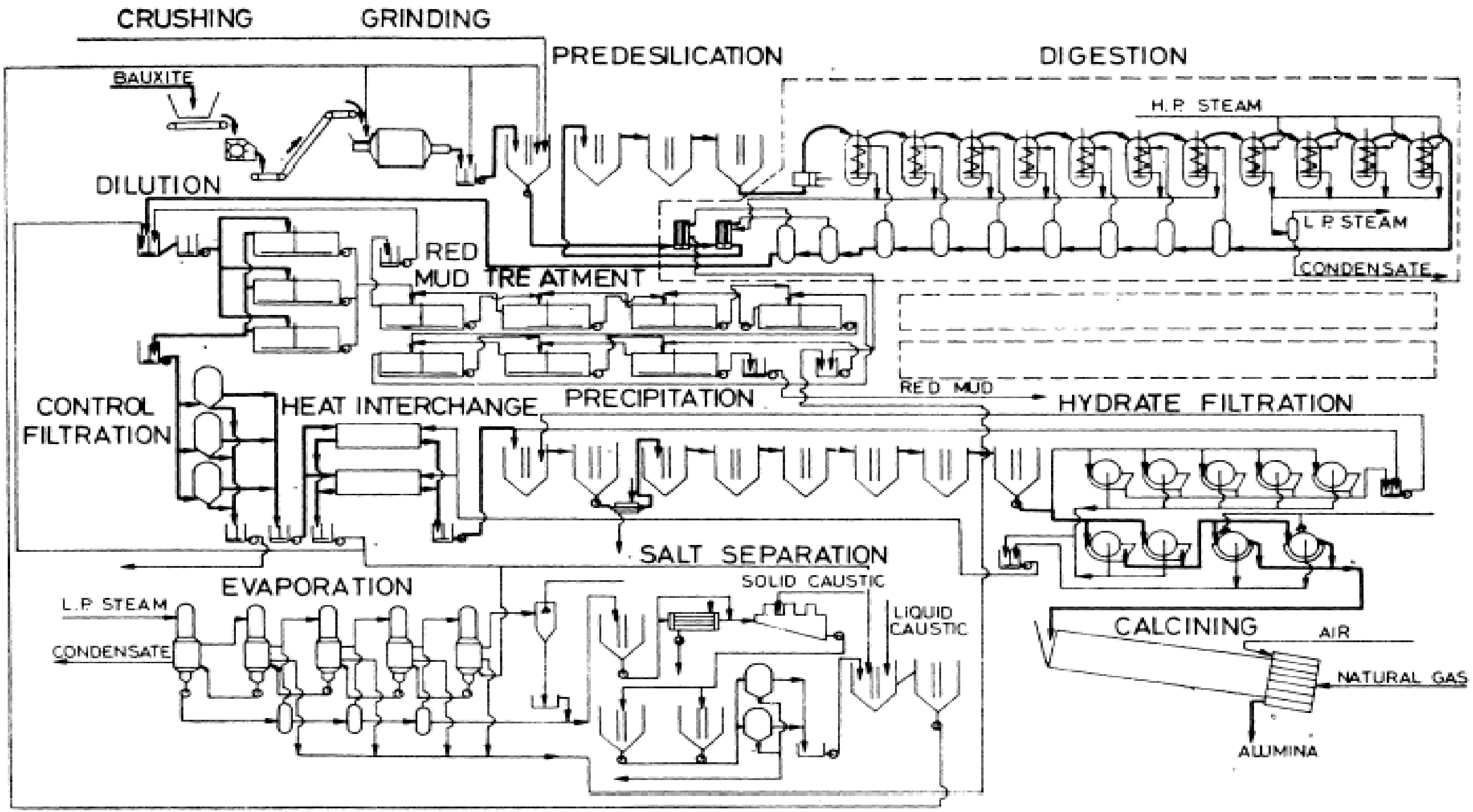
Breakdown of the bauxite carbon content during a low temperature digestion



NOOC – non oxalic carbon

Clegg and Armstrong, AQW, 2005

Process flow diagram of a high temperature Bayer plant



Ajka, 1972, HU

Forward-looking solutions at the Ajka Plant, Hungary

- **No contact heating (eg. predesilication, digestion)**
- **Extensive heat recovery (eg. 9 stage flash cooling in the digestion)**
- **No exotic materials in the HT digestion**
- **Automated Vertical Pressure Filters for the control filtration**
- **No flash cooling for the pregnant liquor (HID), or for the precipitation intermediate cooling**
- **Relatively high liquor productivity in the precipitation (73 kg/m^3)**
- **Disk filters for the filtration of the hydrate**
- **Falling film evaporator (later a Salting out Evaporator was added)**
- **The rotary kilns equipped with effective heat recovery systems for the preheating of the hydrate and air and cooling of flue gas and alumina.**

Increase in the alumina production

The annual alumina production has dramatically increased from the 21 Mtpa in 1970 to 133 Mtpa in 2020 (yearly average nearly 4%).

In the following slides the developments of the last 50 years are indicated with *italicised texts in blue colour*.

Grinding. State of the art in 2020

Two compartment rod-ball mills **have become fairly widespread. Single compartment ball mills can be found in several places. Open or closed circuits. Slurrying only for some lateritic bauxites.**

Predesilication. State of the art in 2020

Gibbsitic bauxites	**Boehmitic/diasporic bauxites**
***introduced in several cases*, preheating of dense slurry by contact heaters, in some cases with indirect preheating.**	***introduced in some cases*, preheating of dense slurry mostly by contact heaters, in some cases with indirect preheating.**

Digestion. State of the art in 2020

Gibbsitic bauxites

140-150°C (170°C) typically double stream digestion, the liquor stream overheated, some % of final heating by contact heating in the 1st autoclave.

Tube digestions with indirect final heating at some places in Japan, China and Vietnam.

