

BUREAU DE RECHERCHES GÉOLOGIQUES ET MINIÈRES
DIRECTION DES RECHERCHES ET DU DÉVELOPPEMENT MINIERS
Mission Arabie Saoudite

CONFIDENTIEL

A DOCUMENTARY STUDY ON ALUMINA EXTRACTION PROCESSES

by

G. BAUDET



SERVICE GÉOLOGIQUE NATIONAL

Département minéralurgie
B.P. 6009 – 45018 Orléans Cédex – Tél.: (38) 63.00.12

77 SGN 061 MIN

Février 1977

A B S T R A C T

A documentary study on alumina extraction processes from materials other than high grade bauxite ores, has been carried out at the request of the B.R.G.M. mission in Saudi Arabia.

Processes which are applicable to alumino silicates and related materials (high silica, high iron bauxites), have been exclusively considered in this study. Because of the lack of large low-silica bauxite and alunite deposits in Saudi Arabia, alumino silicates represent the alternative raw material for alumina production ; two large deposits are known : Dhurma Shales, containing about 27 % Al_2O_3 and Yanbu anorthosites containing about 22 % Al_2O_3 .

This documentary study takes into account alumina extraction processes which have been developed beyond laboratory scale and which can be carried into industrial practice, in a short period of time.

These processes can be subdivided in two groups :

- acid processes which are suitable for "acid" alumino silicates like clays or shales,
- basic processes which are applicable to both "acid" and "basic" alumino silicate rocks like clays, shales, feldspars, nephelites-syenites and a large variety of igneous rocks.

Among the acid processes, the H^+ process from Pechiney-Ugine Kuhlman, presents the lowest energy requirements (about 8,000,000 kcal per ton of alumina), the highest alumina yields (about 90 %), and its technical development at pilot plant scale is the most advanced with respect to the other acid processes which are under development at the present time. Chemical composition of Dhurma shales: low ferrous iron, CaO, MgO, Na_2O and organic matter contents are quite favourable for the H^+ process. Potentially valuable iron oxide and potassium sulfate are produced along with alumina.

Among the basic processes, those involving sintering of the alumina bearing raw material with limestone, limestone + soda ash, and optionally carbon appear to be applicable to Dhurma shales. Large quantity of Portland cement must be

produced along with alumina (about 12 t per ton of alumina), to make the process economically feasible ; it requires about 4.5 tons of shale, 15 tons of limestone and 40,000,000 kCal.

High energy and raw material consumptions for producing alumina alone, make the process unfeasible.

The suitability of a basic process for Yanbu anorthosite treatment is less certain because of the low alumina content and lack of large limestone reserves near the anorthosite deposit.

S U M M A R Y

pages

Abstract

Introduction 1

A DOCUMENTARY STUDY ON ALUMINA EXTRACTION PROCESSES

Part I : Basic processes applied to alumino silicate and high silica - high iron containing bauxites 2

1. PROCESSES INVOLVING SINTERING 4

1.1. Lime sinter process applied to nephelines 4

111. Grinding and mixing 4

112. Sintering 4

113. Leaching 7

114. Desilicification 9

115. Carbonation 17

116. Cement production 19

117. Economic evaluation 21

1.2. The lime soda sinter process 25

1.3. The lime sinter processes (self disintegration processes) 32

131. The Grzymek process 33

132. Evaluation of the lime sinter process in U.S.S.R. 37

133. Lime sinter processes applied to clays in U.S.A. 41

134. The "Seailles" - "Ciments Français" processes 47

1.4. The lime sinter process with a reducing agent 52

1.5. The lime-soda sinter process with a reducing agent 53

2. HYDROMETALLURGICAL PROCESSES 55

2.1. The Ponomarev-Sazhin process 55

211. Leaching 55

212. Regeneration of alkalis 56

213. Utilization of the solid residue 56

214. Other applications of the process 57

2.2. <u>The Manvelyan process</u>	57
3. <u>BAYER-SINTERING SEQUENTIAL METHOD (AND COMBINED HYDROCHEMICAL TREATMENTS)</u>	58
3.1. <u>Bayer-sintering method</u>	58
311. Alkaline pressure digestion	58
312. Sintering	58
3.2. <u>Combined hydrochemical treatments</u>	59
4. <u>PROCESSES INVOLVING ELECTROSMELTING - BLAST FURNACE - OR TUBULAR FURNACE SMELTING</u>	61
4.1. <u>The Pedersen process</u>	61
4.2. <u>The Seailles process, applied to blast furnace slags</u>	61
4.3. <u>Other miscellaneous processes</u>	61
431. Treatment of blast furnace slags	61
432. Treatment of high silica bauxites	63
433. Treatment of red muds	65
5. <u>TECHNICAL EVALUATION OF LIME SINTER AND LIME SODA SINTER PROCESSES</u>	69

°°

<u>PART II : Acid processes applied to alumino silicates</u>	72
1. <u>NITRIC ACID - ION EXCHANGE PROCESS</u>	73
1.1. <u>Calcination of the clay</u>	73
1.2. <u>Nitric acid leaching</u>	73
1.3. <u>Ion exchange extraction of iron</u>	73
1.4. <u>Crystallization of aluminium nitrate nonahydrate</u>	74
1.5. <u>Decomposition of aluminium nitrate nonahydrate</u>	74
1.6. <u>Reduction of the concentration of the nitrates of impurities in the mother liquor</u>	74
1.7. <u>Acid recovery</u>	74

1.8. <u>Basic consumption figures for the nitric acid-ion exchange process</u>	76
2. <u>HYDROCHLORIC ACID ION EXCHANGE PROCESS</u>	77
2.1. <u>Calcination of the clay</u>	77
2.2. <u>Leaching with hydrochloric acid</u>	77
2.3. <u>Iron removal from chloride solution</u>	77
2.4. <u>Crystallization of aluminium chloride hexahydrate</u>	77
2.5. <u>Recovery of the hydrochloric acid</u>	78
2.6. <u>Basic consumption figures for the hydrochloric acid ion exchange process</u>	80
3. <u>THE H⁺ PROCESS</u>	81
3.1. <u>Clay preparation</u>	81
3.2. <u>Sulfuric acid digestion</u>	81
3.3. <u>Primary liquid-solid separation</u>	83
3.4. <u>Counter current water washing of the solid residue</u>	83
3.5. <u>Recovery and separation of the impurities</u>	83
3.6. <u>Separation and purification of the alumina</u>	84
361. <u>Crystallization of aluminium sulfate</u>	84
362. <u>Crystallization of the aluminium chloride hexahydrate</u> ..	84
3.7. <u>Recovery of the acids</u>	84
3.8. <u>Recovery of alumina and hydrogen chloride</u>	85
3.9. <u>Main features of the H⁺ process</u>	85
391. <u>Hot sulfuric acid digestion</u>	85
392. <u>Sulfuric acid</u>	85
393. <u>The selective precipitation of AlCl₃, 6 H₂O</u>	85
394. <u>The acids H₂SO₄ and HCl</u>	85
395. <u>Silica, calcium compounds</u>	85
396. <u>The sodium concentration</u>	86
397. <u>The acids are recycled</u>	86

3.10. <u>Relations between the raw-material characteristics and the H⁺ process</u>	86
3.11. <u>Development of the H⁺ process at the Pechiney company</u>	87
3.12. <u>Evaluation of available raw materials in Saudi Arabia on account of the H⁺ process</u>	89
3.13. <u>Rough evaluation of the H⁺ process</u>	90
4. <u>COMPARISON OF VARIOUS ACID PROCESSES</u>	91
5. <u>THE TOTH PROCESS</u>	93
5.1. <u>Stage_1</u>	93
5.2. <u>Stage_2</u>	93
5.3. <u>Stage_3</u>	93
5.4. <u>Stage_4</u>	94
Conclusion	96
References	103
Appendix : list of patents related to alumina extraction processes from non bauxite ores	116

° °

I N T R O D U C T I O N

A documentary study on alumina extraction processes has been carried out taking into account the will which has been expressed to develop as fast as possible an aluminium industry in Saudi Arabia.

Processes the development of which has reached the pilot plant or continuous bench scale trial stages were selected in this report so that the industrial implementation might be carried out in a short period of time.

A large number of processes have been devised to extract alumina from various materials, but most of these were not developed beyond the laboratory scale [*see patents and references in appendix*].

The lack of high grade bauxites in Saudi Arabia draw attention to alternative alumina raw materials. Large alunite ore deposits have not been found so far in Saudi Arabia, whereas huge alumino silicate deposits containing more than 20 - 25 % Al_2O_3 (anorthosite - shales) are known. Processes which are suitable for these ores have been exclusively considered in this study.

A DOCUMENTARY STUDY ON ALUMINA EXTRACTION PROCESSES

PART I :

Basic processes applied to alumino silicate and high silica -
high iron containing bauxites

Basic processes can be subdivided to four groups :

GROUP n° 1

Processes involving sintering of the alumina bearing raw material with :

- limestone
- or - limestone + carbon
- or - limestone + soda ash
- or - limestone + soda ash + carbon.

All these processes are derived from the french SAINTE-CLAIRE-DEVILLE process (the soda ash sinter process), which was the first industrial preparation of alumina. A mixture of bauxite and soda ash was sintered at 1000-1100° C, the sinter was leached with water, and the solid residue separated from the sodium aluminate solution. Alumina was precipitated by carbonation ; concentration of the pregnant solutions allowed the soda ash to be recycled to sintering.

GROUP n° 2

Hydrometallurgical processes.

Alumino silicates are subjected to pressure leaching in autoclaves with concentrated soda solutions containing lime at about 300° C. This process is under development in U.S.S.R.

GROUP n° 3

Bayer-sintering sequential method.

A siliceous bauxite is treated by the conventional Bayer process. The red mud or solid residue from the alkaline pressure digestion is mixed with lime and soda ash and sintered so as to recover the chemically

bound alumina contained in the mud. Most of the alumina is directly recovered from the alkaline liquor.

GROUP n° 4

Processes involving electrosmelting,

of a mixture of the alumina bearing material containing large amounts of iron compounds, with carbon and limestone. Alumina is recovered from the slag by alkaline leaching, cast iron is produced along with alumina.

All these processes are derived from the Pedersen process, developed in Norway.

1. PROCESSES INVOLVING SINTERING

When sintering aluminosilicates with soda ash alone (Sainte-Claire-Deville process), silica is bound to alumina and soda, forming an insoluble compound having the following approximate formula : $\text{Na}_2\text{O}, \text{Al}_2\text{O}_3, 2 \text{SiO}_2$, thus no alumina could be extracted from raw materials with low $\frac{\text{Al}_2\text{O}_3}{\text{SiO}_2}$ molar ratios ($< 0,5$) for instance : kaolinite and other miscellaneous clays, anorthosite, nephelite, etc...

Limestone thoroughly or partially replacing soda ash, combines with silica to form dicalcium silicate, a low solubility compound in alkaline solutions; alumina combines with soda or lime to form sodium aluminate or calcium aluminate which are soluble in alkaline solutions.

Alumina is extracted from the sinter by alkaline leaching, leaving a dicalcium silicate residue.

Dissolved silica is precipitated from the aluminate solution by heating or lime addition..

The desilicified aluminate solution is subjected to carbonation so as to separate hydrated alumina. The hydrated alumina is calcined to produce α -alumina. The processes involving sintering can be applied to a great variety of raw materials assaying more than 25 - 28 % Al_2O_3 among them :

clays - alkali feldspars - anorthite - shales - mine wastes fly ash - (brown coal ash) - siliceous bauxites - nephelines phonolites, etc...

They are described in detail in the following paragraphs.

1.1. LIME SINTER PROCESS APPLIED TO NEPHELINES.

Nepheline ($\text{Na}, \text{K})\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 2 \text{SiO}_2$), the theoretical composition of which is : 34,2 % Al_2O_3 - 40,3 % SiO_2 - 25,5 % $\text{Na}_2\text{O} + \text{K}_2\text{O}$, is extensively used in USSR as a raw material for alumina production [see paragraph 5],

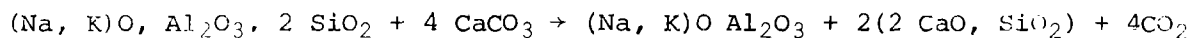
it can be estimated that about 2 million tons of alumina [28,41] are produced in three plants located in the Kola Peninsula and in Central Siberia [28,2-76]. A flowsheet is presented in figure 1 [73].

111. Grinding and mixing.

Ground flotation concentrates assaying 28 to 31 % alumina [28,73] are mixed with finely ground limestone (minus 100 μm to minus 74 μm) so as to form dicalcium silicate during sintering ($\frac{\text{CaO}}{\text{SiO}_2} = 2,14$ $\frac{\text{R}_2\text{O}}{\text{R}'_2\text{O}_3} = \text{about } 1$ at the Volkhov alumina plant [3]).

112. Sintering.

The charge is sintered in rotary kilns at a maximum temperature of about 1215 - 1275° C [27, 28, 1]



Due to high alkali ($\text{K}_2\text{O} - \text{Na}_2\text{O}$) content of the charge the β form of 2 CaO, SiO₂ is stabilized and self disintegration does not take place.

The quality of sinters is determined by porosity measurements [4] in - 20 + 1 mm or - 10 + 1 mm particle size ranges.

Fused sinters which are difficult to leach, are characterized by low porosity : apparent porosity : 10 % total porosity : 22 % (- 20 + 1 mm).

Cooling rate of the sinter at temperatures higher than 1000° C [39], exerts a significant influence on alumina and alkalis recoveries. Slow cooling favours the decomposition of the solid solution of Na₂O, Al₂O₃ in $\beta - 2 \text{CaO}, \text{SiO}_2$, into its components, and in this way Al₂O₃ and Na₂O extractions are enhanced.

It was shown that 88.3 % Al₂O₃ are extracted from the nepheline sinters which are quenched in air, 94 % Al₂O₃ are extracted from sinters cooled at a rate of 1.1° C/min.

Normal sinters [4] are characterized by :

- apparent porosity : 28 to 28.5 %	} - 10 mm + 1 mm
- total porosity : 37 to 40 %	

Weak sinters [4] are related to an insufficient degree of reaction, and are characterized by :

- apparent porosity : 35 to 37.5 %	} - 10 mm + 1 mm
- total porosity : 43 to 44 %	

Typical analysis of nepheline concentrates and sinters are presented in tables 1 and 2.

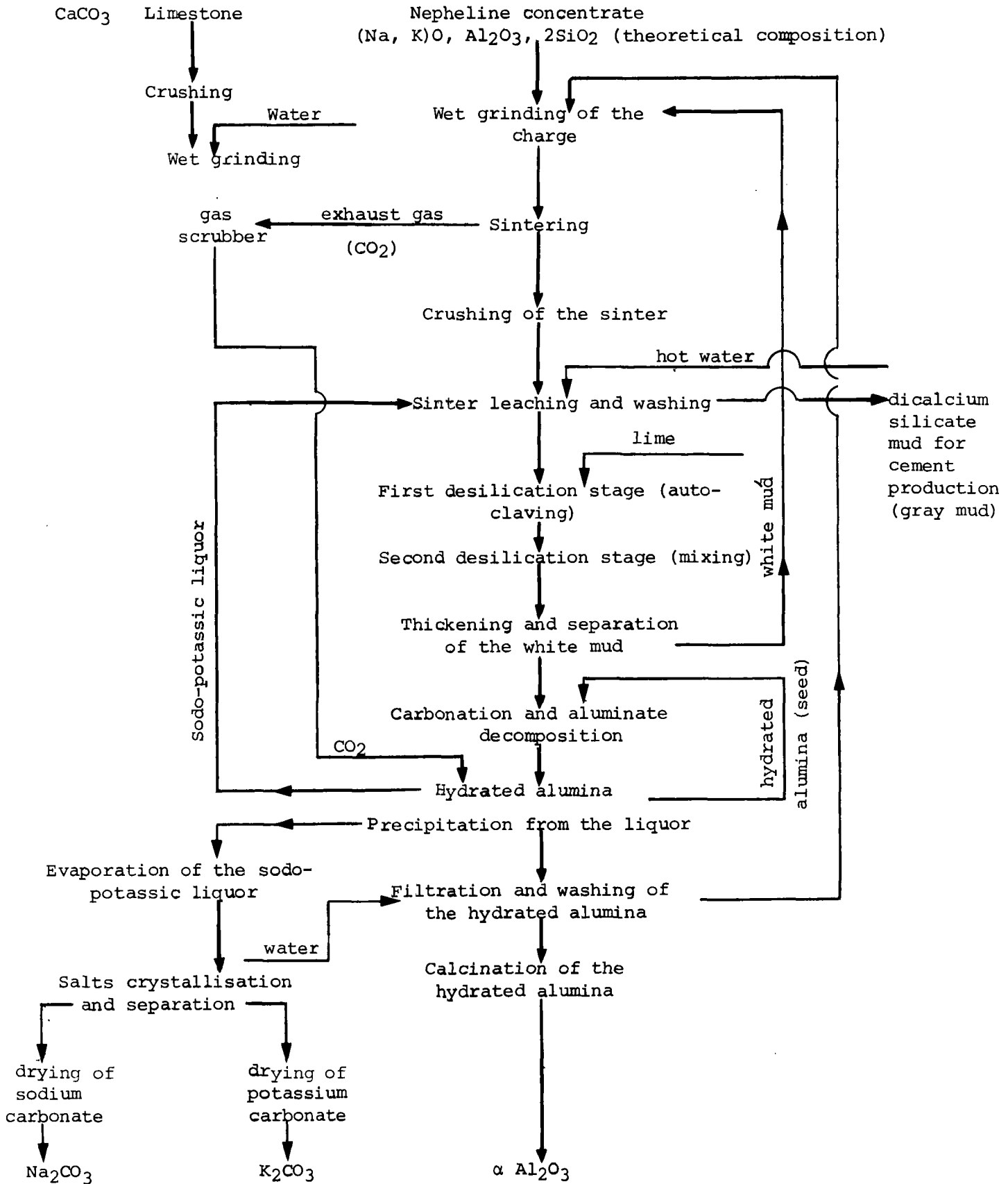


Figure 1 : Flowsheet for alumina production from nepheline or nepheline-syenite rocks [73] .