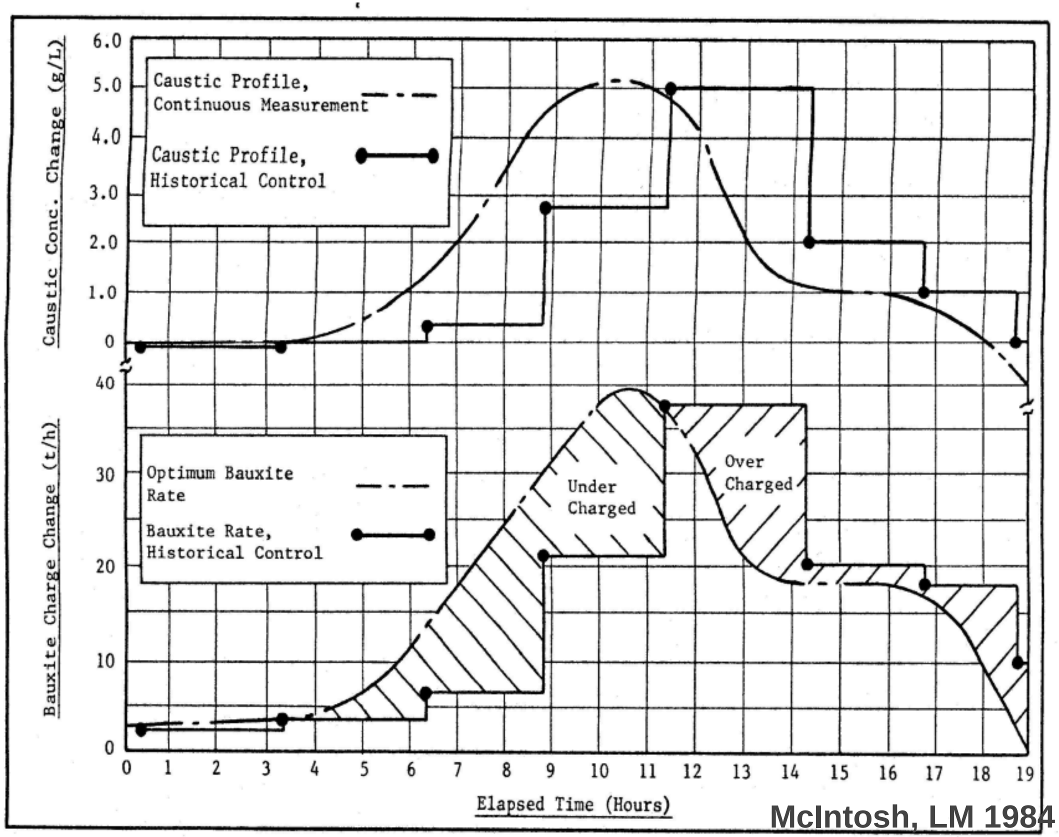
The atmospheric digestion at 108°C is being replaced with low temperature digestion in India.

Boehmitic/diasporic bauxites

240-270°C, double stream digestion, final heating with contact heating, single stream digestion in autoclave trains and *tube digestion, final heating with indirect heating* in most cases. Several places „sweetening process" was introduced. *In some places (in India and US) double digestion for mixed gibbsitic-boehmitic bauxite. With new types of reliable valves the isolation of a part of a digester line has been made possible for cleaning, meanwhile the rest of the line is operable.*

Consequences of bauxite undercharge and overcharge

When bauxite is undercharged, more extractable alumina could have been charged and dissolved. When bauxite is overcharged, part of the extractable alumina is lost, the undissolved alumina comprises seed for secondary alumina losses in the settling and washing. If A/C control was more accurate, the equilibrium solubility could be better approached, the safety margin could be reduced.



McIntosh, LM 1984

Significant improvements in the process control

The safety margin at the digestion A/C ratio control has been reduced from about 0.04 to about 0.005. This allowed to

- **increase the plant production capacity**
- **decrease the specific consumption of bauxite and steam.**

In general, the combination of the feedforward and the feedback control has been proven to be the most accurate.

Separation of bauxite residue (BR), washing of BR. State of the art in 2020

The starch-based flocculants have been replaced with synthetic ones**, settlers of somewhat conical bottom are still widespead at temperatures close to the atmospheric boiling point.**

In several refineries *high rate thickeners (deep cone settlers/washers) have been introduced.* In some refineries in USA and India *pressure decanters have been introduced in connection with the double digestion*.

Alcan *Deep Cone Thickeners*

Dewatering of BR. State of the art in 2020

In several refineries deep cone washers (high rate thickeners) have been introduced at least as last washers. In some refineries in Australia "Superthickeners" were implemented.

There are refineries where *the last washer U/F is submitted* to vacuum drum filtration, *recently rather to press filtration.*

In an exceptional case (Indonesia) Hi-Bar Filters have been introduced for the same service.

Bauxite residue disposal. State of the art in 2020

By 2016 the disposal of BR in sea was ceased. *By 2020 the estimated worldwide amount of dry mud disposal has reached about 50%*, the rest is in ponds. Intensive R&D activities have been carried out for the environment friendly closures of the BRDAs, such as in Australia, India, Jamaica and Ireland.

The amount of accumulated BR globally is more than 4.5 Gt. By now only 2-3 % is being utilized for various purposes, *this rate is expected to grow in medium term*. *Extensive R&D activities are going on with the objective of processing the BR (in Greece, India, Abu-Dhabi/UAE, etc.)*

Lagoon type disposal (red mud pond)

Ganja 2012

Tipping of vacuum drum filtered BR for dry mud stacking

Alunorte, 2005

BR cake from a plate and frame filter

AdG 2008

Remediation of a BRDA without topsoil

Kirkvine Pond 7: November 2007

Kirkvine pond 7: December 2013

Jamaica

Evans-Bánvölgyi, IMFORMED 2019

Encouraging efforts for the extensive use of BR

Increase of the amount of the BR can be seen in clinker raw meal (Hindalco) India and in supplementary cementitious materials, inorganic polymers and hybrid binders ≥ 50-85% at KU Leuven (Belgium), Greece, etc.