113. Leaching.

The sinters are leached at a temperature of about 70° C with a circulating aqueous solution of causticized alkalis, alkalis aluminate, alkalis carbonate : (100 to 200 g/l R₂O total $\frac{R_2O}{Al_2O_3}$ (molar) = 2.2 alkali carbonate content : about 5 % of total R₂O, caustic ratio : about 2) in two stages [5, 6] :

- leaching counter currently the crushed sinter in rotating tubular apparatus, (this process involves diffusion as a principle of leaching),
- grinding the sinter (- 1 mm) at the outlet of the tubular reactor in a rod mill and leaching the ground slime in a stirred tank ($\frac{\text{liquid}}{\text{solid}}$ ratio = 3). A combination of hydrocyclones and thickeners are used for separating leach liquor from the slimes.

Al₂O₃ and alkalis extraction yields amount respectively to 87-90 % and 89-90 % [7] total contact time is about 1 hour.

	Khibiny (Kola) Nepheline flotation concentr. %	Nepheline rock origine unknown %	Kol'skii nepheline concentr. %	Limestone (Pikalaevo) %	Nepheline rocks %	
SiO ₂	42 to 45	39.70	43.70	1.2	52.0	40.9
Al ₂ O ₃	19 to 30	27.55	30.10	0.35	21.6	24.0
Fe ₂ O ₃	2 to 4	4.72	3.4	0.1	1.1	2.7
FeO					2.6	6.1
Na ₂ O	12 to 15		17.25		7.1	8.5
K ₂ O	5 to 8		?		6.6	1.5
CaO	1.5 to 2.5	7.35	1.0	54.9	4.6	8.3
MgO		1.08	0.7	0.38	0.6	1.6
H ₂ O ⁺						
H ₂ O ⁻						
TiO ₂		0.42			0.6	1.1
L.o.I.	~ 1	3.0	1.0	43.5		
P ₂ O ₅						1.0
<i>($\frac{Na}{K}$ ratio is usually $\frac{3}{1}$)</i>						

Table 1: Typical chemical analysis of : nepheline rocks and concentrates and limestone used for alumina production in U.S.S.R.

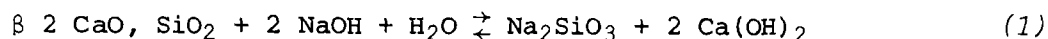
	Kol'skii nephelite concentrate + limestone	Volkhov*** alumina plant sinter
SiO ₂	18.0	24.3
Al ₂ O ₃	11.4	15.5
Fe ₂ O ₃	1.7	3.1
Na ₂ O	6.9	9.6 *
K ₂ O	?	
CaO	33.3	45.5
MgO		
L.o.I.	29.0	
TiO ₂		0.18
P ₂ O ₅		0.22
* Na ₂ O equivalent to Na ₂ O + K ₂ O		
*** Phase composition : 25.1 % alkali aluminate 69.8 % dicalcium silicate		

Table 2 : Chemical compositions of charges before or after sintering.

The following basic reactions are involved during the leaching step :

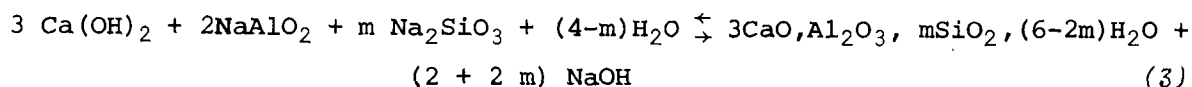
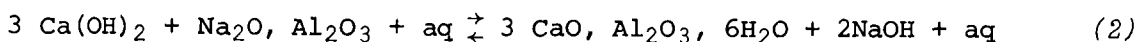
a) dissolution of NaAlO₂ and K AlO₂,

b) partial dissolution of dicalcium silicate :



[8] (same reaction with K)

c) interaction of alkalis aluminates with the products of the previous reaction [11] :



(same reaction with K)

This latter reactions account for secondary alumina losses in insoluble compounds : hydrated calcium aluminate and hydrogarnets.

d) formation of low solubility potassium and sodium hydroaluminates of approximate composition R₂O, Al₂O₃, 1.5-2 SiO₂, n H₂O [16] [18] giving rise to additional alumina losses.

Secondary alumina and alkalis losses depend on dicalcium silicate solubility. The amount of silica which passes into the solution, can be decreased by using leaching solutions containing silica (non desilicified solutions) and by using short contact time between leaching solutions [8.9] and sinter or slime, the amount of carbonate in compounds must be low.

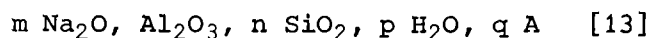
On the other hand, it has been reported that decomposition of α' $2 \text{ CaO}, \text{ SiO}_2$ in aluminate solutions is more important than decomposition of β $2 \text{ CaO}, \text{ SiO}_2$ [12], thus giving higher alumina losses during leaching. Low sintering time or temperature ($\theta < 1150^\circ \text{ C}$) as well as low $\frac{\text{SiO}_2}{\text{CaO}}$ ratios (< 2) lead to α' dicalcium silicate stabilization.

114. Desilicification.

The alkalis-aluminate liquor containing metastable sodium silicate (about 85-100 g/l Al_2O_3 and 1.6-4 g/l $\text{SiO}_2 - \frac{\text{R}_2\text{O}}{\text{Al}_2\text{O}_3}$ (molar) = 1.5 caustic ratio = 1.20 - 1.25, $\text{K}_2\text{O} = \sim 25$ to 50 % R_2O), can be desilicified in different ways.

1141. Autoclaving at about 175° C for 2 or 3 hours without additive.

Silica is separated in a solid deposit, the main component of which is sodium hydroaluminosilicate (and potassium hydroaluminosilicate) :



(where $\text{A} = \text{CO}_3^{2-}, \text{SO}_4^{2-}$ or 2 Cl^-) with sodalite like crystalline structure.

m : about 1.15 to 1.30

n : about 1.72 to 1.87

p : about 0.8 to 1.4

q : 0 to about 0.3

(corresponding potassium hydroaluminosilicate has the approximate composition : $\text{K}_2\text{O}, \text{ Al}_2\text{O}_3$ 1.7-1.8 SiO_2 $n \text{ H}_2\text{O}$).

Separation of silica gives rise to alkalis and alumina losses. The degree of desilicification depends on the true solubility of the sodium hydroaluminosilicate in the aluminate solutions at the end of the thermal treatment. Sodium hydroaluminosilicates formed with addition of Na_2SO_4 or Na_2CO_3 (5 to 25 g/l) [14] before autoclaving are the less soluble compounds [13.38].

It is worth while noting that desilicification of potassium aluminates is less efficient than desilicification of sodium aluminates, with and

without additives [15].

The solubility of sodium hydroaluminosilicates in aluminate solutions with caustic modulus of 1.8 depends on the following parameters [38] :

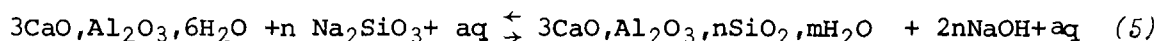
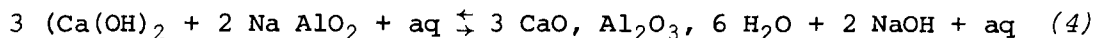
- concentration of the aluminate solution. The silica equilibrium concentration in the desilicified solution decreases from 0.170 g SiO₂/l down to 0.044 g/l as the alumina concentration in the starting solution decreases from 90 g Al₂O₃/l down to 30 g Al₂O₃/l (for $\theta = 175^\circ \text{ C}$, [Na₂O carb] = 30 g/l),
- concentration of the Na₂O from carbonate ([Na₂O carb]) in the starting solution. The silica equilibrium concentration decreases regularly as Na₂O carb concentration increases from 0 to 30 g/l,
- temperature of thermal treatment. The silica equilibrium concentration reaches a minimum at a temperature of about 125° C.

Table 3 summarizes these effects [38].

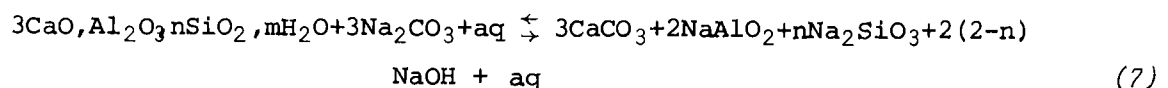
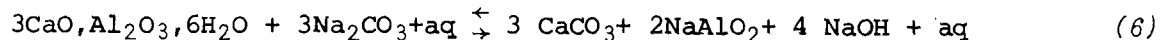
1142. Autoclaving at about 175° C for 2 or 3 hours with additive :

Lime, gray slime (dicalcium silicate residue from the leaching operation) or white slime (recycled solid residue from desilicification stage).

11421. With Lime : average lime concentration is about 10 g/l. Low solubility products : hydrated calcium aluminate and hydrogarnets (entrapping silica) are formed according to the following sequences [19] (for Na and for K) :

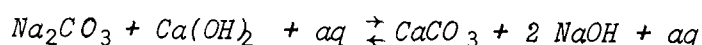


decomposition of these latter products may occur, depending Na₂CO₃ concentration **, according to :



The amount of lime added represents several times more than

** In the same time caustification of Na₂CO₃ occurs :

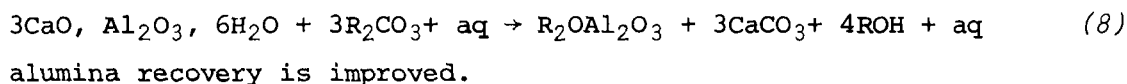


Equilibrium Concentration of SiO_2 and Equilibrium Silicon Modulus (M_{sil}) in Aluminate Solutions with $\alpha_c = 1.8$

No. of solution	Temp., °C	$\text{Na}_2\text{O}_{\text{cb}}$ content, g/l	Al_2O_3 content, g/l							
			30		50		70		90	
			$[\text{SiO}_2]$	M_{cr}	$[\text{SiO}_2]$	M_{cr}	$[\text{SiO}_2]$	M_{cr}	$[\text{SiO}_2]$	M_{cr}
1	98	0	0.066	451	0.115	440	0.182	390	0.298	311
2		10	0.049	612	0.085	588	0.132	532	0.218	432
3		30	0.046	652	0.079	630	0.126	555	0.200	453
4		50	0.043	698	0.078	633	0.125	558	0.212	430
5	125	0	0.076	392	0.103	471	0.167	417	0.246	368
6		10	0.049	608	0.078	655	0.122	580	0.197	474
7		30	0.044	682	0.074	688	0.111	652	0.171	532
8		50	0.039	764	0.070	697	0.107	660	0.161	557
9	150	0	0.075	400	0.118	437	0.184	380	0.274	337
10		10	0.049	618	0.079	625	0.129	538	0.200	461
11		30	0.039	774	0.074	662	0.120	585	0.173	521
12		50	0.038	790	0.066	743	0.115	603	0.170	533
13	175	0	0.080	378	0.129	380	0.210	330	0.272	333
14		10	0.050	600	0.085	600	0.150	465	0.208	450
15		30	0.044	675	0.074	680	0.132	530	0.170	528
16		50	0.041	730	0.070	706	0.133	523	0.171	527

Table 3 : Solubility of sodium hydroaluminosilicate in aluminate solution [38].

the stoichiometric value needed to combine alumina in hydrogarnet compounds [17]. Separation of hydrated calcium aluminate may be responsible for large alumina losses during desilicification when using large amounts of lime. Alumina contained in $3 \text{ CaO}, \text{ Al}_2\text{O}_3, 6 \text{ H}_2\text{O}$ may be recovered by washing the white mud (hydrogarnet + hydrated calcium aluminate) with alkali solution: [20], 100 g R_2O per liter at 95° C , for 1 hour :



Presence of MgO in limestone promotes good desilicification [21].

11422. Gray slime (or gray mud) : addition amounts to 5 g/l up to 10 g/liter [22] of aluminate solutions to be treated.

Dicalcium silicate, the main component of the gray slime, is not stable in aluminate solutions containing free alkalis: it decomposes according to reaction (1) giving :

- free lime Ca(OH)_2 , acting as a desilicifying reagent according to reactions (4) and (5) [14.17],
- alkaline hydroaluminosilicate with the following average composition : $\text{Na}_2\text{O}, \text{ Al}_2\text{O}_3, 1.7 \text{ SiO}_2, n \text{ H}_2\text{O}$ [17]. This second product acts as an active seed, promoting further precipitation and crystallization of alkalis hydroaluminosilicates, thus improving desilicification of solutions [17].

Desilicifying ability of gray slime depends on the solubility in aluminate solutions of alkalis hydroaluminosilicates which are formed.

11423. White slime (or white mud).

Large additions to aluminate solutions are recommended [17], the order or magnitude being 100 g/l.

The main components of the white slime are alkalis-hydroaluminosilicates [23.17] acting as centers of crystallization or seeds for precipitation and crystallization of alkalis hydroaluminosilicates from the aluminate solution, silica contained in the solution being entrapped in these low solubility compounds during thermal treatment.

1143. Two-stage desilicification process.

In industrial practice, pressure vessel desilicification, carried out at 175-200° C for 1 to 3 hours, with or without additive, is usually followed by additional mixing of the autoclave pulp in open vessels at about 100-105° C for 3 to 6 hours [21].

This latter operation greatly improves desilicification of the aluminate solution [17,22,24] as it is shown by silicon modulus * increase of the solution after post-autoclave treatment :

The Pikalevo aluminate solution ^{is} subjected to two stages desilicification [17] :

Stage I : autoclaving at 170° C for 1 hour or 3 hours

Stage II : mixing the autoclave pulp at 100° C for 4 hours

presents the following silicon modulus :

	1 hour autoclaving		3 hours autoclaving
Additive for autoclaving	none	Gray slime 10 g/l	Gray slime 10 g/l
Starting silicon modulus	50	50	50
Silicon modulus after autoclaving	300	380	-
Silicon modulus after mixing	423	585	630

Efficiency of desilicification, when using solutions with high potassium aluminate contents, is greatly improved by high lime additions (10 to 15 g/l), high autoclaving temperature : 200° C instead of 175° C or time [24] and high mixing contact time after autoclaving, as it is indicated by these partial results of Manvelyan experiments.

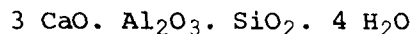
* Silicon modulus is defined as follows : $\frac{Al_2O_3 \text{ concentration (g/l)}}{SiO_2 \text{ concentration (g/l)}}$ in aluminate solution.

	Autoclaving time hours	Mixing time at 100° C hours	Lime addition g/l before autoclaving	SiO ₂ concentr. in aluminate solution after desili- cification	Silicon modulus after desili- cification
$\frac{\text{Na}_2\text{O}}{\text{K}_2\text{O}} = \frac{1}{4}$ in original solution	1 - 175° C	0	10	0.356	237.7
	1 - 175° C	1	10	0.321	259.4
	1 - 175° C	3	10	0.283	295.9
	1 - 175° C	6	10	0.264	314.6
	3 - 175° C	0	10	0.189	420.0
	3 - 175° C	1	10	0.176	472.9
	3 - 175° C	3	10	0.154	534.4
	3 - 175° C	6	10	0.153	533.3
	1 - 175° C	0	15	0.150	542.9
	1 - 175° C	1	15	0.136	633.4
	1 - 175° C	3	15	0.112	745.4
	1 - 175° C	6	15	0.101	814.0
	3 - 175° C	0	15	0.081	1003.3
	3 - 175° C	1	15	0.052	1601.6
	3 - 175° C	3	15	0.040	1982.0
	3 - 175° C	6	15	0.040	2000.0
$\frac{\text{Na}_2\text{O}}{\text{K}_2\text{O}} = \frac{1}{9}$ in original solution	3 - 175° C	0	15	0.220	363.6
	3 - 175° C	1	15	0.180	440.0
	3 - 175° C	3	15	0.125	640.7
	3 - 175° C	6	15	0.070	1143.7
	3 - 175° C	0	15	0.120	658.6
	3 - 175° C	1	15	0.100	796.0
	3 - 175° C	3	15	0.090	877.9
	3 - 175° C	6	15	0.070	1128.6

These results clearly demonstrate that desilicifying efficiency decreases as potassium content increases in aluminate solutions.

Two stages desilicification, involving gray slime addition, is used at Achinsk Alumina plant in Central Siberia.

In order to avoid any high alumina losses in insoluble compounds like :



(approximate composition for calcium hydro alumino silicate deposit, formed according to reaction (5)) with $\frac{\text{SiO}_2}{\text{Al}_2\text{O}_3} = 1$, when desilicifying with

lime addition, desilicification should be carried out in two stages [20] :

Stage I : desilicification in autoclaves without additive at about 175° C for 1 to 3 hours, giving alkali-hydro alumino silicate with a molar ratio $\frac{\text{SiO}_2}{\text{Al}_2\text{O}_3}$ of about 1.7.

Stage II : desilicification with lime addition corresponding to a molar ratio : $\frac{\text{CaO}}{\text{SiO}_2}$ of about 5 to 8.

With low $\frac{\text{CaO}}{\text{SiO}_2}$ ratio, the solid deposit consists of a mixture of alkalis and calcium hydro alumino silicates, more soluble than the mixture of hydrated calcium aluminate and calcium hydro alumino silicate which is formed when higher $\frac{\text{CaO}}{\text{SiO}_2}$ ratio are used.

This second stage may be carried out in open vessels at 105° C or in pressure vessels at 170° C, for 5 hours, this latter procedure provides a higher silicon modulus in a shorter period of time.

Washing the solid deposit (white mud) with alkali solution allows alumina to be partially recovered (Al_2O_3 combined in $3 \text{ CaO}, \text{Al}_2\text{O}_3, 6 \text{ H}_2\text{O}$ is regenerated, $3 \text{ CaO}, \text{Al}_2\text{O}_3, \text{SiO}_2, 4 \text{ H}_2\text{O}$ is insoluble in alkali solutions).

The higher is the alkali carbonate content in the aluminate solution after the first desilicification stage *, the lower the desilicifying ability of lime will be for the second stage desilicification [19], this phenomenon can be explained through reactions (6) and (7). Large additions of lime are required for desilicifying (second stage) solutions containing large amounts of alkali carbonate.

With potassium aluminate solutions, simultaneous additions of white mud (15-25 g/l) and lime (15-25 g/l), followed by autoclaving at 200° C for 3 hours, lead to high silicon modulus in desilicified solution and low alumina losses in solid deposits [29].

* carried out in autoclave without additive.

1144. Heating in open vessels at atmospheric pressure and 100-105° C.

11441. With addition of white mud.

Large amounts of white slime, about 100 g/l, are added to solutions obtained from the leaching of sinters. The mixture is treated for 2 to 6 hours at about 100° C [17, 23, 25] in stirred tanks .

Silica is separated from the solution as an insoluble alkali hydroalumino silicate, white mud acts as a seed or centers of crystallization, activating the precipitation of this latter compound.

Silicon modulus is increased from 30-40 up to 700-1600 [17, 25]. Additional alumina losses (alumina trihydrate) may arise from hydrolysis of aluminate solutions which is favoured by low temperatures (80° C) and impurities. Decomposition of aluminate solutions can be determined through caustic modulus increase, when this factor increases to more than 0.1, desilicification is associated with decomposition of the aluminate solution [26].

The desilicified solution is separated from the white mud by thickening and filtering, the white mud is recycled to the desilicification section. Activity of the white mud is regenerated by washing with alkali solution. The alumina trihydrate that promotes decomposition of aluminate solutions, and the impurities decreasing the white slime activity, are removed from the recycled white mud [25, 26].

11442. With addition of lime.

High silicon modulus (up to 3400) can be reached, using lime addition (10 to 20 g/l) and mixing for one hour to 6 hours at 90-100° C [23, 26], with alumina solutions previously subjected to a first desilicification stage (with white mud addition).

1145. Alumina recovery after desilicification.

Alumina losses in solid deposits formed during desilicification range between 2 and 11.7 % of the original Al_2O_3 content in the solution. Average alumina losses can be estimated at about 5 % [23, 14, 30, 29] under normal conditions.

Alkali losses in solid deposits (white mud) make it possible to recycle the latter to the sintering process.

1146. Comparison of desilicifying additives.

As it was outlined above, lime and gray slime (dicalcium silicate) chemically interact with silica and alumina contained in aluminate solutions, giving rise to additional alumina losses (hydrated calcium aluminate) and formation of insoluble hydrated calcium aluminosilicate compounds with low $\frac{\text{SiO}_2}{\text{Al}_2\text{O}_3}$ ratio. Additional alumina and alkali losses, when using gray slime are proportional to the weight quantities of the slime addition [17].

Rather small amounts of lime or gray slime are needed : about 2.5 to 20 g/l (average usual addition : 10 g/l).

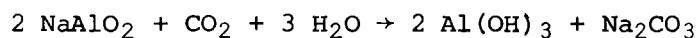
Using lime additive implies additional consumption of limestone and energy for decarbonation and additional equipment for preparation. Gray slime does not require additional raw materials or equipment.

Unlike lime and gray mud, white slime does not react chemically with aluminate solution. Because it acts as a seed, promoting crystallization of hydrated alkali aluminosilicates, the alumina losses are the same as when desilicifying without chemical additives [17] [25] ($\frac{\text{SiO}_2}{\text{Al}_2\text{O}_3} \geq 1.7$ in the precipitate formed).

Large amounts of white slime are needed (about 100 g/l) so as to achieve a thorough desilicification, however the alumina and alkali losses does not depend on quantity of white slime added, this feature is a great advantage in respect to lime and gray slime.

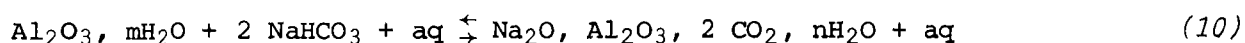
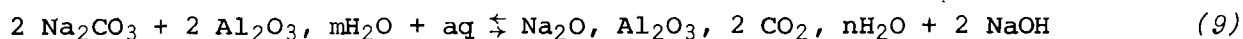
115. Carbonation.

Alumina recovery is carried out by carbonation of alkali aluminate solutions at 75° C [31] leading to alumina hydrate (usually alumina trihydrate) precipitation, according to the following simplified reaction :



Washed gas from kilns, having a 10-12 % CO₂ content is used, carbonation rate is low (neutralization of 10 to 5 g/l caustic Na₂O per hour) and total residence time in carbonators, ranges between 6 and 12 hours [35].

If the carbonation process is carried out completely, then aluminium hydroxyde will pass into the precipitate, together with nearly all the silica contained in the solution (coprecipitation of sodium hydroaluminosilicate along with alumina hydroxyde), as well as a good deal of alkali, because of the formation of alkali hydro aluminocarbonate [32]. These latter compounds form in accordance with the following reactions [33] :



where $n = 2$ to 3

This compound forms at the end of the carbonation process [reaction (10)].

Aluminate solutions with high silicon modulus (700 to 1,000 subjected to carbonation, till a 55 %-80 % decomposition [34], only exhibit small decrease in silica concentration, that implies the precipitation of alumina with a low silica content.

With a silicon modulus of 1,150, the silica content of the aluminium hydroxyde remains at a very low level : $< 0,04$ % until 88 % of the total alumina is separated [30], for higher separations, there is a sharp increase in the SiO_2 content of the hydrated alumina.

Low carbonation rates and long residence time in carbonators, allow for a better crystallization of hydrated alumina and formation of larger crystals. Addition of hydrated alumina seeds (seeding ratio \ast : 0.5 to 2) improves particle size distribution of the precipitated alumina and increase the rate of hydrated alumina crystallization. With a seeding ratio of 1, this rate equals the rate of caustic Na_2O neutralization [36].

When seed crystals are added to a solution, the silica content of the precipitated hydrated alumina is very low, until the recovery of alumina in the solid phase reaches 40 to 90 % depending on the silicon modulus of the starting solution (470 to 1,150 [34]).

\ast seeding ratio : ratio of Al_2O_3 in the seed to the Al_2O_3 in the solution [37].

Chemical composition of the hydrated alumina obtained from nepheline depends on :

- the silicon modulus of the desilicified aluminate solution,
- the degree of separation (recovery in solid phase) of hydrated alumina or the thoroughness of the carbonation process (specially for SiO_2 and Na_2O content),
- the presence of seed crystals.

For instance, with a low silicon modulus of 550 it is possible to produce calcined alumina assaying : 0.04 % SiO_2 - 0.32 % Na_2O and 0.018 % Fe_2O_3 for a recovery of 87 % [37].

The solubility of silica in aluminate solutions increases as temperature decreases [40] therefore it is possible to carry out decomposition of these solutions in two stages in order to avoid precipitation of silica at the end of the carbonation process :

First stage : carbonation of the solutions in the presence of seed crystals, at 75-85° C for 7 to 9 hours until a 83-85 % decomposition is reached,

Second stage : further decomposition of the remaining mother liquor from the previous hydrated alumina separation stage, for 18 to 25 hours, with a gradual temperature reduction down to 40-45° C, until 92-93 % degree of decomposition is reached.

Using this combined process, high quality alumina can be obtained (SiO_2 : 0.05 %).

116. Cement production.

1161. Manufacture of an usual Portland cement.

The solid residue (gray mud) from the leaching operation is mainly composed of dicalcium silicate. Typical Chemical analysis of these muds are presented in the following table (table 4) :

	% (Volkhov)	% (Achinsk)
SiO ₂	27.63	28.63
Al ₂ O ₃	4.34	3.13
Fe ₂ O ₃	2.55	4.80
Na ₂ O	2.22	2.18
CaO	53.62	52.97
MgO		2.12
TiO ₂	0.25	0.30
P ₂ O ₅	0.26	0.48
L.O.I.	6.10	3.89

Table 4 : typical analysis of dicalcium silicate mud for cement production.

The gray mud is carefully wet ground and blended with calculated amounts of bauxite, pyrite cinders and limestone so as to provide a suitable Portland clinker composition.

The slurry is dried and fired in a rotary kiln at 1350-1400° C giving a clinker with the following composition [2] :

3 CaO, SiO₂ : 51.9 %

2 CaO, SiO₂ : 27.5 %

After grinding with gypsum addition, the resulting Portland cement, characterized by a Blaine fineness of 3,100 cm²/g, presents the following compressive strengths [2] :

Setting time day	Compressive strength kg/cm ²
1	185
3	384
7	439
28	521

In an other method, gray mud is mixed with limestone and a small proportion of a mineralizer (CaF₂ : 0.34 % on dry crude basis) [2].

The cement (ground to 3,080 cm²/g) presents the following characteristics :

Setting time day	Compressive strength kg/cm ²
1	275
3	430
7	473
28	567

Flowsheets of the Portland cement production are presented in figures 2 and 3.

1162. Manufacture of a "nepheline cement".

Gray mud is wet ground, along with hydrated lime or quicklime and gypsum , in ball mills.

The resulting slurry is dried and subjected to a thermal treatment at 500-600° C.

The cement obtained, is characterized by its good resistance to frost and corrosive waters [28].

Because of its high dicalcium silicate content the rate of hardening of this cement is low, so that, activating agents, such as calcium carbide, [28] have to be added so as to increase the rate of hardening when necessary.

A flowsheet for the manufacture of nepheline cement is presented in figure 4 .

117. Economic evaluation.

A rough economic evaluation of the nepheline process can be computed from basic consumption figures quoted in reference [76]. These figures were obtained from the bimonthly magazine : SOVIET EXPORT.

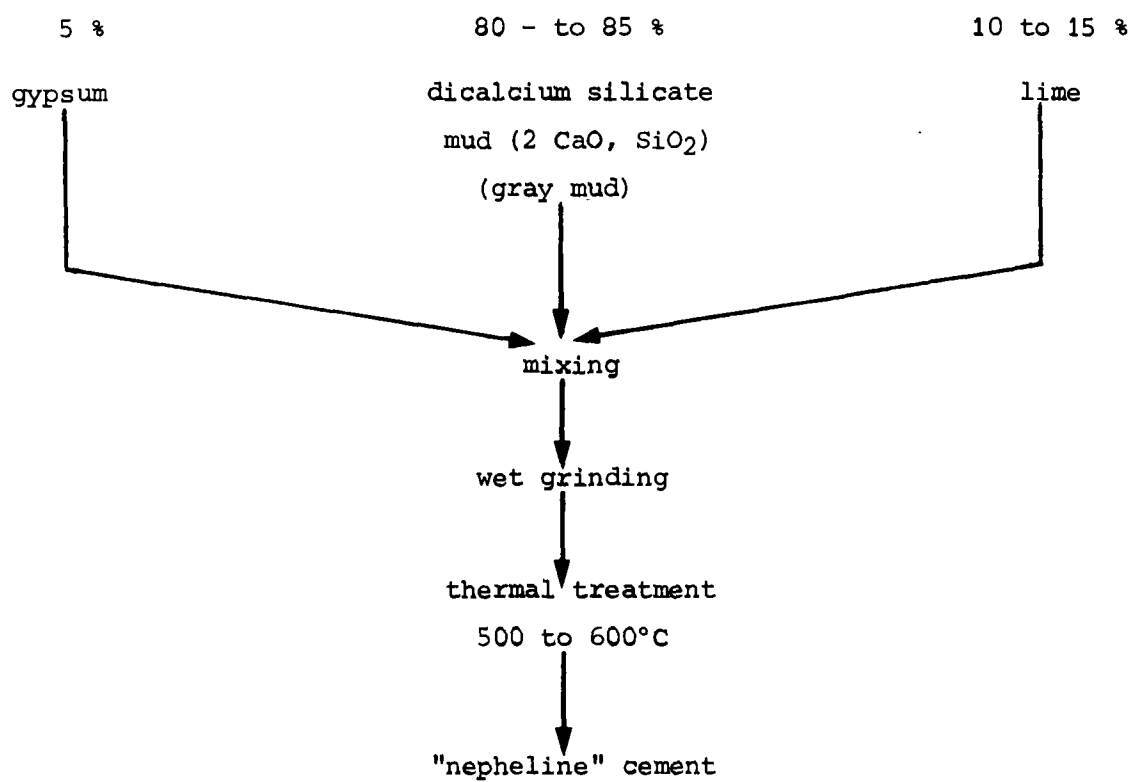


Figure 4 : Manufacture of nepheline cement .

Consumption	}	Alumina recovery	: 83-86 % (estimated)
		Nepheline concentrate	t/t Al ₂ O ₃ : 4
		Total limestone	t/t Al ₂ O ₃ : 12
		Fuel	t/t Al ₂ O ₃ : 2.7
		Steam	t/t Al ₂ O ₃ : 6 (4.25.10 ⁶ kcal)
		Electric power	kWhr/t Al ₂ O ₃ : 2,000
Production	}	Soda	kg/t Al ₂ O ₃ : 700
		Potash	kg/t Al ₂ O ₃ : 300
		Gallium	kg/t Al ₂ O ₃ : 0.1
		Portland cement	t/t Al ₂ O ₃ : about 8.5

It is claimed that, using gray mud for producing cement, the rotary kiln output is increased by 25-30 % and fuel consumption is reduced by 20-25 %.

Overall operating costs are 10-15 % lower than for separate stage production :

- alumina from bauxites in the Bayer process
- soda from ammonia
- potash
- cement from limestone and clay.

Soviet technology and patents are available through an American company, the Southwire Corporation [75], which is the sole agent in the U.S. (and probably in the Western World) of Licenzentorg, the Russian licensing agency.

According to reference [28] the 800.000 tons alumina/year capacity plant at Achinsk (Central Siberia) would produce : 300 kg of caustic soda, 100 kg of potassium sulphate, and 6 to 9 tons of gray mud per ton of alumina.

It is worth while pointing out that Southwire is engaged in a feasibility study for the construction of an aluminum plant with a capacity of 225,000 tons/year, near Djubail [77].

1.2. THE LIME-SODA SINTER PROCESS.

This process is quite similar to the lime sinter process using nephelins, it consists of the same unit operations.

The alumina bearing material is sintered with limestone and soda ash, silica and lime combine to dicalcium silicate, alumina and sodium oxide combine to sodium aluminate.

Sodium aluminate is extracted from the sinter by leaching with a hot soda ash or soda solution, the dicalcium silicate residue, mixed with limestone, can be used for producing Portland cement.

The aluminate solution is desilicified in one, or two stages with or without additives, according to the desilicifying processes which have been previously described.

The hydrated alumina is separated by carbonation and seeding, the precipitate is calcined at about 1100° C so as to obtain α alumina. The remaining solution containing soda ash and residual sodium aluminate is recycled to the sintering and leaching sections.

The flowsheets [44, 45] are shown in figures 5 and 6.

This process can be applied to :

basic raw materials such as anorthosite the theoretical composition of which is : CaO , Al_2O_3 , 2SiO_2 , (theoretical alumina content : 36.7 %), but the natural rocks consist of a mixture (solid solution) of anorthosite and alkali feldspar, (albite : Na_2O , Al_2O_3 , 6SiO_2) with a higher $\frac{\text{SiO}_2}{\text{Al}_2\text{O}_3}$ ratio, and an alumina content ranging between 20 and 34 %.

Rocks assaying 26 to 28 % Al_2O_3 are required for lime-soda sinter process or lime sinter process, with this latter process low alkali content is required, so as to allow the self disintegration of the sinter through $\beta \rightarrow \gamma$ inversion of dicalcium silicate.

It is worth while pointing out that a large variety of basic rocks can be treated by the lime-soda sinter process.

acid raw materials such as clays or shales, containing : kaolinite ($2 \text{H}_2\text{O}$, Al_2O_3 , 2SiO_2), with 39.5 % alumina content - illite (potassium

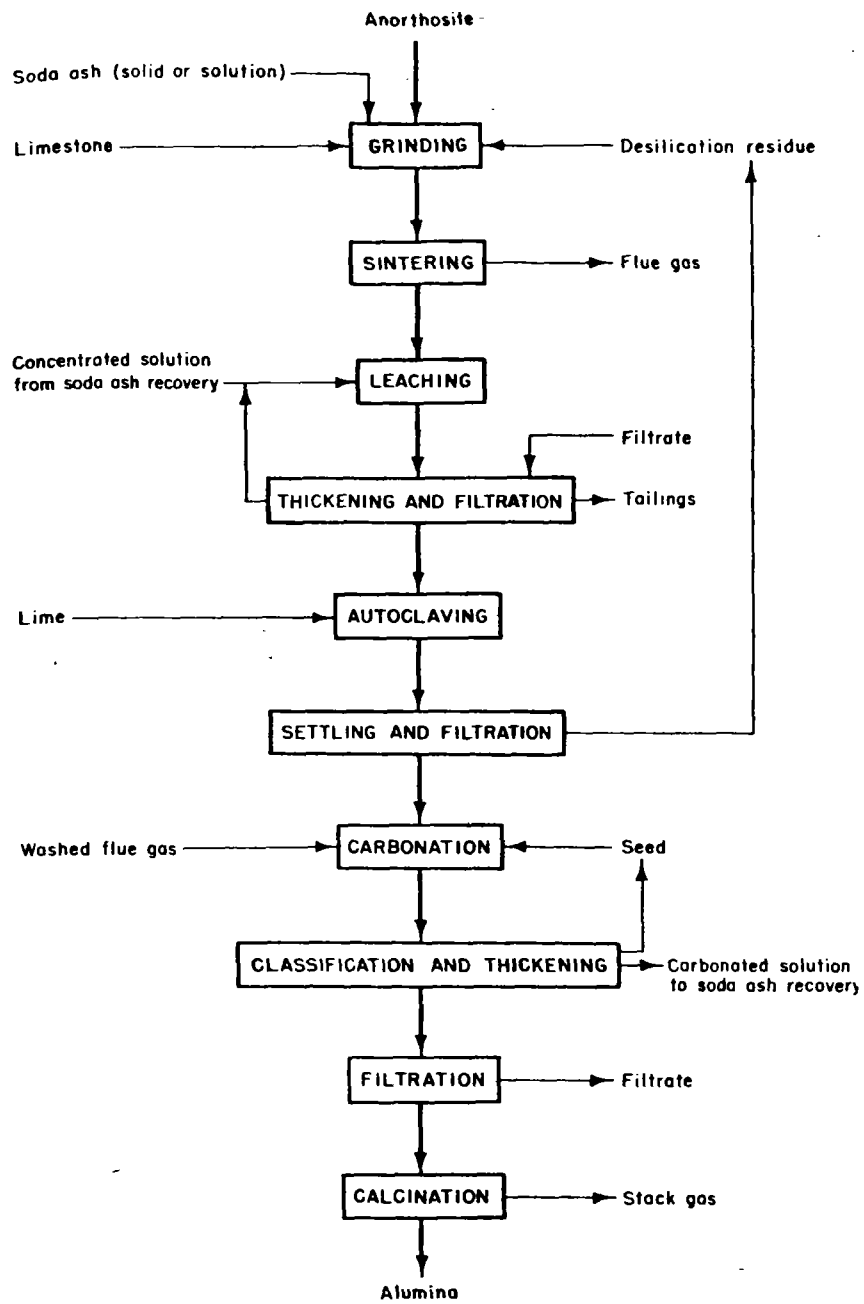


Figure 5 : Flowsheet of the lime - Soda sinter process applied to anorthosite [44].