Recovery of Ga from BR eg. in Greece and Russia.

Recovery of iron e.g. in China and Russia. The latter rather in the iron ore preparation.

Complex use of BR ≥ 50-100% in UAE, embedded into UAE Green Agenda Compliance (strong support by the Government).

Control filtration. State of the art in 2020

Automated Vertical Pressure Filters have been introduced in several places. Continuously added TCA with optimised particle size distributions has become the common filtration aid and it almost doubled the throughput (per square meters of filter area).

Outdated Kelly filters are rare, but they are still in use in some places.

A Kelly filter

Utah, USA, cc. 1900

An Automated Vertical Pressure Filter

Bokela, BPF

Heat Interchange Department (HID). State of the art in 2020

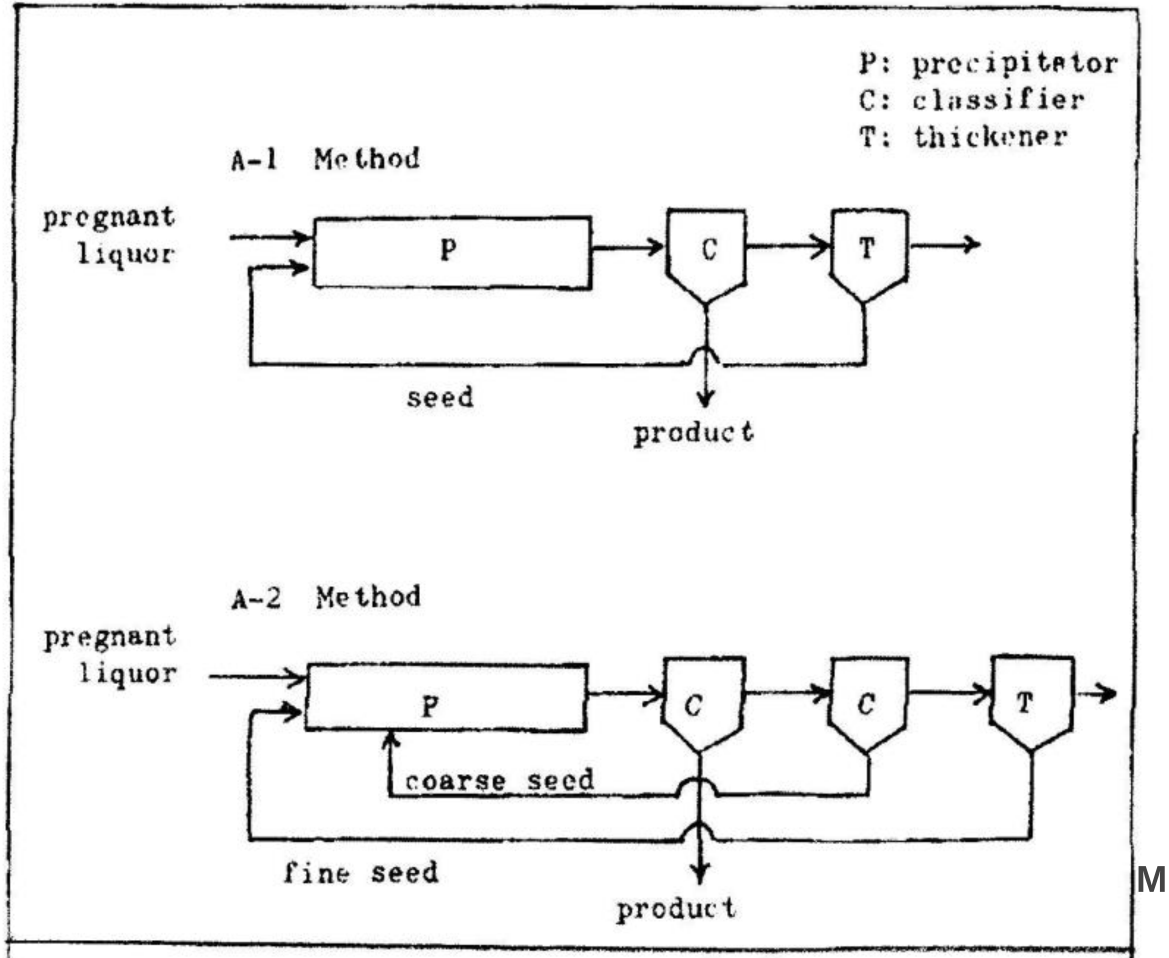
Gibbsitic bauxites

Flash cooling of the pregnant liquor remained widespread.