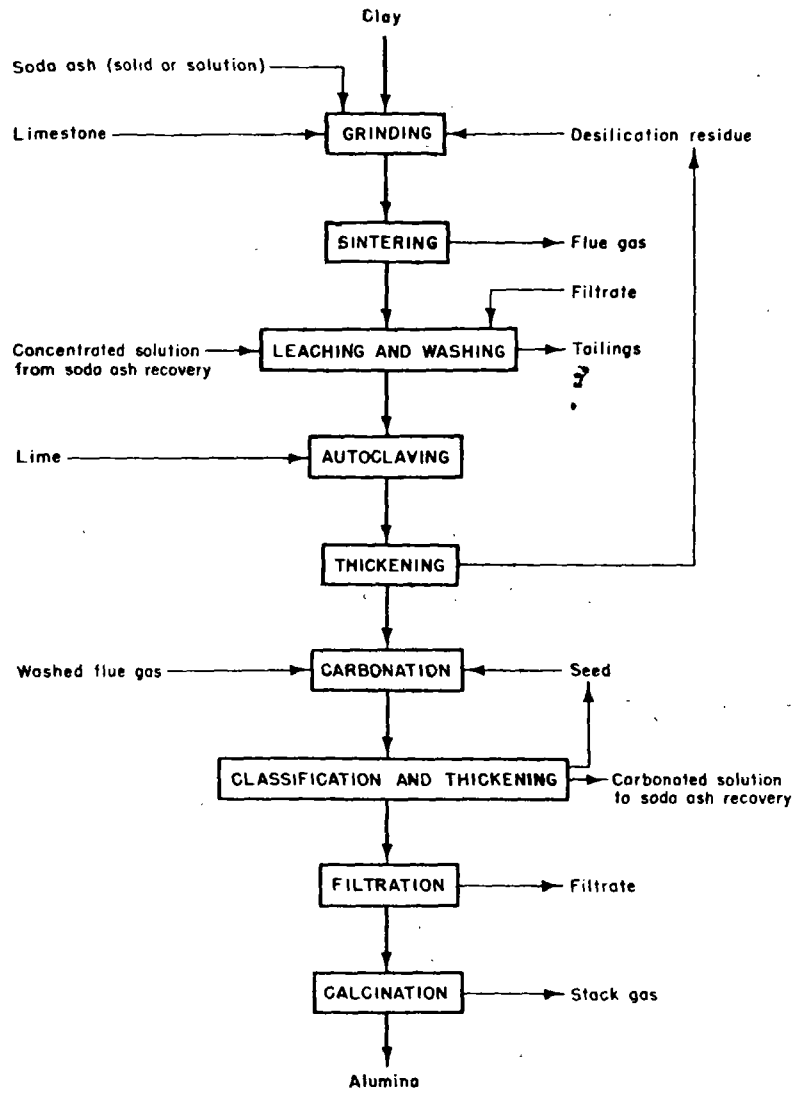


Figure 6 : Flowsheet of lime-sinter process applied to clays [45].

hydroalumino silicate), with 20-25 % alumina content and about 7 % K_2O content - montmorillonite and chlorite, with about 20-27 % alumina content - as main alumina bearing minerals - and silica (quartz), as a main impurity.

Extensive laboratory and pilot plant experiments have been carried out in U.S.A. by U.S.B.M. using both clays and anorthosite.

siliceous bauxites, which are not suitable for Bayer process, usually assaying more than 10 % SiO_2 (13 to 25 % SiO_2) and more than 10 % Fe_2O_3 . Ores with large Fe_2O_3 contents are sintered with limestone and carbon - or limestone, soda ash and carbon, so as to reduce iron compounds.

red muds, or solid residues from the treatment of bauxite by the Bayer process.

Large alumina plants are operated in Socialist Countries specially in U.S.S.R., and Yugoslavia using the lime-sinter process to treat siliceous bauxites or to recover the residual alumina from red muds produced from low quality bauxites by the Bayer process.

In the Urals (U.S.S.R.) low quality bauxites [42] assaying 7-13 % SiO_2 are processed so as to produce a high quality bauxite concentrate with a silicon modulus of 7 or more which is suitable for the Bayer process, and tailings with a low silicon modulus (≤ 2) which can be converted to alumina through a lime-soda or lime sinter process.

A large alumina plant is operated at Tikhvin [40, 43] in U.S.S.R.

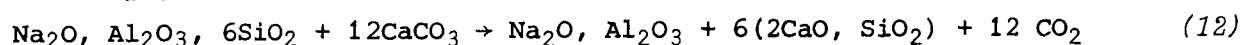
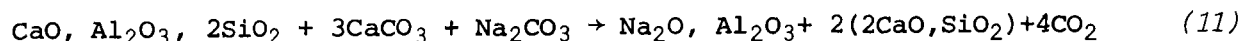
The lime soda sinter process differs from the nepheline sinter process by the sintering conditions. The product to be sintered, is finely ground (- 74 μm [44-45] or - 90 μm [42-46]), the mixture is composed of : an alumina bearing material : anorthosite, clay, siliceous bauxite or red mud - limestone - soda ash (recycled soda ash + addition for compensating the losses) and the desilicification residue (white mud) containing :

- hydrated tricalcium aluminate :
3 CaO, Al_2O_3 , 6 H_2O ,
- hydrated calcium hydroalumino silicate with the approximate composition 3 CaO, Al_2O_3 , SiO_2 ,
4 H_2O ,

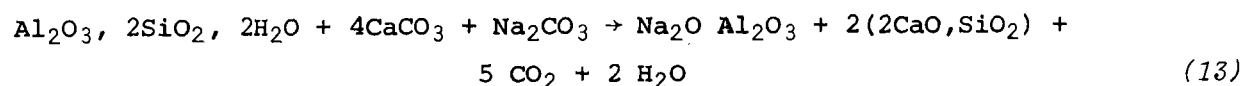
- sodium hydroalumino silicate
of the sodalite group :
 $\text{Na}_2\text{O}, \text{Al}_2\text{O}_3, 1.7 \text{SiO}_2, n\text{H}_2\text{O} -$
 CaCO_3 and $\text{Ca}(\text{OH})_2$

The reactions that occur during sintering may be expressed as follows :

for anorthosite [44]



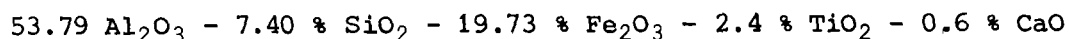
for kaolinitic clay [45]



The dicalcium silicate has the β form.

The sintering temperature is 1200°C with anorthosite, clay and bauxite assaying 24.8 % SiO_2 [42, 44, 45], the total retention time in the kiln is 2.5 hours [44, 45].

With bauxite assaying :



The optimum sintering temperature range was found to be $1,200-1,300^\circ \text{C}$ 46 . Below $1,200^\circ \text{C}$, sinters contain unreacted starting materials and intermediate products (sodium or calcium alumino silicates, sodium and calcium aluminates or silicates like : N.C.S., N AS_2 , $\text{N}_2\text{C}_8\text{S}_5 - \text{N}_2\text{C}_3\text{A}_5$ * [42, 12], which are insoluble during leaching and account for alumina and alkali losses) above $1,300^\circ \text{C}$, solid solution formation and melting take place.

In addition to reactions (11) and (12) lime and soda react with TiO_2 and Fe_2O_3 leading to the formation of CaTiO_3 and $\text{Na}_2\text{O}, \text{Fe}_2\text{O}_3$ [42, 47], it is therefore necessary to take into account the possibility for these compounds to form when calculating the charge composition : the molar ratio $\frac{\text{CaO}}{\text{SiO}_2 + 0.5 \text{TiO}_2}$ must be usually greater than 2:2.05 to 2.1 [42].

* $N = \text{Na}_2\text{O} - C = \text{CaO} - S = \text{SiO}_2 - A = \text{Al}_2\text{O}_3 - F = \text{Fe}_2\text{O}_3$

The molar ratio $\frac{\text{Na}_2\text{O}}{\text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3}$ must be greater than 0.67 (0.7 up to 1.05) [42-46].

With a constant ratio $\frac{\text{Na}_2\text{O}}{\text{R}_2\text{O}_3}$ of 1.05 the maximum alumina extraction with an alkaline leaching is obtained for a molar ratio $\frac{\text{CaO}}{\text{SiO}_2}$ in the 2 to 3, range [46].

For high lime addition, CaO, Fe₂O₃ gradually replaces Na₂O, Fe₂O₃ [46], high $\frac{\text{CaO}}{\text{SiO}_2}$ ratio promotes a good crystallization and enlargement of the structural constituents within the sintered mass and favours formation of a sinter structure [46].

It is reported [39] that slow cooling of the sinter, increases the alumina and alkali yields owing to the decomposition of the solid solution of Na₂O, Al₂O₃ in β 2 CaO.SiO₂.

Dolomitized limestone might replace pure limestone when sintering bauxites with soda ash [48], in that case, silica, CaO and MgO combine to merwinite 3 CaO, MgO, 2 SiO₂, which remains insoluble during leaching; alumina is combined to Na₂O, Al₂O₃ and iron oxide is combined to Na₂O. Fe₂O₃.

Compounds like gehlenite : 2 CaO, Al₂O₃, SiO₂ - brownmillerite : 4 CaO, Al₂O₃, Fe₂O₃ - nepheline or carnegiete : Na₂O, Al₂O₃, 2 SiO₂ and Na₂O, CaO, SiO₂, lead to alumina and alkali losses since they are low - solubility compounds in leaching solutions.

Low $\frac{\text{CaO}}{\text{SiO}_2}$ (< 2), $\frac{\text{Na}_2\text{O}}{\text{R}_2\text{O}_3}$ (< 0.67) molar ratios favour formation of Na₂O, CaO, SiO₂ and carnegiete [42, 12] as well as fast heating rate, low temperature and large pellet size.

According to U.S.B.M. experiments related to clay or anorthosite treatments, presence of hydraulic compounds like 3 CaO, SiO₂ or calcium aluminates [49, 50] in poorly sintered products, provokes gelation of the aluminate slurry obtained when leaching the ground sinter (about - 250 μm) with soda or soda ash solution.

Gelation is likely due to the hydration and setting of the hydraulic compounds increasing viscosity of slurry, forming hard or highly swollen solid deposits.

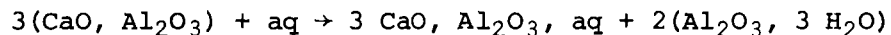
These properties raise difficulties in handling slurries, and decrease alumina recovery.

Addition of sugar, starch or guar gum (about 5 to 10 kg/ton of sinter) depresses gelation and improves alumina recovery. Increasing iron content in the sinter up to 8-9 % [50] contributes to decrease the formation of hydraulic compounds, resulting in better alumina recovery.

Laboratory investigations revealed [49] that a $\frac{\text{Al}_2\text{O}_3}{\text{SiO}_2}$ molar ratio higher than 0.9 in the sinter resulted in good alumina and alkali recoveries and suppressed any tendency toward gelation.

Gelation is considered as the main source of alumina losses. It must be pointed out that a high degree of sintering for the charge prevents aluminate slurry from gelation: fine grinding, good blending of the mixture, small pellet size [50], appropriate heating and cooling rates as well as a high temperature, are factors, the influence of which reduce gelation.

It is also worth while noting that gelation might be related to calcium aluminate supersaturation in leach liquor giving rise to hydrolysis and precipitation according to the reaction [55] :



a reaction that implies alumina losses in a solid deposit and setting (due to hydrated calcium aluminate precipitation).

Appropriate conditions of alkali and aluminate concentrations as well as an appropriate temperature during leaching might help in controlling alumina losses and gelation of the leach slurry.

For an hypothetical clay assaying :

- Al_2O_3 : 30 % - Fe_2O_3 : 3 % - SiO_2 : 50 % - L.O.I. : 15 %,

an hypothetical anorthosite assaying :

- Al_2O_3 : 27 % - Fe_2O_3 : 2 % - SiO_2 : 53 % - Na_2O : 4 % -
CaO : 11 %

and an hypothetical limestone assaying :

CaO : 54 % - CO_2 : 42,4 % - Al_2O_3 : 0,4 % - SiO_2 : 16 %

The U.S.B.M. ^{has} computed the basic consumption figures [44, 45] for the lime-soda sinter process applied to clay and anorthosite, taking into account average laboratory and pilot plant results. These figures are shown in the following table.

	Clay**	Anorthosite**
Alumina content in alumina raw material Al ₂ O ₃ %	30	27
Alumina raw material requirement : t/t Al ₂ O ₃	4.58	4.86
Limestone requirement for sinterization t/T Al ₂ O ₃	8.30	8.81
Soda ash consumption **** : kg/t Al ₂ O ₃	22.6	77.1
Electric power for alumina production**** kWhr/t Al ₂ O ₃	578	893
Steam consumption**** : t/t Al ₂ O ₃	0	0
Total water consumption**** : m ³ /t Al ₂ O ₃ (including cooling and process water)	55.7	61.8
Natural gas { kcal/t Al ₂ O ₃ **** *** { t/t Al ₂ O ₃	13,950x10 ³ 1.22	16,259x10 ³ 1.42
Alumina recovery %	72.8	76.2
* wet grinding before sinterization. ** 8.000 kcal/Nm ³ - 0.7 kg/N.m ³ . **** assuming, published data on short ton and U.S. gal. basis .		

1.3. THE LIME-SINTER PROCESSES (SELF DISINTEGRATION PROCESSES).

These processes were studied before the second World War in France (SEAILLES and VON EUW), Soviet Union, and Poland (Doctor Engineer Jerzi GRZYMEK), but its industrial development began in Poland on 1954 when a large pilot plant was built near GROSZOWICE [52]. It is claimed that several thousands tons of aluminium oxide or aluminium hydroxide have been produced since the plant was put in operation, giving sufficient data to improve the process and determine the technical and economic parameters.

131. The Grzymek process.

The process involves simultaneous production of alumina and Portland clinker, starting from limestone (assaying more than 53 % CaO), and alumina bearing raw materials : clays, shales industrial and mine wastes, clayey tailings from coal processing, fly ash from brown coal, aluminous steel slags assaying more than 30 % Al₂O₃, typical chemical analyses of which are :

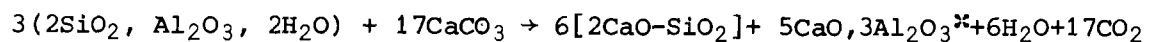
	Al ₂ O ₃ %	Fe ₂ O ₃ %	SiO ₂ %	CaO %	I.L. %
Clay	31.32	2.27	51.17	0.82	10.80
Siliceous bauxite	31.15	2.45	34.16	1.47	30.00
Fly ash from brown coal	32.96	6.86	50.87	2.38	3.00

Limitation in the alumina content of the raw materials are imposed by economical considerations rather than technical ones.

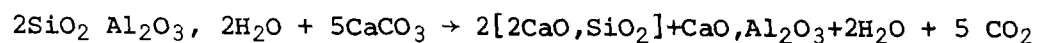
The manufacture of alumina consists of the following operations (simplified principle) :

1311. Grinding and blending in ball-mills the alumina raw material with a calculated amount of limestone so as to form mainly 2 CaO - SiO₂ and 5 CaO - 3 Al₂O₃ or CaO - Al₂O₃ during sintering of the mixture (Fe₂O₃ may be engaged in garnet type compounds and 4 CaO - Al₂O₃ - Fe₂O₃).

1312. Sintering the charge in rotary kilns (cement making type) at a maximum temperature of about 1350-1400° C. For a kaolinitic clay, the reaction is represented by :



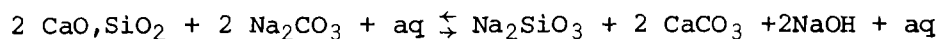
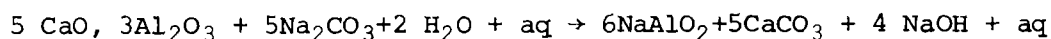
and



* 5 CaO, 3 Al₂O₃ formation is generally more important than CaO, Al₂O₃ formation.

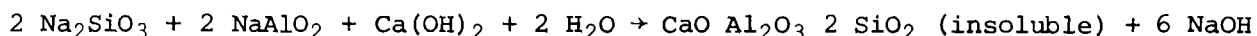
1313. Slow cooling of the sintered mass so as to favour the transformation $2 \text{ CaO}, \text{ SiO}_2/\beta \rightarrow 2 \text{ CaO}, \text{ SiO}_2/\gamma$ which occurs with a volume increase of 10 % and giving rise to self disintegration of the clinker.

1314. Leaching the self disintegrated mass with soda ash solution. Calcium aluminates and a part of the calcium silicate, are dissolved according to the following simplified reactions :



the dicalcium silicate residue is thickened, washed and filtered.

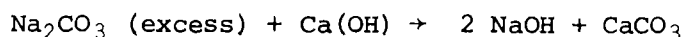
1315. Desilicification of the sodium aluminate solution with lime under atmospheric pressure at 98-100° C :



(this reaction is simplified, the insoluble product is a mixture of a complex calcium alumino silicate of the form :

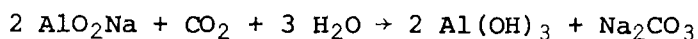
$\text{CaO}, \text{ Al}_2\text{O}_3, 2 \text{ SiO}_2, 2 \text{ H}_2\text{O}$ or $3 \text{ CaO}, \text{ Al}_2\text{O}_3, \text{ SiO}_2, 4 \text{ H}_2\text{O}$ and sodium hydro alumino silicate of the form : $\text{Na}_2\text{O}, \text{ Al}_2\text{O}_3, 1.8 \text{ SiO}_2, \text{ H}_2\text{O}$)

A secondary reaction takes place during desilicification :

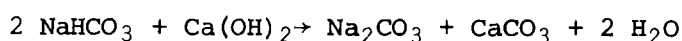


The aluminate solution is subjected to thickening and filtration so as to separate the insoluble silica compounds.