Boehmitic/diasporic bauxites

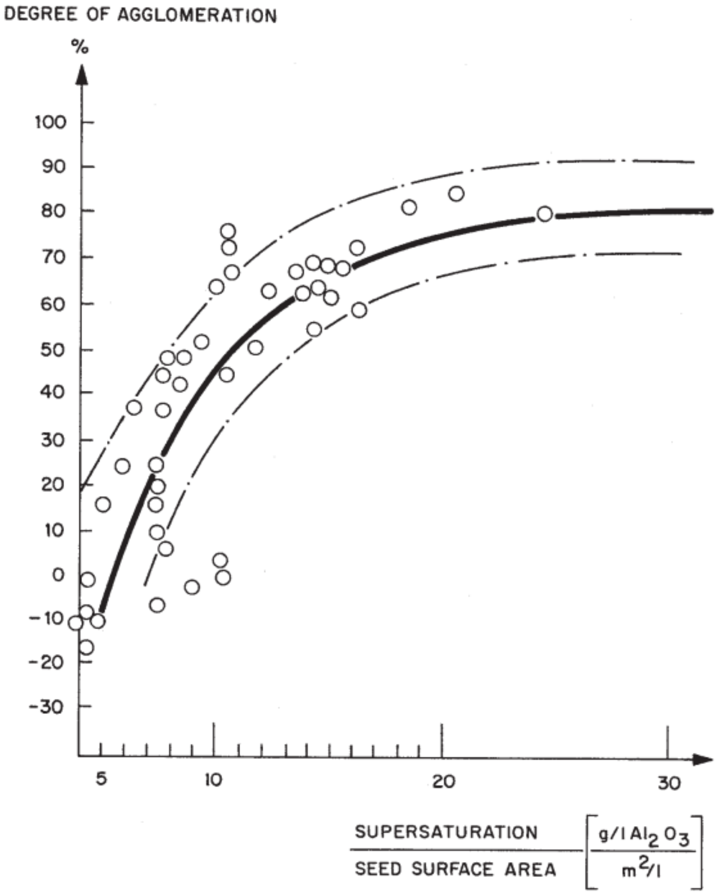
Flash cooling of the pregnant liquor can still be found. ***Several refineries use plate heat exchangers.***

Simplified precipitation scheme



Minai et al. LM1978

Fundamentals of the agglomeration



Tschamper LM 1981

Precipitation. State of the art in 2020

Gibbsitic bauxites

The precipitation circuits have become of continuous operation. The pregnant liquor concentration has increased up to about 265 g/L C, the agglomeration has been intensified. The liquor productivity has been increased from 40-50 kg Al_2O_3/m^3 to about 75-90 kg Al_2O_3/m^3 pregnant liquor. Interstage cooling with welded plate heat exchangers. **The product is sandy type hydrate with** *improved properties. Increased use of crystal growth modifiers.*

Boehmitic/diasporic bauxites

Precipitation circuits use relatively high liquor concentration up to about 275 g/L C, agglomeration then high seed ratio for the crystal growth. *The liquor productivity has increased from 70 to about 75-90 kg Al_2O_3/m^3 pregnant liquor. Interstage cooling with welded plate heat exchangers. The product has shifted from floury to sandy type hydrate (and alumina) with improved properties. Increased use of crystal growth modifiers.*

Hydrate classification and filtration. State of the art in 2020

Gibbsitic bauxites

Primary and secondary hydroseparators are used for the product hydrate and the coarse seed. *In some refineries the hydroseparators and/or hydrate thickeners have been replaced with hydrocyclones.* The product hydrate is filtered and washed on pan filters or belt filters or disk filters. The coarse seed is filtered with disk filters. In several plants two-stage filtration for the fine seed is introduced, Na-oxalate is separated from the dewatered fine seed.

Boehmitic/diasporic bauxites

***In most refineries some sort of hydrate classification was introduced.* The coarsest particles comprise the product hydrate. The fine particles are the seed hydrate for agglomeration. The coarse seed filtered with disk filters is used for crystal growth.**

Evaporation. State of the art in 2020

Gibbsitic bauxites

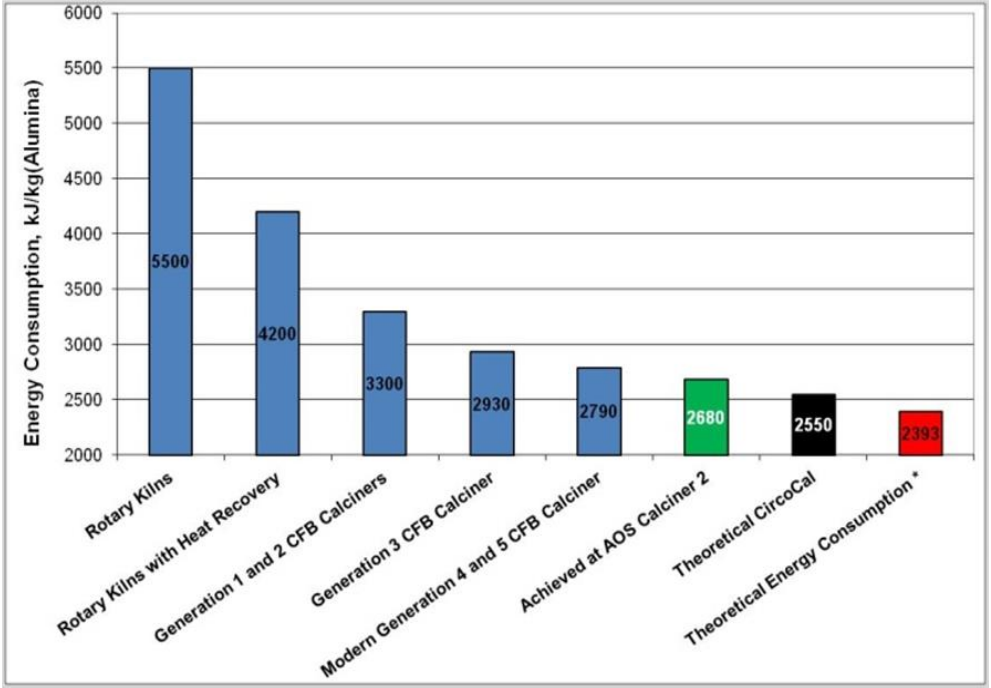
Flash type multi-effect evaporators are typical. In some refineries part of the strong liquor is concentrated further in *salting out evaporators* so that sodium carbonate and sodium organics salts be separated afterwards.

Boehmitic/diasporic bauxites

In quite a few refineries counter-current falling film evaporators (GEA-Kestner) typically with 5 effects are in use. In some refineries part of the strong liquor is concentrated further in *salting out evaporators* so that sodium carbonate and sodium organics salts be separated afterwards.

Calcination. State of the art in 2020

Several rotary calciners are still in use with different sorts of heat recovery system. ***The new calciners are stationary ones with significantly less primary heat consumption*****.**



The primary heat consumptions of different types of calciners.