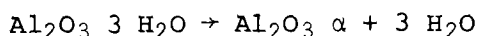
1316. Carbonation of the sodium aluminate solution, with CO_2 contained in the exhaust gas of the sintering kilns, according to the following simplified reactions : (Al(OH)_3 is used as a seed to promote precipitation)



The precipitate of alumina trihydrate is thickened, washed, and filtered, the alkaline solution is evaporated to concentrate soda ash which is recycled to the leaching stage. Sodium bicarbonate formed by thorough carbonation is first converted to carbonate, after contact with lime, as it is shown by the reaction :



1317. Calcination of the alumina trihydrate at 1100° C in rotary kilns to produce α Al_2O_3 according to :

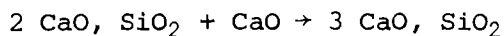


Typical chemical analysis of the alumina is :

Al_2O_3	:	about 99,50 %
Na_2O	:	0.15 to 0.30 %
SiO_2	:	0.02 to 0.06 %
Fe_2O_3	:	0.004 to 0.010 %

1318. Portland cement production.

The Portland cement is manufactured according to the following basic reaction :



(tricalcium silicate or alite which is the main component of the clinker).

The insoluble silicate residue from the operation n° 4, is mixed with limestone, the amount of which is calculated in order to obtain a lime saturation factor of about 0.95, taking into account the chemical composition of the product.

The mixture is wet ground in a ball mill, dried and fired in a rotary kiln at about 1400° C, the clinker is cooled, mixed with gypsum and ground down to $80 \mu\text{m}$ (Blaine fineness : 3000 to 3800 cm^2/g).

The compressive strengths of the cements ranged between 400 and 500 kg/cm^2 after 28 days, depending on the fineness.

A simplified flowsheet of the Polish pilot plant is given in figure n° 7 .

1319. Economic evaluation.

For the Polish pilot plant, basic consumption figures for 1 metric ton of Al_2O_3 are given as follows :

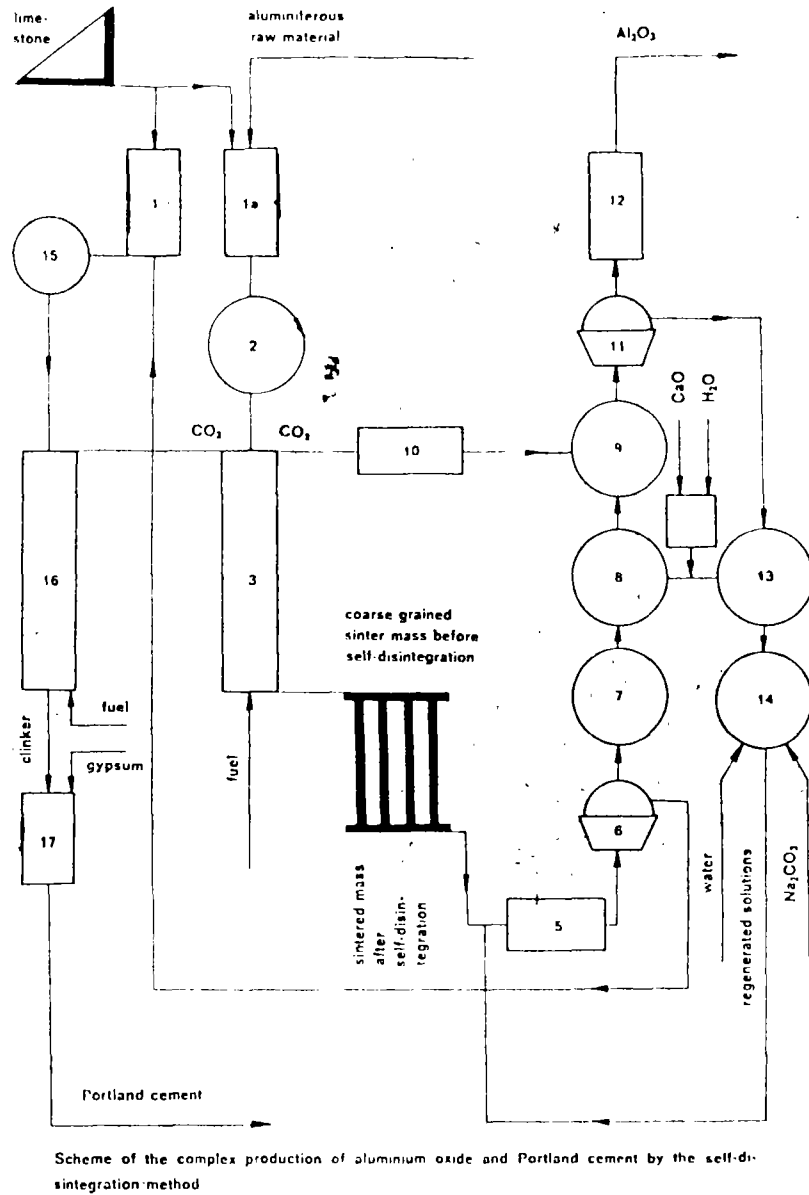


Fig. 4 - Esquema de la producción conjunta de óxido de aluminio y cemento Portland por el método de auto-desintegración

limestone - caliza; *aluminiferous raw material* - primera materia aluminifera; *fuel* - combustible; *gypsum* - yeso; *Portland cement* - Cemento portland; *course grained sinter mass before self-disintegration* - masa sinterizada de grano grueso antes de la auto-desintegración; *sintered mass after self-disintegration* - masa sinterizada después de la auto-desintegración; *water* - agua; *regenerated solutions* - soluciones regeneradas

Figure 7 : Flowsheet of the lime sinter process (Grzymek process [52]).

Limestone	:	12	m.tons
Alumina raw material (31% Al ₂ O ₃)	:	4.5	m.tons
Coal for sinterisation	:	2.0	m.tons
Soda ash	:	0.22	m.tons
Lime	:	0.20	m.tons
Fuel oil (9500 kcal/kg)	:	0.16	m.tons (consumption for cement manufacture is not included)
Steam	:	4.20	m.tons
Electric power	:	1,100	kWhr (consumption for cement manufacture is not included)
Al ₂ O ₃ recovery	:	about 71.7 %	(calculated)
(Al ₂ O ₃ losses during sintering* , alkaline leaching and desili- cification account for total alumina losses)			

Depending on the chemical composition of the raw materials, the cement production ranges between 9 and 12 tons per ton of Al₂O₃.

132. Evaluation of the lime sinter process in U.S.S.R.

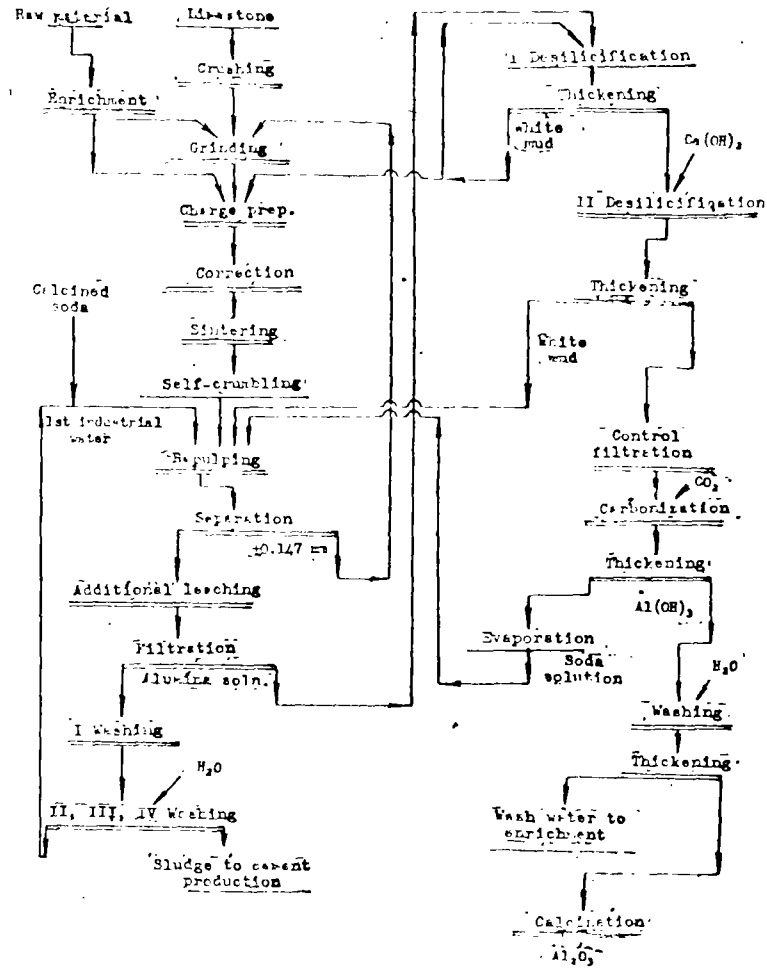
A russian author V.A. MAZEL reviewed the experiments carried out at the LOZ VAMI pilot plant on 1962-1963 [53]. The principles involved in alumina and cement manufacture are very similar to the basic operations used in the Polish pilot plant, a flowsheet is presented in figure n° 8 .

Some features of the process are quoted in the MAZEL report :

- particle size of the sintered mass after self disintegration :
80-85 % less than 147 μm (> 90 % expected for an industrial plant),
- Al₂O₃ recovery in leach liquor : 85-86 % , temperature for leaching : 60-70° C, retention time in extractor : 30 min, soda number** : 1.5, Al₂O₃ concentration : 70 g/l in the final solution,

* alumina engaged in less soluble compounds like gehlenite and aluminoferrite.

** $\frac{\text{Number of Na}_2\text{O moles}}{\text{Number of CaO moles chemically bound with Al}_2\text{O}_3}$



Flowsheet of the production of Al_2O_3 from aluminosilicates by sintering with limestone

Figure 8 : Flowsheet of the production of Al_2O_3 from aluminosilicates by sintering with limestone [53].

- desilicification is carried out in two stages :

- a) precipitation of sodium hydro alumino silicates by heating ($\sim 105^{\circ} \text{C}$),
- b) addition of lime and precipitation of calcium hydro-alumino silicates.

- basic consumption figures (consumptions expressed in metric tons).

Al ₂ O ₃ content in alumina raw material %	34.6	32	30
Natural gas for sinterization t/t Al ₂ O ₃ ***	0.67 } **	0.77 }	0.85 }
	1.04 }	1.26 }	1.45 }
Steam consumption t/t Al ₂ O ₃			
for desilicification	1.47	1.46	1.43
for slime-wash water heating	0.77	0.86	0.95
for aluminium hydroxyde wash-water heating	0.23	0.26	0.29
for boiling out mother liquor	0.93	1.12	1.33
Total steam consumption t/t Al ₂ O ₃	3.4	3.7	4.0
Soda ash consumption kg/t Al ₂ O ₃			
to compensate for chemical losses	106	120	130
to compensate for mechanical losses	27	32	35
Total consumption kg/t Al ₂ O ₃	133	152	165
Alumina raw material needs t/t Al ₂ O ₃	3.5	3.9	4.2
Limestone needs for sinterisation t/t Al ₂ O ₃	8.0	9.2	10.1
Limestone needs for clinkerisation of silicate residue t/t Al ₂ O ₃	~ 3.3	~ 3.9	~ 4.5
Alumina recovery % (calculated)	82.6	80.1	79.4
Portland cement production t/t Al ₂ O ₃	9.76	10.81	11.76
Natural gas for calcination (estimated on specific heat consumption of 1200 kcal/kg of alumina t/t Al ₂ O ₃)	0.1	0.1	0.1
Natural gas for clinkerization (1.450 kcal/kg) of silicate residue obtained for 1 t of alumina t/t Al ₂ O ₃	1.24	1.37	1.49
Electric power for alumina plant kWhr /t Al ₂ O ₃	~ 920	$\sim 1,020$	$\sim 1,100$
Electric power for cement plant kWhr/t Al ₂ O ₃	~ 750	~ 830	~ 900

** Second figure corresponds to 30 % water content of alumina raw material and 57 % water content for the slurry.

First figure corresponds to 0 % water content.

*** Natural gas : 8.000 kcal/Nm³ - specific weight $\sim 0.7 \text{ kg/Nm}^3$

It is reported that small amounts of alkalis ($\text{Na}_2\text{O} + \text{K}_2\text{O}$) in raw materials are very beneficial in lowering sodium (or potassium) carbonate consumption. In treating clay with 32-33 % Al_2O_3 and 1.7 % Na_2O (mica or hydro-mica) contents, soda ash is only added to compensate for mechanical losses, the consumption amounts to about : 30-35 kg/t Al_2O_3 .

The cement kilns output is increased by about 30 % in respect to normal operating conditions*, by using the dicalcium silicate residue.

(In polish pilot plant the percent increase in output is at least 25 %, the percent decrease in thermal consumption per ton of cement is at least 15 %).

A typical chemical analysis of this dicalcium residue obtained at the LOZ VAMI pilot plant is given as follows :

SiO_2 : 22.6 % - CaO : 57 % - Al_2O_3 : 2.7 % - Fe_2O_3 : 1.2 % - Na_2O : 1 %

Loss on ignition and other elements : 14.10 %.

V.A. MAZEL and V.P. MEL'NIKOVA [54] carried out investigations related to effects of impurities contained in raw materials (dolomitized limestone, and alkalis in kaolinitic clay) on self disintegration of the sinter and alumina extraction yields. Their conclusions can be summarized as follows :

- increasing MgO content, for constant molar $\frac{\text{CaO}}{\text{Al}_2\text{O}_3}$ ratio of 1.5 and $\frac{\text{CaO}}{\text{SiO}_2} = 2$, gives lower alumina yields,
- deleterious effect of MgO (0.6 to 4.5 % MgO in the sinter) when treating low alkalis alumino silicates can be offset by using higher $\frac{\text{CaO}}{\text{Al}_2\text{O}_3}$ ratio : 1.8 for instance, instead of 1.3 to 1.66. When treating alumino silicates containing alkalis, this latter ratio can be lowered down to 1.6,
- the alkalis content in the sinter should not exceed 1.2 % so as to preserve self disintegration properties of the clinker (the $\beta \rightarrow \gamma$ inversion of C_2S is hindered by high alkalis content or oxides like : $\text{P}_2\text{O}_5 - \text{B}_2\text{O}_3 - \text{Cr}_2\text{O}_3 \dots$).

As a conclusion, partially dolomitized limestone could be used as well as clays containing a significant amount of alkalis (Dhurma clays for instance).

* Wet processing.

133. Lime-sinter processes applied to clays in U.S.A.

1331. Double-leach process.

In U.S.A., during second World War (1942-1945), the Tennessee Valley Authority carried out laboratory and pilot plant investigations in view of extracting alumina from kaolin [51] according to the lime sinter process.

This process was used in a 1 ton of sinter per day pilot plant [51], it is quite similar to the processes developed in Poland-USSR and France, (SEAILLES process), except that alkaline leaching of the crushed sinter (- 0.75 mm) is achieved in two stages :

- 75 % of the sinter is leached for 40 min at 50° C with solutions (soda ash + sodium aluminate) from the second leaching stage. The slurry is settled, the thickened solids are fed to the second leaching stage, the aluminate solution is directed to the desilicification stage,
- 25 % of the sinter, mixed with the solid residue from the first leaching stage, is leached for 50 min at 50° C, with concentrated soda ash and sodium bicarbonate solutions. The slurry is thickened and washed, the dicalcium silicate residue is separated from the liquor (soda ash + sodium aluminate) which is directed to the first leaching stage.

The final aluminate solution leaving the first stage leaching has a very high silicon modulus (500) [51], 0.2 % SiO₂ in respect to alumina content, due to the double leaching process which limits dicalcium silicate solubility in alkaline liquors Al₂O₃ recovery is 85 %. The final aluminate solution is desilicified with lime* at 80° C for 30 min at atmospheric pressure.

The desilicified solution has a silicon modulus of about 5,000, the sodium and calcium hydro alumino silicates precipitating from the solution contain 3 % of the entering alumina, this precipitate is recycled to sintering.

* white mud can also be used as a desilicifying agent.

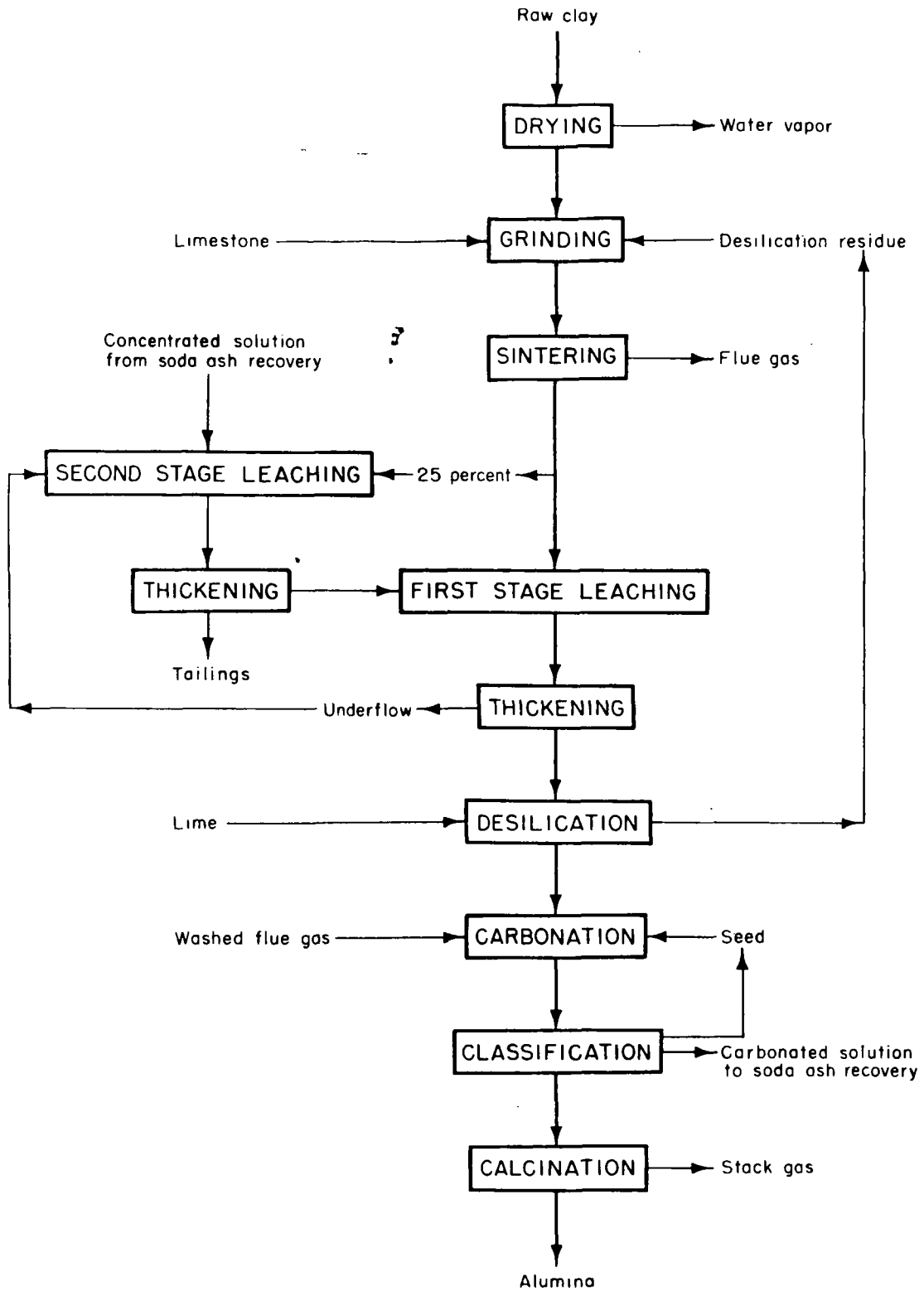


Figure 9 : Flowsheet of the lime sinter double leach process [51].