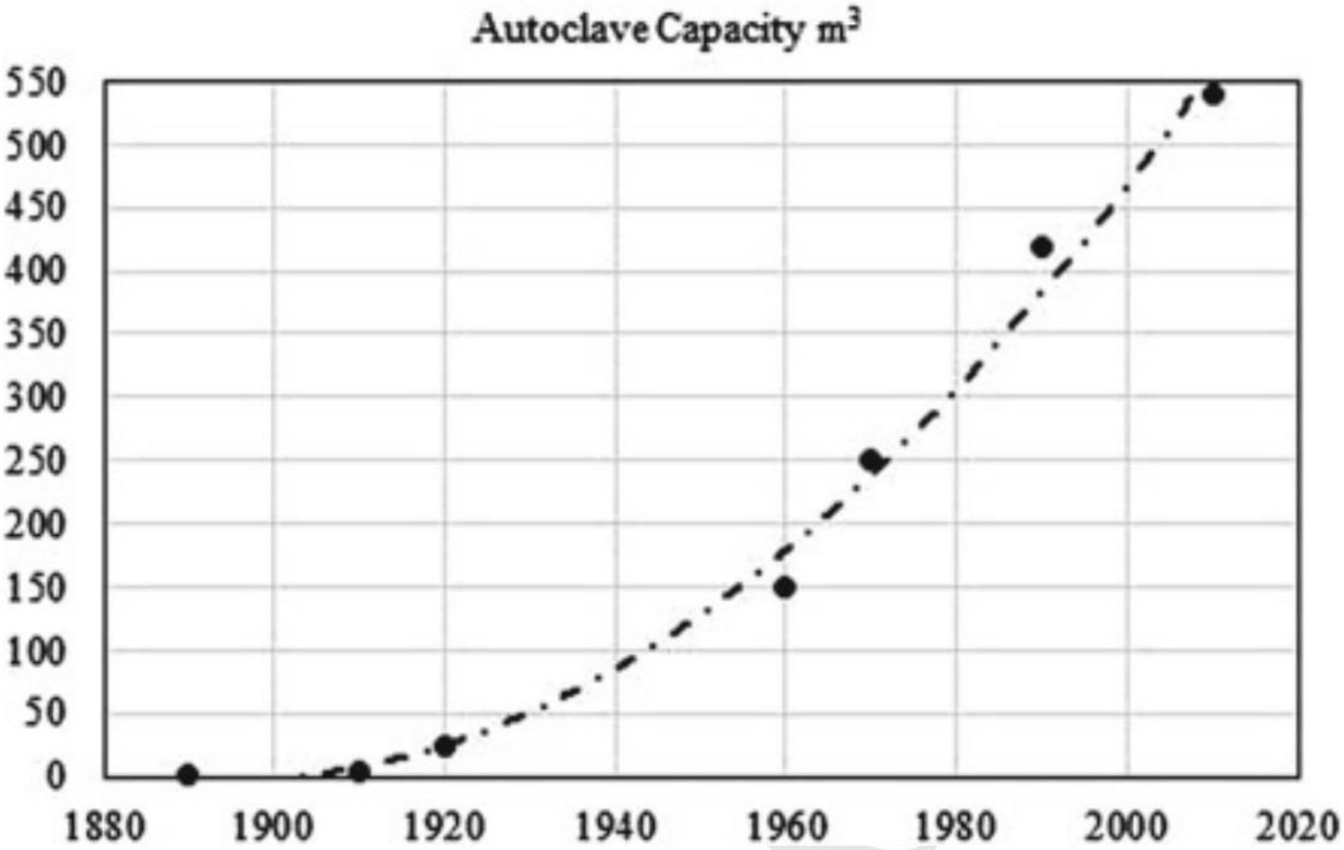
Metson, LM 2022

Evolution of the Bayer unit capacity

The Bayer unit capacity has evolved from about 600-800 ktpa to about 1500-2000 ktpa, however, most refinery use not more than about 1300 ktpa.

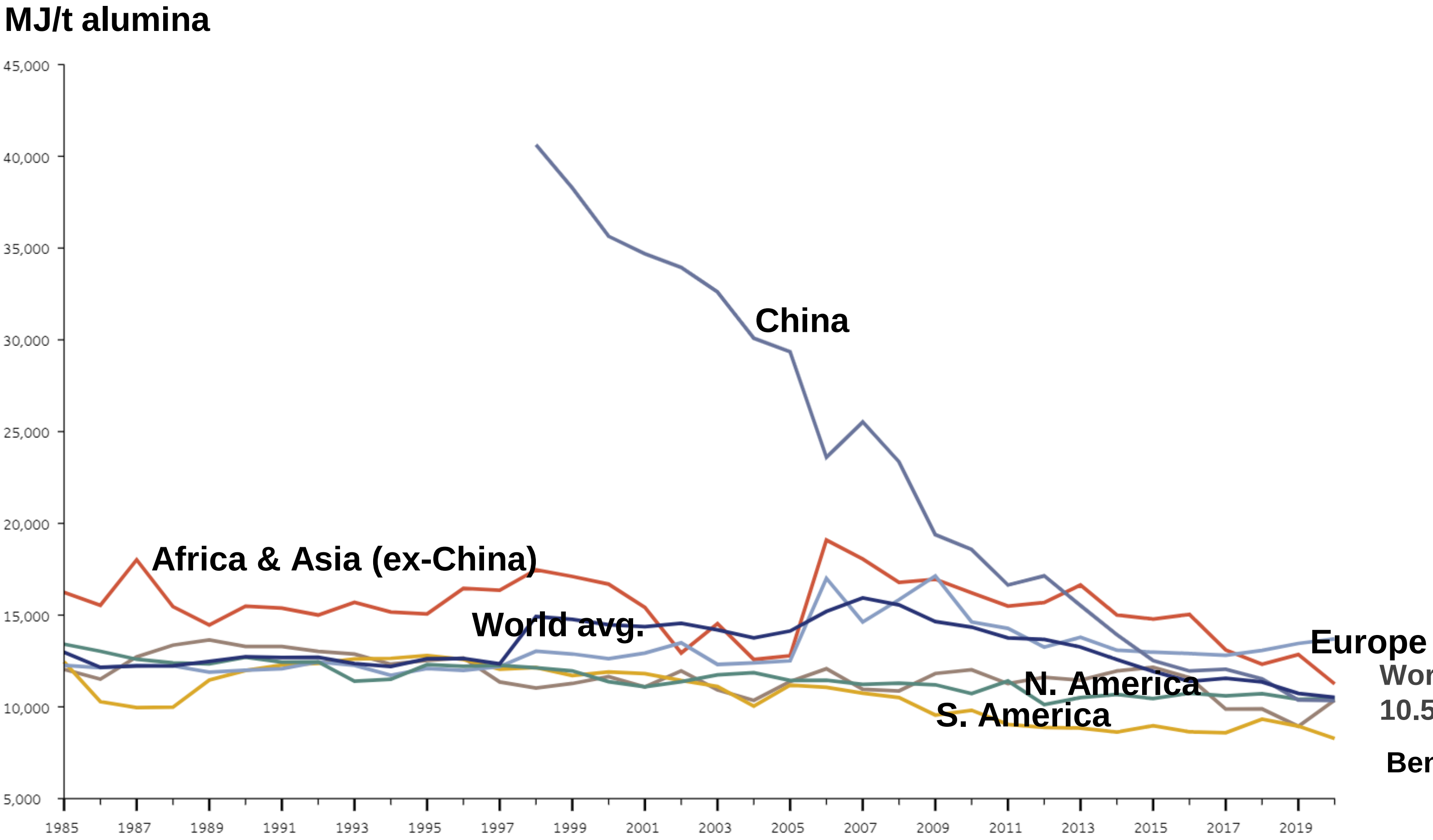
There are alumina refineries with production capacities of about 4 Mtpa, even one wih 6.3 Mtpa capacity (Alunorte, Brazil). The latter consists of 5 production lines, 1250 ktpa average. The power plant is being converted from heavy fuel oil to natural gas. ***Very recently an electric boiler has been implemented. The next anticipated stage is conversion of primary fuel to hydrogene. (Going for the „green alumina".)***

Evolution of principal equipment



B. Hanemann_'Smelter Grade Alumina from Bauxite', Chapter 4_Springer, 2022

Evolution of refinery energy consumptions



World average 2020: 10.5 GJ/t

Benchmark: 7.5 GJ/t

IAI, 2020

Outlook for the next 20 years

Further reduction of the process liquor impurities.

Higher precipitation liquor productivity, probably 90-100+ kg/m^3.

Exhaustion of several „easy access” high quality bauxite deposits, extensive processing of „more difficult” ores such as sub-economic ones.

Closures of plants in USA and Europe, move prodn eg. to China.

Significantly less NaOH consumptions, further decrease of energy consumption, move to „green power”.

Higher level of process control, more reliable sensors.

The bauxite residue becomes a by-product, not a hazardous waste, will be processed further in increasing quantities.

The BR will not be disposed of in ponds any more.

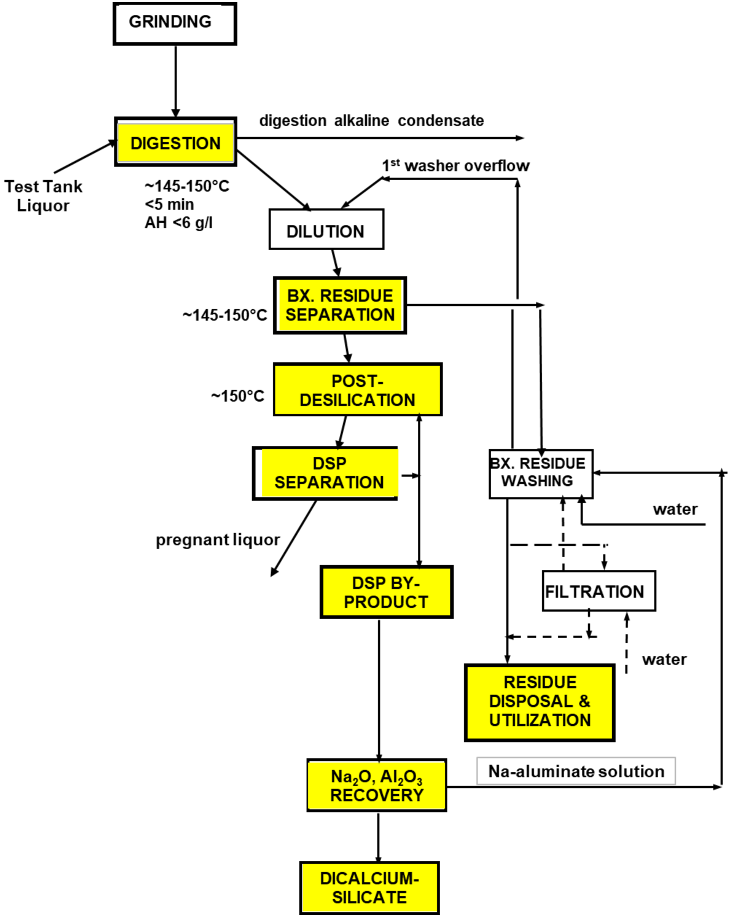
Minimum make up water, zero effluent discharge

The reduction of the make up water and the effluent discharge(s) have been objectives of the research and development for several years. These goals are to be considered along with the other unit operations. The more perfect of the washing and dewatering of BR the more difficult to achieve low level of contaminants in the process liquor.