Aluminate solution is subjected to carbonation at 50° C for 20 hours, high carbonation rate allows 98 % of the alumina to precipitate while high CO₂ content of the remaining solution, which is concentrated and recycled to the second leaching step, favours carbonation of the free lime in the sinter during leaching. Fine alumina tri hydrate is used as a seed, with a seeding ratio of 0.4.

High degree of desilicification before carbonation is necessary because the alumina precipitation by carbonation is nearly complete.

Dry grinding and mixing of the raw materials is an important feature of this process.

Calcined alumina assaying : 99.3 % Al₂O₃ - 0.5 % Na₂O - 0.02 % SiO₂ can be produced [51].

The flowsheet is presented in figure 9 .

1332. Single leach process.

An other american company, the ANCOR CORPORATION operated a 50 tons per day pilot plant in Harleyville (South Carolina) between 1944-1946 [51].

Limestone, recycled soda ash solution (containing a small amount of sodium aluminate) and clay were wet ground and mixed, then dried and sintered at 1,370° C (molar ratio : $\frac{\text{CaO}}{\text{SiO}_2} = 2 - \frac{\text{CaO}}{\text{Al}_2\text{O}_3} = 1.7$ in the charge).

The sinter is leached at 63° C for 45 min with a recycled concentrated solution of soda ash containing a small amount of sodium aluminate (because alumina is not thoroughly precipitated during the carbonation stage). CO₂ is admitted during leaching so as to obtain a suitable concentration. The dicalcium silicate residue is separated and washed, the remaining aluminate solution is directed to desilicification. Due to the leaching conditions used, dicalcium silicate is more soluble in leaching solution than in the case of the double leach process [51].

Desilicification is carried out in autoclave at 177° C for 2 hours with lime addition, because the silica content of the aluminate liquor is high.

The desilicified aluminate solution is subjected to carbonation until 85 % of the alumina is precipitated, this latter proportion cannot be exceeded in order to avoid precipitation of a large amount of silica along with alumina trihydrate.

The precipitated alumina is washed and calcined to produce metallurgical grade.

The flowsheet is presented in figure 10 .

1333. Economic evaluation.

For an hypothetical clay assaying : Al_2O_3 : 30 % - Fe_2O_3 : 3 % - SiO_2 : 50 % - L.O.I. : 15 %, an hypothetical limestone assaying :

CaO : 54 % - CO_2 : 42.4 % - Al_2O_3 : 0.4 % - SiO_2 : 1.6 %

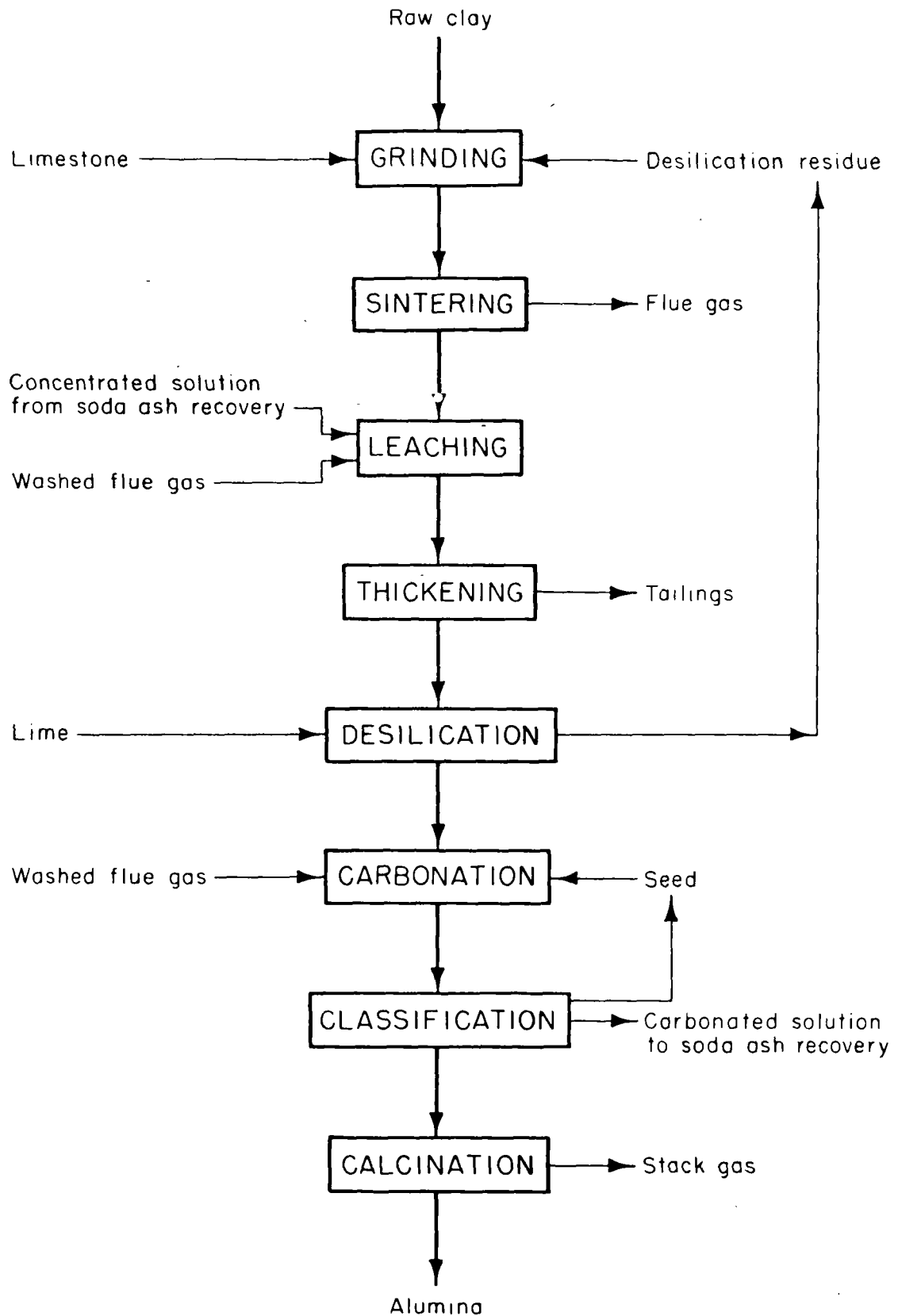


Figure 10 : Flowsheet of the lime sinter single-leach process [51].

U.S.B.M. [51] computed the basic consumption figures presented in the following table :

	Double * leach process	Single *** leach process
Alumina content in alumina raw material	30	30
Alumina raw material requirement : t/t Al ₂ O ₃	4.75	4.98
Limestone requirement for sinterization : t/t Al ₂ O ₃	9.61	10.41
Soda ash consumption***** : kg/t Al ₂ O ₃	29	29
Electric power for alumina production ***** : kWhr/t Al ₂ O ₃	642	611
Steam consumption***** 2.1 kg/cm ² t/t Al ₂ O ₃	2.97	-
Steam consumption***** 17.3 kg/cm ² t/t Al ₂ O ₃	-	5.26
Total water consumption*****: m ³ /t Al ₂ O ₃ (including cooling and process water)	211.7	164.2
Natural gas***** { kcal/t Al ₂ O ₃ { t/t Al ₂ O ₃	16,780x10 ³ 1.47	23,088x10 ³ 2.02
Alumina recovery %	70.18	66.93
* Dry grinding *** Wet grinding ***** 8.000 kcal/Nm ³ - 0.7 kg/Nm ³ ***** Assuming published data on short ton and U.S. gal basis		

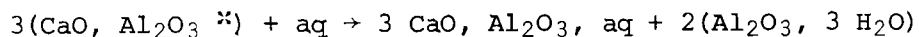
1334. Alumina losses through "gelation" of the leach slurry.

Gelation of the leach slurry may occur when using the lime sinter process [51].

Gelation might be related to the instability of alkaline sodium aluminate solutions (caustic ratio 1.7 to 2) in the presence of calcium aluminate [55].

According to VON EUW [55] calcium aluminate is less soluble in the presence of sodium aluminate ; in certain conditions of temperature and concentration, the leach liquor is supersaturated with respect to calcium

aluminate, causing hydrolysis of the latter and precipitation, of hydrated alumina and hydrated calcium aluminate :



formation of needle shaped crystals of $3 \text{CaO}, \text{Al}_2\text{O}_3, \text{aq}$ and precipitation of hydrated alumina may account for the observed effects during gelation :

- viscosity increase of the slurry,
- swelling and gelatinous appearance of the mud at the beginning of the precipitation process,
- setting of the mud due to $3 \text{CaO}, \text{Al}_2\text{O}_3, \text{aq}$, which is an active hydraulic binder,
- large alumina losses during leaching under inappropriate conditions.

Careful control of leaching conditions may contribute to reduce gelation tendency.

134. The "Seailles" - "Ciments Français" processes.

The following information was obtained from, the Société des Ciments Français, it is the english translation of a short note written by Mr Von EUW, Director of the Research and Development Department [78].

The "Société des Ciments Français" was interested in processes binding cement manufacture to alumina production. It owns patents taken in common with its Consulting-Engineer Mr J.C. SEAILLES, and it is associated with other companies, and specially with Compagnie de Saint-Gobain, to undertake the research at an industrial scale.

The basic principle involved in these processes consisted in producing by an appropriate way, a mixture of soluble calcium aluminates and self crumbling dicalcium silicate starting from low grade bauxites, shales and limestone. Following alumina extraction, the remaining mud is corrected (by limestone addition) so as to obtain a Portland cement composition, a second and very cheap firing leads to clinker production.

* the same reaction may occur with $5 \text{CaO}, 3 \text{Al}_2\text{O}_3$.

In a first step, the mixture of aluminates and dicalcium silicate is obtained by sintering in a rotary kiln designed for cement production (Guerville pilot plant (78) France, operated by Ciments Français) and alumina was extracted by leaching with water.

In a second step, the sinter is leached with soda ash solution, and the liquor subjected to carbonation, providing very pure hydrated alumina, with a low silica content ($\text{SiO}_2 < 100 \text{ ppm}$), which is very important for aluminium production.

The pilot plant, located at Aubervilliers (93) France, was operated between 1949 and 1951 by Cie de Saint-Gobain.

With a derived process studied by 1940, the limestone was replaced by gypsum before sintering, permitting sulfuric acid production along with a mixture of soluble aluminates and dicalcium silicate. Industrial trials were carried out at the Miramas plant (13) owned by Poudrerie Nationale de Saint-Chamas.

In a last step, sintering in rotary kiln was replaced by production of self crumbling aluminous slags in blast furnace*, along with pig iron production. The disintegrated slag was leached with soda ash solution so as to extract alumina.

Industrial trials were carried out, using 500 t blast furnaces at Decazeville (France, 12) and Muttengewerk Rheinhausen (West Germany).

Alumina recovery from the slag was carried out at Aubervilliers (93) pilot plant.

Various industrial projects were elaborated, in France and other countries, they did not materialize for two essential reasons :

- the investments were very important because they had to lead to the construction of industrial complexes, combining the alumina

* a derivative of the Pedersen process.

industry and the Portland cement industry or the alumina, the cement industries and iron metallurgy,

- the discovery of very large new aluminium ore deposits (laterites, bauxites), in various locations throughout the world, called the advisability of such investments in question again.

The Seailles processes are briefly described in a thesis presented by Marcel VON EUW [55].

The limestone and the alumina bearing material mixture is sintered in a rotary kiln (1350-1400° C)-or the limestone-aluminosilicate, coke and iron ore are melted in a shaft furnace, giving cast iron and a self crumbling slag.

In order to hinder formation of gehlenite $2 \text{CaO}, \text{Al}_2\text{O}_3, \text{SiO}_2$ insolubilizing the corresponding proportion of alumina, the molar ratio $\frac{\text{CaO}}{\text{Al}_2\text{O}_3}$ must be higher than 1.3 while $\frac{\text{CaO}}{\text{SiO}_2}$ is 2. Gehlenite slowly decomposes to $2 \text{CaO}, \text{SiO}_2$ and $\text{CaO}, \text{Al}_2\text{O}_3$ at about 1350° C, but practical conditions of cooling do not permit any decomposition in a significant proportion, however maintaining the sinter or the slag at 1350° C, during a sufficient period of time can decrease the amount of gehlenite before leaching. Slow cooling favours $\beta \rightarrow \gamma$ inversion of $2 \text{CaO}, \text{SiO}_2$ and self disintegration of the sinter or the slag.

The disintegrated sinter or slag is leached with soda ash solution at 60° C. The following reactions are observed :

- $\text{Na}_2\text{CO}_3 + \text{CaO Al}_2\text{O}_3 \rightarrow \text{Na}_2\text{O Al}_2\text{O}_3 + \text{CaCO}_3,$
- slight solubilization of $2 \text{CaO}, \text{SiO}_2$ in soda ash solution giving sodium silicate and a calcium carbonate precipitate,
- sodium aluminate and silicate combine partially to give an insoluble hydrated sodium aluminosilicate,
- with an excess of sinter or slag and with a prolonged agitation of the solution, CaO interacts with sodium aluminate, soda is regenerated and the hydrated calcium silico aluminate precipitates.

The sodium aluminate is desilicified with an addition of Portland cement milk, leading to the formation of an insoluble hydrated calcium

alumino silicate through Ca(OH)_2 contained in the cement milk.

Lime in excess interacts with soda ash to precipitate calcium carbonate.

Hydrated alumina is precipitated from the desilicified solution by carbonation, with a seed addition. Sodium carbonate is regenerated and recycled to leaching stage.

The process flowsheet is presented in figure 11 .

During the second World War (1944-1945), an aluminium plant was operated, according to the SEAILLES process, in Germany at STREMBERG, producing 5,000 t alumina per year and about 60,000 t of Portland cement. Coal shales or fly ash (assaying 27.85 % Al_2O_3 - 5.55 % Fe_2O_3 and 44.5 % SiO_2) were used as alumina bearing materials. 20 t of shales and limestone or 18 t of fly ash and limestone gave 1 t of alumina and 12 t of Portland clinker [67].

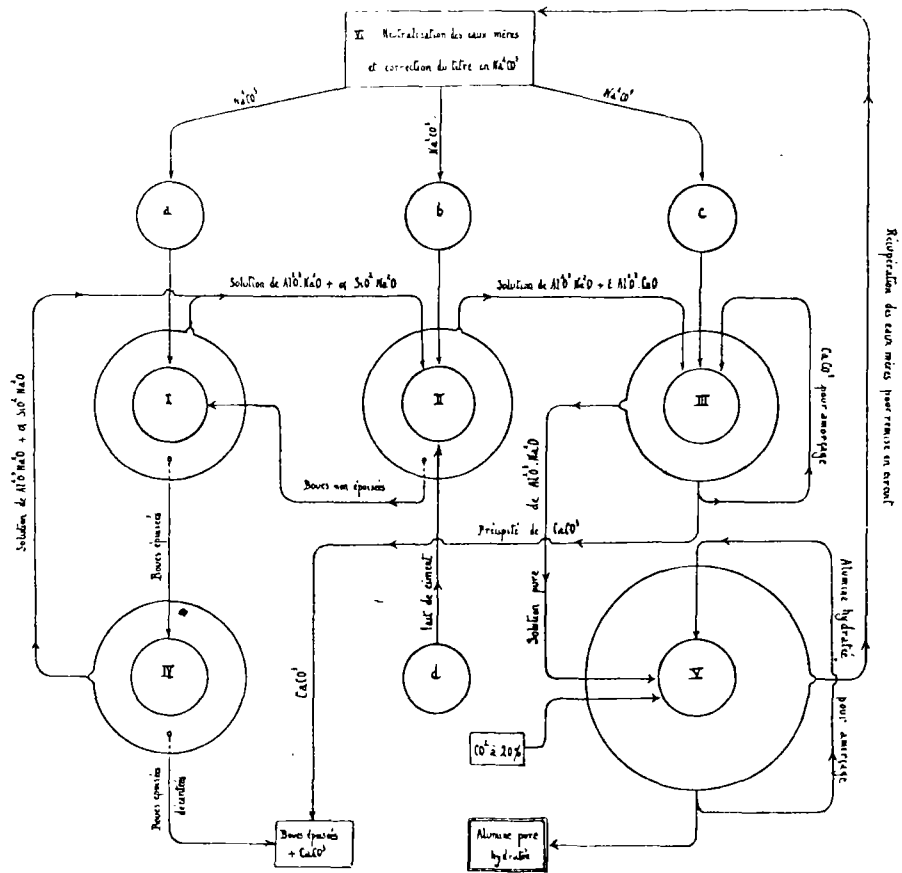


Figure 11 : Flowsheet of the SEAILLES - Ciments Français process [55].