Other objectives are the substantial reduction of the chemically combined soda content and moisture in BR, the higher utilisation rate of BR, consequently the less amount of BR to be disposed of, possibly none.

A novel process route: the updated ILTD Process

A possible way to process even subeconomic bauxites and similar materials is the updated Improved Low Temperature Digestion (ILTD) Process



GRINDING

DIGESTION

digestion alkaline condensate

Test Tank Liquor

~145-150°C
<5 min
AH <6 g/l

1st washer overflow

DILUTION

~145-150°C

BX. RESIDUE SEPARATION

~150°C

POST-DESILICATION

DSP SEPARATION

BX. RESIDUE WASHING

water

pregnant liquor

FILTRATION

DSP BY-PRODUCT

water

RESIDUE DISPOSAL & UTILIZATION

Na_2O, Al_2O_3 RECOVERY

Na-aluminate solution

DICALCIUM-SILICATE

Highlighted in yellow: modifications for the ILTD Process from CLTD

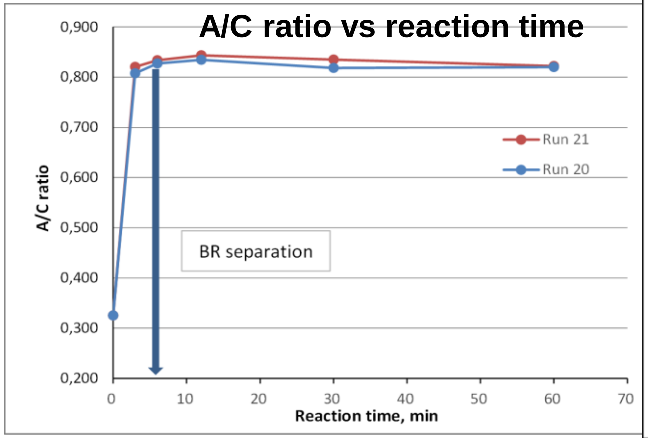
Bánvölgyi ICSOBA 2021

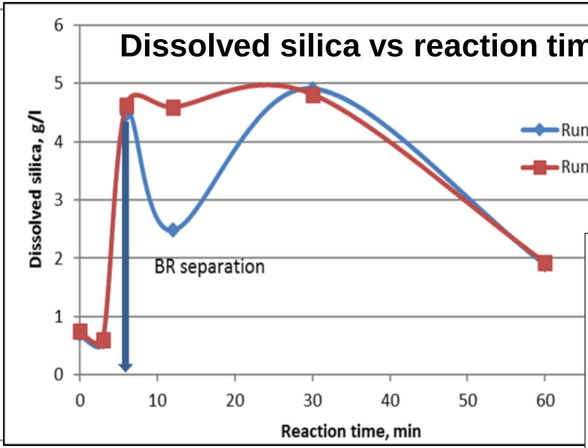
ILTD bench scale kinetic tests 1of2

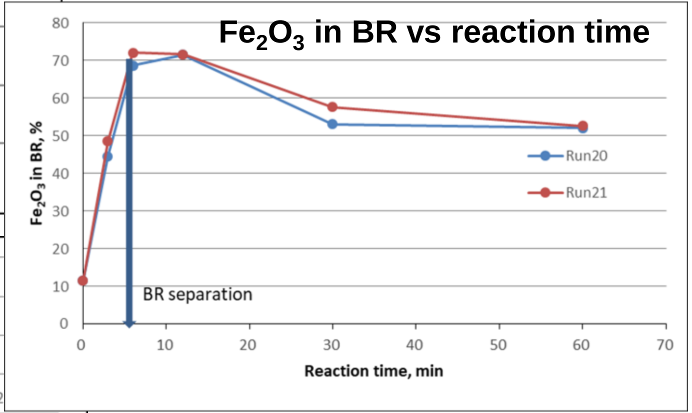
<u>Conditions</u>

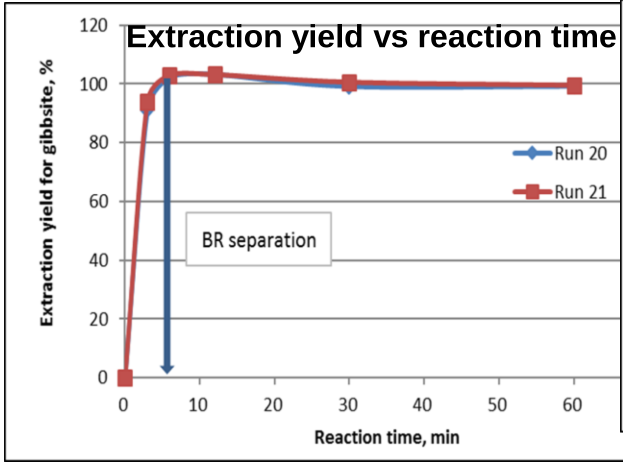
- Feedstock: Trombetas bauxite
- Physical modeling of the two-stream digestion
- 150°C digestion temperature (130-<u>150°C</u>)
- Achieved A/C ratios ≥ .83
- Repeated digestion tests
- Fairly vigorous agitation (rpm <u>200/min</u> and 400/min)
- Equilibrium A/C ratios by the equation of Siklósi
- Reference of Runs 20 and 21: G. Bánvölgyi, P. Siklósi, The Improved Low Temperature Digestion (ILTD) Process: an Economic and Environmentally Sustainable Way of Processing Gibbsitic Bauxites. Light Metals 1998, reprinted in the “Essential Readings in Light Metals, Vol. 1, Alumina and Bauxite”, TMS - Springer, 2016