- a, b, c* - soda ash distributors.
- d* - cement slurring and complementary addition of soda ash.
- I* - dissolution tank for complementary leaching of muds by an excess of Na_2CO_3
- II* - dissolution and purification tank (precipitation of silica by an excess of cement)
- III* - purification tank (precipitation of excess CaO by an excess of Na_2CO_3)
- IV* - thickener for washed muds
- V* - carbonator - thickener (hydrated alumina precipitation)
- VI* - neutralization of the mother-liquor and correction of soda ash concentration.

1.4. THE LIME-SINTER PROCESS WITH A REDUCING AGENT.

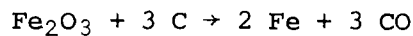
The basic principles involved in this process is quite similar to the usual lime sinter process, but it applies to high iron containing raw materials.

The alumina bearing material (siliceous bauxite, clay or shale) and limestone are finely ground (about - 100 μm) and mixed together with fine petroleum coke or charcoal (- 150 μm).

The charge is sintered at about 1200° C-1300° C (depending on the melting point of the charge) and leached with hot soda or soda ash solution (recycled solution containing alkali aluminate). The aluminate solution is subjected to desilicification, and alumina trihydrate is precipitated from the desilicified solution by carbonation.

Limestone quantity is calculated so as to obtain 2 CaO SiO₂ and 12 CaO 7 Al₂O₃ in the sinter cake [56].

Ferric oxide is reduced by carbon according to the simplified reaction:



(reduction by CO involves Fe₃O₄ and FeO formations - reduction occurs in the following sequences : Fe₂O₃ → Fe₃O₄ → FeO → Fe metal)

The amount of C which is added, corresponds to 50 up to 300 % of the stoichiometric quantity, as indicated by the latter reaction. A mixture of FeO and Fe is obtained [57].

Ferrous oxide is a basic oxide and do not form compounds like calcium ferrite : CaO, Fe₂O₃ ; metallic iron does not combine to alumina and silica as ferric iron does (brownmillerite : 4 CaO, Al₂O₃, Fe₂O₃) thus :

- there is no need to introduce additional limestone in the charge to bind ferric iron,
- alumina yields are increased because no alumina is bound to insoluble compounds like C₄ AF * .

Complete formation of Fe₃O₄ occurs at 800° C with 300 % addition of reducing agent, that of FeO occurs at 1200° C, metallic iron appears at about 800-900° C. Final iron compounds consist of ferrous iron oxide and metallic iron [56].

* cement chemistry notation.

1.5. THE LIME-SODA SINTER PROCESS WITH A REDUCING AGENT.

This process is quite similar to the lime sinter process but soda ash partially replaces limestone so as to obtain sodium aluminate which is readily soluble in alkaline leaching solutions.

Without a reducer, ferric iron, in interacting with soda, lime and alumina forms sodium ferrite, calcium ferrite, and brownmillerite, accounting for additional consumption of raw materials and alumina losses. With a reducer [57] the final interaction products are sodium aluminate, dicalcium silicate, ferrous oxide and metallic iron.

Ferric iron reduction takes place within a temperature range of 700-900° C ; at 900° C, 17 % of the iron is metallic iron, at 1200° C this proportion is 62 %.

It was established [57] that alumina recovery in the leach liquors is greater, the more completely the iron is reduced.

Laboratory and pilot plant tests carried out in U.S.S.R. with Turgai bauxites and red muds demonstrated the efficiency of reduction sintering [57] with respect to conventional sintering :

- sintering temperature is reduced by about 100° C,
- alumina and alkali extractions were 82 % and 93 % without a reducer, 87 % and 91.8 % with a reducer,
- the material flow per ton of alumina for the charge with the reducer, was about 18 % less than the charge without the reducer (due mainly to the reduction of the $\frac{\text{Na}_2\text{O}}{\text{R}_2\text{O}_3}$ ratio).

In U.S.S.R., siliceous and sideritic bauxites were treated according to the following process [58] :

- decarbonation of siderite in a fluidized bed at 600-700° C leading to Fe_3O_4 formation,
- alkaline pressure digestion of the roasted ore, yielding sodium aluminate and red mud containing the magnetite,
- sintering the red mud with limestone and soda so as to recover alumina entrapped in a complex sodium hydro aluminosilicate .

During the latter stage of the treatment it was shown that magnetite in the red mud does not react with soda or lime under the sintering conditions, this makes it possible to reduce the amount of alkali in the original charge, and with the same alumina recovery in leach liquor, to increase the alkali extraction.

It is worth while pointing out that metallic iron or magnetite can be extracted magnetically from the leaching residue [56].

2. HYDROMETALLURGICAL PROCESSES

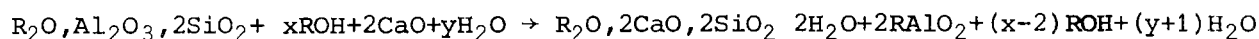
These processes were first developed in U.S.S.R., two types of which have been tried at a laboratory and pilot plant scale.

2.1. THE PONOMAREV-SAZHIN PROCESS.

This latter process was first developed for nephelites and consists of high pressure decomposition of ground nepheline (about - 100 μm), containing about 28-30 % Al_2O_3 , with concentrated soda solution (350-650 g NaOH/l) in the presence of CaO for combining SiO_2 to an insoluble alkali calcium silicate * at 260-300° C [59] for 15 to 30 minutes, with a $\frac{\text{liquid}}{\text{solid}}$ ratio of 3 and molar $\frac{\text{CaO}}{\text{SiO}}$ of about 1 to 1.1. Soda combines with alumina to form soluble alkali aluminate.

211. Leaching.

The pressure leaching stage can be represented by the following simplified reaction (I) [59] [61] :



High alumina recovery (≥ 90 %), in alkali aluminate solution sharply depends on values of the initial molar ratios $\frac{\text{CaO}}{\text{SiO}_2}$ (1.1) and $\frac{\text{Na}_2\text{O}}{\text{Al}_2\text{O}_3}$ (>12) [60].

Alkalis are regenerated from the hydrated alkali calcium silicate deposit, thus, the KOH concentration increases on account of the number of the leaching cycles.

It was demonstrated [59] that increasing KOH concentration, decreases Al_2O_3 extraction, $\frac{\text{K}_2\text{O}}{\text{R}_2\text{O}}$ molar ratio must be lower than 0.38 [60] - 0.40 [63] to keep Al_2O_3 yield at an acceptable level.

In a continuous process, that feature implies separation of alkalis.

* soluble sodium silicate interacting with $\text{Ca}(\text{OH})_2$ leads to precipitation of Na_2O , 2 CaO , 2 SiO_2 , 2 H_2O .

Under inappropriate leaching conditions : $\frac{\text{Na}_2\text{O}}{\text{Al}_2\text{O}_3} < 12$, for the whole system, or $\text{NaOH} \leq 200$ g/l or $\frac{\text{CaO}}{\text{SiO}_2} \leq 0.97$ or low temperature leaching : 160°C for instance, alumina which is extracted, according to reaction (I), further combines to silica, lime or lime and alkalis and precipitates as sodium calcium hydroaluminosilicate, sodium hydroaluminosilicate, cancrinite or hydrogarnet [60].

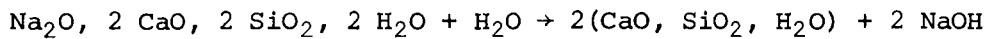
212. Regeneration of alkalis.

Alkalis are regenerated from the hydrated alkali calcium silicate deposit, using one of the following methods :

autoclaving with lime at 210°C and 18 kg/cm^2 for 1 hour, lime is added so as to obtain the insoluble $2 \text{ CaO}, \text{SiO}_2, n \text{ H}_2\text{O}$. The concentration of solutions is approximately $70\text{--}75$ g/l Na_2O [59]

autoclaving without lime at 230°C - 30 kg/cm^2 for 2 hours [59]

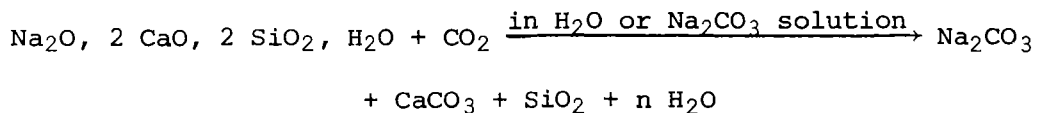
According to reaction :



the solid deposit is hydrolyzed, and releases free alkali, but at a very low concentration : $20\text{--}25$ g/l Na_2O .

carbonation at atmospheric pressure without heating the following, conditions : $\frac{\text{solid autoclave deposit}}{\text{liquid}} = \frac{1}{4}$, time : 60 minutes, CO_2 gas bubbling through the slurry, are used, with an aqueous medium or with a soda ash solution (40 to 100 g/l Na_2O carb.)

Alkali recovery amounts to 86% up 96% [59-62]. The carbonation process can be represented by the following reaction :



213. Utilization of the solid residue.

The final solid residue from the alkali regeneration step :

- hydrated dicalcium silicate

or - hydrated monocalcium silicate

or - mixture of calcium carbonate and colloidal silica

can be thickened and mixed with limestone, bauxite and pyrite cinders to produce Portland cement.

214. Other applications of the process.

Because of their fine particle size distribution giving a good reactivity, clays are probably the best materials to use for this process [60].

A large variety of aluminosilicates can be treated : microcline, albite, oligoclase, labradorite, muscovite, andesite and anorthite, this latter order corresponds to the approximate order of reactivity [60] .

Minerals like kyanite gave low alumina extraction yields [60].

Red mud or solid residue from the Bayer process can be treated hydrochemically according to the Ponomarev-Sazhin process. Alumina recovery is reported to be 90 % [64].

Alumina contained in aluminosilicate slag produced by electrosmelting of red muds, can be extracted hydrochemically. The alumina recovery ranges between 90-95 % [61].

Alumino silicate slag produced by blast-furnace smelting of aluminous iron ore concentrate with limestone, is mixed with nepheline concentrate and hydrochemically treated in autoclave with lime and concentrated soda solution [63]. Alumina extraction in the solution is reported to be : 87-91 %.

2.2. THE MANVELYAN PROCESS.

This process has been devised to treat nepheline-syenite rocks. Few details related to this process are available in the literature.

The basic principle involves hydrochemical etching of nephelinite with solutions which have a specific $\frac{\text{Na}_2\text{O}}{\text{K}_2\text{O}}$ ratio [65].

Na_2O combines to a part of silica and is recovered as an alkali-siliceous solution of Na_2O , while K_2O remains insoluble in a pure potassium alumino silicate (concentrate).

The potassium alumino silicate concentrate is sintered with limestone, the sinter is leached with potassium alkali, and alumina is recovered as a pure potassium aluminate solution. Aluminate solution is desulfurated, and alumina trihydrate precipitated by carbonation.

3. BAYER-SINTERING SEQUENTIAL METHOD (AND COMBINED HYDROCHEMICAL TREATMENTS)

These methods are only applied to high silica high iron bauxites.

3.1. BAYER-SINTERING METHOD.

It consists of two stages :

311. Alkaline pressure digestion.

Alkaline pressure digestion of such a bauxite in autoclave, using the conventional Bayer process leads to large alumina losses in red muds due to the formation of an insoluble sodium hydrated alumino silicate (S.H.A.S.) with the approximate following formula : $3 \text{ Na}_2\text{O}, 3 \text{ Al}_2\text{O}_3, 5 \text{ SiO}_2, 5 \text{ H}_2\text{O}$.

The higher is the silica content, the higher will be the alumina losses (1 ton of silica gives rise to losses of approximation, 1 t of alumina and 1 t of soda ash).

Part of the alumina is recovered as a sodium aluminate solution which is cooled, then filtered before hydrated alumina precipitation occurring through seeding and hydrolysis of the liquor.

312. Sintering.

The insoluble residue or red mud, containing S.H.A.S., iron oxides and titanium is ground and mixed with limestone and soda ash or with limestone, soda ash and carbon so as to obtain molar ratios of : [57] [39]

$$\frac{\text{CaO}}{\text{SiO}_2 + 0.5 \text{ TiO}_2} = 2 \quad \text{to} \quad 2.1 \quad \frac{\text{Na}_2\text{O}}{\text{Al}_2\text{O}_3} = 1.35 \quad \text{to} \quad 1.6 \quad \frac{\text{CaO}}{\text{Fe}_2\text{O}_3} = 2$$

without a reducer.

* One must take into account iron bound with soda.

and molar ratios of :

$$\frac{\text{Na}_2\text{O}}{\text{Al}_2\text{O}_3} = 1.1$$

$$\frac{\text{CaO}}{\text{SiO}_2 + 0.5 \text{TiO}_2} = 2 \text{ to } 2.1.$$

$$\frac{\text{C}}{\text{Fe}_2\text{O}_3} = 1.5 \text{ to } 3.0$$

with carbon.

As it is mentioned in a previous section, ferric iron reduction impedes formation of compounds like sodium or calcium ferrite and brownmillerite that accounts for non soluble alumina in the sinter and large soda ash and limestone consumptions.

Sintering is carried out in rotary kilns at about 1150° C for the charge without a reducer, and at about 1050-1100° C for the charge with carbon.

Leaching the sinter with soda ash solutions allows alumina to be extracted, alumina recovery in the leach liquor ranges between 85 and 92 % soda ash recovery in the leach liquor ranges between 89 and 92 %.

Recovery of alumina and soda depends on the reducing and cooling conditions of the sinter. Typical chemical compositions of red muds are presented in the following table :

	Red mud from Turgay % bauxites	Unknown origin %
Al ₂ O ₃	22.37	22.6 - 21.3
SiO ₂	19.50	19 - 20.4
Fe ₂ O ₃	29.54	27.5 - 30.7
CaO	1.44	1.5
Na ₂ O	10.7	11.3 - 12.0
TiO ₂	4.96	4.5 - 5.2
L.o.I.	10.37	12.8

3.2. Combined hydrochemical treatments.

As it was mentioned in a previous section, red muds from Bayer process can be subjected to hydrochemical treatment according to the Ponomarev Sazhin process, so as to extract alumina [64].

With a Bayer mud assaying :

18.8 % SiO_2 - 20.8 % Al_2O_3 - 31.95 % Fe_2O_3 - 0.97 % CaO - 10.71 % Na_2O -
4.95 % TiO_2 - L.O.I. 0.53 %,

leached in autoclave under the following conditions : - 280° C for 1 hour -
concentration of the starting solution 470 g/l Na_2O - pressure : 40 $\text{kg}\cdot\text{cm}^{-2}$ -
lime addition corresponding to $\frac{\text{CaC}}{\text{SiO}_2} = 1.5$.

Alumina recovery in the solution amounts to 90 %. It was reported that
prolonged contact of the autoclave residue, (sodium, calcium hydrosilicate +
ferric oxides), resulted in large alumina losses due to the formation of hy-
drogarnets [64].

Thus, solid-liquid separation and washing have to be carried out by
filtration rather than slow settling and counter current washing in thicke-
ners.

4. PROCESSES INVOLVING ELECTROSMELTING - BLAST FURNACE - OR TUBULAR FURNACE SMELTING

4.1. THE PEDERSEN PROCESS.

It consists of melting the alumina bearing material with iron ore, coke, and limestone in an electric furnace. Alumina is recovered by alkaline leaching of the slag. It has been used in Norway to treat high-iron, low silica, boehmite bauxite, it has also been used experimentally to treat anorthosite [66]. Technical and economic data are presented in reference [72].

4.2. THE SEAILLES PROCESS, APPLIED TO BLAST FURNACE SLAGS.

The last derivative of the SEAILLES processes (1945-1955) is basically similar to the PEDERSEN process. Experimental assessment of the process was carried out at an industrial scale, using 500 t blast furnaces at Decazeville and Muttenwerk Rheinhausen, between 1950 and 1955 [67]. Iron ore, coke, alumina raw materials, limestone, the two latter components added in suitable amounts* so as to form aluminosilicate self crumbling slags, were melted in a blast furnace, producing cast iron and slag assaying 27-30 % Al_2O_3 .

Leaching with soda ash, resulted in 82 % alumina recovery.

4.3. OTHER MISCELLANEOUS PROCESSES.

Extensive studies were achieved in U.S.S.R. both at a laboratory and a pilot plant scales in attempting to recover alumina from fused slags.

431. Treatment of blast furnace slags.

As an alternative resource of alumina, slags produced from smelting of aluminous iron ore concentrates, can be considered.

4311. Isakov et al [63] carried out laboratory experiments and cost estimate of the process using such a material.

* Limestone addition is calculated so as to obtain dicalcium silicate-calcium titanate and $\frac{CaO}{Al_2O_3}$ 1.3 for the remaining CaO.

Lisakovsky iron ore concentrates assaying 61.5 % Fe - 6.2 % Al_2O_3 - 5 % SiO_2 - 0.9 % CaO - 0.6 % MgO - 2.0 % P_2O_5 - 0.19 % V_2O_5 - coke and limestone in suitable amounts, were smelted, producing cast iron, and self crumbling slag. Too low a lime content in the slag, resulted in formation of a rather large amount of gehlenite, ($\text{C}_2, \text{A}, \text{S}$)* insoluble in soda ash leaching solutions.

The chemical compositions of the slags were in the range : 25-30 % Al_2O_3 - 16-20 % SiO_2 - 46.50 % CaO and 2-3 % MgO, the following phases were present : C_2S (40-50 %) - $\text{C}_2, \text{A}, \text{S}$ (20-35 %) - $\text{C A} - \text{C}_5\text{A}_3$ and spinel $\text{MgO}, \text{Al}_2\text{O}_3$.

Direct leaching of the slag is not advantageous because of the high gehlenite content.

The slag (55 %) was mixed with nepheline (45 %) assaying : 29 % Al_2O_3 , 40.4 % SiO_2 , 6.3 % CaO, 1.3 % MgO, 11.55 % Na_2O , 2.95 % K_2O , 4.4 % Fe_2O_3 - and the mixture was subjected to hydrochemical treatment in autoclave according to the Ponomarev- Sazhin process.

Alumina extraction was 87-91 % and that of alkali, about 85 %. Potassium carbonate is produced along with alumina.

4312. Khazanov [68] describes a process which consists of subjecting to reduction smelting, in a blast, electric or shaft furnace, high alumina iron ore, high iron -high silica bauxite (or an alumino silicate or red mud), carbon, limestone***.