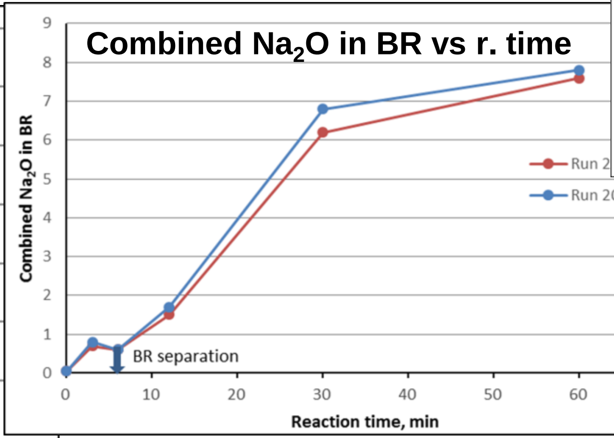
ILTD bench scale kinetic tests 2of2


A/C ratio vs reaction time


Dissolved silica vs reaction time


Fe_2O_3 in BR vs reaction time


Extraction yield vs reaction time


Combined Na_2O in BR vs r. time

Compositions of aluminous laterite, BRs, DSP and C_2S

			Conventional LTD Process	Updated ILTD Process (with Na_2O, Al_2O_3 recovery from DSP)		ILTD Process (no Na_2O, Al_2O_3 recovery from DSP)	
		Eastern Ghats aluminous laterite	Bauxite residue (BR)	Low soda bauxite residue	C_2S (belite)	Low soda bauxite residue	DSP, CO_3^- sodalite
Compositions	%			by-product	by-product	by-product	by-product
Al_2O_3 (Total)	%	38.2	13.4	10.9		10.9	28.7%
av. Al_2O_3 (145°C)	%	30.8	1.0	0.5		0.5	
Al_2O_3, in boehmite	%	0.9	1.4	1.7		1.7	
Al_2O_3, in diaspore	%	0.0	0.0	0.0		0.0	
SiO_2 (Total)	%	6.7	10.8	7.7	34.9%	7.7	33.8%
r.SiO_2 in bx, r. SiO_2 and SiO_2 in DSP	%	5.6	9.0	5.5		5.5	
Fe_2O_3	%	33.10	53.5	65.2		65.2	`~0.1%
TiO_2	%	1.9	3.1	3.7		3.7	
Na_2O	%	0.0	6.3	1.2		1.2	23.3%
CaO	%	0.01	0.8	1.0	65.1%	1.0	
C_{org}	%	0.11	0.0	0.0		0.0	
Other constituents	%	0.66	1.1	1.3		1.3	
LOI (calculated/estimated)	%	19.29	11.0	9.0		9.0	14.3%
Total		100.0	100.0	100.0	100%	100.0	100.0%
Amounts, dry matter	t/ta	3.68	2.28	1.57	0.25	1.67	0.27

M&E cost savings from Base Case

		Base case		Updated ILTD process		ILTD process	
	Unit prices	Conventional Low Temp Digestion process		ILTD Process (with Na_2O, Al_2O_3 recovery from DSP)		ILTD Process (no Na_2O, Al_2O_3 recovery from DSP)	
	USD/t	Specific consumptions	USD/t_a	Specific consumptions	USD/t_a	Specific consumptions	USD/t_a
Wet bauxite, t/ta	20	3.96	79.2	3.32	66.5	3.54	70.8
NaOH, t/ta	370	0.223	82.6	0.064	23.7	0.140	51.8
CaO for digestion+security filtr., t/ta	100	0.039	3.9	0.033	3.3	0.034	3.4
$CaCO_3$, for DSP sintering, t/ta	30	0.00	0.0	0.288	8.7	0.00	0.0
Coal for sintering, t/ta	65	0.00	0.0	0.042	2.8	0.00	0.0
Process steam, t/ta	20	2.20	44.0	1.93	38.5	1.93	38.5
BR disposal (70% for ILTD), t/ta	7.5	2.28	17.1	1.10	8.2	1.17	8.8
Low Soda BR for sale (30% for ILTD	-5	0.00	0.0	0.47	-2.4	0.50	-2.5
C_2S for sale, t/ta	-20	0.00	0.0	0.248	-5.0	0.00	0.0
DSP for sale, t/ta	-35	0.00	0.0	0.00	0.0	0.27	-9.6
		Sum of items	226.7	Sum of items	144.3	Sum of items	161.2
M&E Cost savings, from Base Case				Savings	-82.3	Savings	-65.5

Commercial scale references of principal units of ILTD Process

- **The largely equivalent solution with the ILTD digestion operated in the Sumitomo alumina refinery for 7 years**
- **The pressure decanter has been in operation in three refineries (two in India and 1 in the USA) and was in operation in two more places (Japan and Australia)**
- **The Hi-Bar filters have been in operation in other industries at temperatures up 160ºC**
- **The seeded pressure desilication has been (or was) in operation where the sintering process has been (or was) used for decades in about 12 refineries**
- **The sintering process which is suitable for the viable processing of the DSP by-product of the ILTD Process has been (or was) in operation for decades in about 12 refineries.**

Status of the updated ILTD Process

✓Material and energy costs savings: about 15-40%

✓Payback period: about 1.5 years (result of a recent Case Study for a 1.5 Mtpa capacity alumina refinery)

✓Economic viability – proven

✓All major steps on a commercial scale – proven

✓Process concept – ready for commercialization

Bánvölgyi, ICSOBA 2021

Closing remarks

The updated ILTD Process might be the most viable process route of the future alumina production where bauxite reserves, subeconomical bauxite resources and aluminous laterites would comprize the feedstock ores. The aggregated amount of the feedstock materials is at least double of the bauxite reserves.

The updated ILTD Process is matured for the commercialization starting with the pilot scale implementation.

Recovery of Na_2O and Al_2O_3 from the DSP by-product boosts the viability of the updated ILTD Process. This option makes recoverable substantial portion of Al_2O_3 which originally is in kaolinite in bauxite and rightfully not considered soluble by the conventional Bayer process.

Thank you for your attention.

Questions, comments are welcome.