Pig iron and self crumbling slag are produced (if the silica content is sufficiently high).

The slag is ground in the presence of an alkaline solution, the calcium aluminates are solubilized as sodium aluminate which is recovered. The remaining insoluble matter, mainly composed of carbonated lime, C_2S

* cement chemistry notation. *** limestone addition is calculated so as to obtain dicalcium silicate, calcium titanate and $\frac{\text{CaO}}{\text{Al}_2\text{O}_3} = 1.5$ to 2 for the remaining CaO.

and C_2AS , is mixed with a ground alkaline alumino silicate rock in a suitable proportion for obtaining :

$$\frac{R_2O}{Al_2O_3} \text{ (molar)} = 1 \text{ to } 1.5 - \frac{CaO}{SiO_2} = 2 - \frac{CaO}{TiO_2} = 1 - \frac{CaO}{P_2O_5} = 3$$

The latter mixture is sintered at about $1250^\circ C$ and the sinter obtained is leached with a circulating solution of soda ash and sodium aluminate. The total aluminate solution is subjected to desilicification and carbonation to precipitate hydrated alumina. Alkalis are also produced along with alumina. The remaining slimes (C_2S) or solid residue from the second leaching stage can be used for cement production.

Average extractions of alumina and R_2O from sinters amount to 85 % while alumina recovery from the slag ranges between 22 and 57 % (average value in normal conditions : 35 %).

A simplified flowsheet is presented in figure 12 .

432. Treatment of high silica bauxites.

V.D. PONOMAREV [61] proposes a method to treat high iron high silica bauxites.

The bauxite is leached with recycled soda (caustic Na_2O : 200-240 g/l) and sodium aluminate, containing solution at $105^\circ C$ for 2 hours so as to extract alumina (yield : 76.5 %, starting from siliceous bauxite assaying : 10.7 % SiO_2 - 43 % Al_2O_3 - 17.4 % Fe_2O_3).

The slurry is diluted for washing, and thickened to separate sodium aluminate from red mud which is mixed with 3 % carbon and directed to reduction electrosmelting at $1550^\circ C$ for 20 minutes (flux is not added). Electrosmelting requires about 3,000 to 3,500 kW.hrs per ton of pig iron produced [71].

96.8 % of the iron is extracted in a pig iron, while alumina, titanium dioxide and most of the alkalis remain in the slag assaying : 30.3 % SiO_2 , 38.4 % Al_2O_3 , 12.5 % TiO_2 , 1.5 % Fe, 15 % Na_2O .

The slag is then subjected to hydrochemical treatment in autoclave according to the Ponomarev-Sazin process. The alumina is selectively

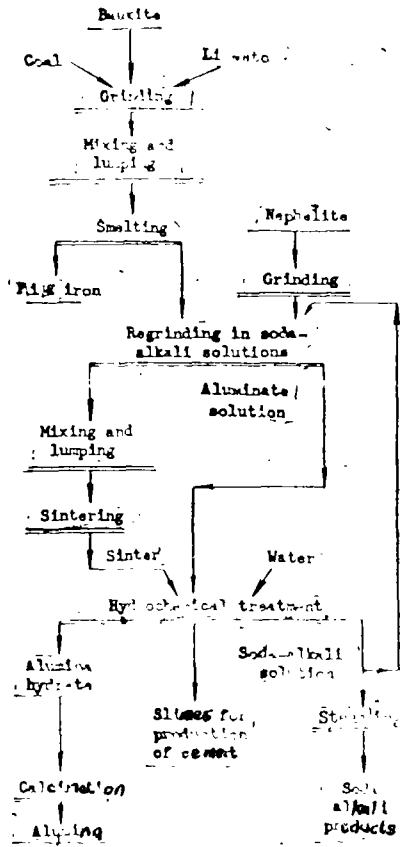


Figure 12 : Flowsheet for the complex treatment of high-iron, alumina-containing, and alkaline aluminosilicate rocks.

extracted from the slag (alumina yield : 90 %, under conditions : Na_2O caustic : 350-500 g/l at 280°C - 50 kg/cm² for 15 min - $\frac{\text{CaO}}{\text{SiO}_2} = 1.1$)

Alkaline leaching of the autoclave solid residue provides a 90-95 % Na_2O extraction and a final slime containing titanium dioxide.

A flowsheet is presented in figure 13 .

433. Treatment of red muds.

A combined flowsheet involving reduction of red mud, and independent smelting of the reduced product in rotary furnaces, was developed at a laboratory scale (Institute of Metallurgy in Sverdlovsk) [70] and experimented at a pilot plant of the Alapaevsk Metallurgical Combine [69].

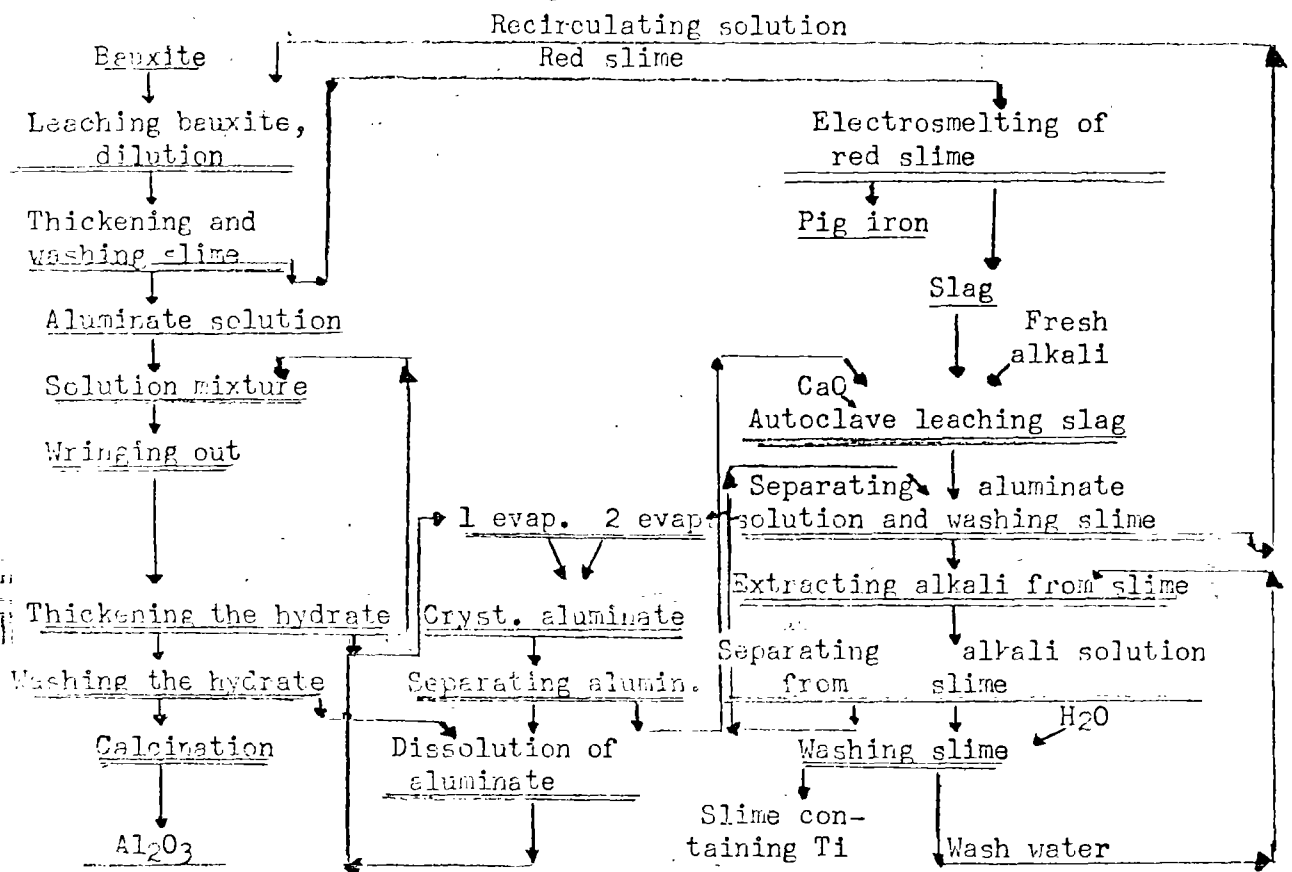
The process consists of reducing the red mud with carbon in a tubular rotary furnace at 1050°C [69] for 4 to 6 hours [71].

The reduced mud and limestone (used as a flux and for the self crumbling slag formation) are melted in a rotating melting furnace heated by a fuel oil burner at $1400-1450^\circ\text{C}$. Due to wearing properties and basicity of the semi-solid slag, the lining is made of chrome-magnesite bricks.

The smelting furnace is operated on a semi continuous way, molten metal is discharged through a tap hole at regular intervals, while the high basicity, semi solid slags ($\frac{\text{CaO}}{\text{SiO}_2} = \text{about } 3$) are discharged continuously. Smelting 8 to 20 tons requires 6-8 hours : high slag basicity provides high quality cost iron with a titanium content lower than cost iron obtained from blast or electric furnace [71] : Ti : 0.1 % - P : 0.35 % - S : 0.02 % - Si : 0.015 %.

The self crumbling slag (due to $\beta \rightarrow \gamma$ inversion of dicalcium silicate) is leached with soda ash solution, the aluminate liquor is desilicified and carbonated to precipitate hydrated alumina.

The solid residue from the leaching stage (gray mud or belite mud) mainly composed of dicalcium silicate is used for producing Portland cement (grade 500 - compressive strength : 500 kg/cm² after 28 days setting).



Flow sheet for complex treatment of high-silica and high-iron bauxites

Figure 13

The following basic consumption figures, were computed from pilot plant data [70] :

Red mud with chemical composition :

Fe : 31.3 % - Al_2O_3 : 13-14 % - SiO_2 : 8-10 % - Na_2O : 2-4 % - P_2O_5 : 1-1.3% -
 V_2O_5 : 0.15 % - CaO : 9-10 %

t/t of alumina	:	9.81
coke fines t/t of alumina	:	1.63
limestone t/t of alumina	:	3.53
fuel oil t/t of alumina	:	0.82
production of cast iron t/t of alumina	:	3.27
production of belite mud for producing cement	} t/t of alumina :	6.20
alumina recovery %	:	75.5
Slag yield per ton of cast iron, t	:	1.973
Slag yield per ton of alumina , t	:	6.450

More detailed cost estimate studies are given in references : [69][70][71]. A flowsheet is presented in figure 14 .

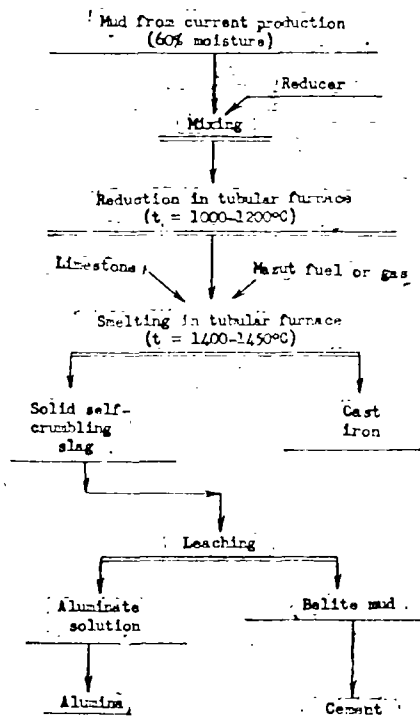


Figure 14 : Flowsheet for the complex treatment of red mud involving tubular furnace utilization.

5. TECHNICAL EVALUATION OF LIME SINTER AND LIME SODA SINTER PROCESSES

Advantages provided by these basic processes may be presented as follows :

- utilization of classical equipment ; the technology of unit operations involved are well known both in the cement industry and the alumina industry,
- these processes have been proved feasible on a technical point of view at a pilot plant scale and semi-industrial scale (order of magnitude for alumina output ~ 5000 t/year),

pilot plant operations :

POLAND (Grzymek process) : lime sinter process with self disintegration of the sinter. Location : Groszowice, in operation since 1954.

Further informations may be obtained from : Polish Institute for scientific investigation and Industry, this institute can be contacted through POLSERVICE VARSAW, UL. POZNANSKA, 15.

FRANCE (Société des Ciments Français in association with J.C. SEAILLES and VON EUW consulting engineers).

Studies on the lime sinter process with self disintegration of the sinter were carried out between 1930 and 1955.

Two pilot plants were operated :

- . GUERVILLE near Paris - before and during 2nd World War,
- . AUBERVILLIERS near Paris - (1949-1951) in association with St Gobain and Hauts Fourneaux de DECAZEVILLE
pilot plants trials were performed at MUTTENWERK RHEINHAUSEN (F.R. of Germany) on 1954-1955 with steel slag from a 500 t/day shaft furnace.

A 5000 t/year alumina plant was designed and operated during 2nd World War (1944-1945) at STREMBERG (Germany), and produced aluminium for military planes.

Two aluminium plants in HUNGARY and RUMANIA (Tornaverni) were operated during 2nd World War according to the Seailles process.

U.S.A. . A 50 t/day plant (50 t of charge) was built at Laramie (Wyoming) during 2nd World War, it was financed by the Defense Plant Corporation. U.S.B.M. operated the plant on 1952 to treat anorthosite with the lime-soda sinter process.

ITALY . A pilot plant is operated in Italy, using lime-soda sinter process on leucite with an output of 1.6 tons/hour of sinter. Further informations can be obtained from Laboratorio Ricerche Alumetal - Porto Marghera Italy.

NORWAY. Construction of a pilot plant for treating alkaline rocks and anorthosite by the lime sinter or lime soda sinter process, is in project, at an industrial scale.

U.S.S.R. Several large alumina plants are operated since 1951, consuming non conventional alumina ores.

Nepheline concentrates, (from the apatite flotation process) are treated at Volkhov and Pikalevo (Kola Peninsula) alumina plants, with a lime sinter process.

Nepheline concentrates are also used with the same process at ACHINSK (Central Siberia). Total capacity of alumina production for these last three plants is estimated to be more than 1 million tons alumina per year (last estimations for 1974 : about 2 millions tons alumina per year [41]).

Siliceous bauxites are processed by sintering with soda and limestone in several large alumina plants at Tikhvin and Siberia.

Several semi-industrial plants are operated on low grade bauxites, clays, shales, red muds from Bayer processing, nephelines, nepheline-syenite and feldspars, according to lime-soda sinter or lime sinter process.

Alumina obtained from basic processes is similar to Bayer alumina and is more suitable for Hall-Heroult electrolysis cells.

Expensive corrosion resistant materials which are necessary with acid processes are not needed with basic processes, mild steel or other ordinary steel equipment is sufficient to handle alkaline solutions.

Clays as well as a great variety of natural and alkalis alumino silicates can be treated by these processes.

Portland cement produced along with alumina (and sometimes potash and soda) is of a suitable quality for local conditions of utilization in Saudi Arabia : low alumina content of the raw materials (mainly dicalcium silicate sludge and limestone) provides salt resistant hydraulic binders (low C_3A content) and lower hydration heat than conventional cements. Compressive strengths as high as 500 kg/cm^2 or more, after 28 days setting can be easily obtained.

Utilization of dicalcium silicate residue gives rise to 25 % increase in the capacity of rotary kilns and 18-20 % decrease in the heat consumption

for cement production, in respect to conventional raw materials used for wet processes.

Simultaneous productions of alumina, Portland cement, and sometimes alkalis do not involve any tailings disposal problem.

PART II :

Acid processes applied to aluminosilicates

"Acid" alumina raw materials, such as clays, or shales represent the most suitable raw materials to use with acid processes.

When using basic processes, solubility of silica in alkaline leaching solutions entails difficulties in removing silica before carbonation of aluminate solutions, when using acid processes, solubility of iron in acid solutions gives rise to difficulties in removing iron from solutions, before precipitation of alumina.

The United States Bureau of Mines evaluated several processes for producing alumina from clay, using acid processes, references [79] to [88], present detailed technical descriptions of these processes as well as the cost estimates.

Among the processes which were considered, two processes :

- Nitric acid - ion exchange process (derived from the Arthur D. Little process),
- Hydrochloric acid - ion exchange process,

exhibit the lowest operating costs [86].

Brief descriptions are presented in the following paragraphs.

1. NITRIC ACID - ION EXCHANGE PROCESS [86]

It consists of the following operations :

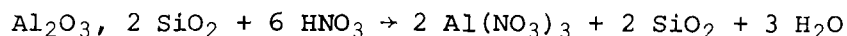
1.1. CALCINATION OF THE CLAY.

The clay is crushed at about 6.5 mm dried and calcined in a rotary kiln at a low temperature, (about 700° C), in order to allow the crystallization water to evolve and break the clay structure (formation of amorphous metakaolin), without forming low solubility compounds like mullite.

1.2. NITRIC ACID LEACHING.

The calcined clay is crushed at about 0.8 mm and then digested with 50 % HNO₃ for 4 hours, at atmospheric pressure, and 125° C.

About 90 % of the alumina is recovered into the solution as an aluminium nitrate by using 95 % of the stoichiometric quantity of HNO₃, required to combine total alumina in the clay :



A small quantity of Fe₂O₃ passes into the solution. The solid residue is washed with water and the solution is filtered.

1.3. ION EXCHANGE EXTRACTION OF IRON.

A synergistic extractant combination of di-(2 ethylhexyl) phosphoric acid and tributyl phosphate, carried in kerosene, is used to extract iron from the nitrate solution.

The raffinate solution is ready for crystallization, the stripping organic phase is contacted successively with water, HCl, and water to remove successively nitric acid, iron and HCl from the solvent which can be recycled.

Ferric ions contained in the hydrochloric solution from the second contacting stage are removed with ion exchange resins, pure HCl can be recycled to the solvent purification stage.

1.4. CRYSTALLIZATION OF ALUMINIUM NITRATE NONAHYDRATE.

Concentration of solution by evaporating them under vacuum, allows aluminium nitrate nonahydrate $Al(NO_3)_3 \cdot 9 H_2O$ to crystallize-85 % of the alumina is precipitated. The crystals are washed with 60 % HNO_3 solutions. Part of the mother liquor is recycled to leaching.

1.5. DECOMPOSITION OF ALUMINIUM NITRATE NONAHYDRATE.

The crystals are melted and decomposed at $200^\circ C$ leaving impure alumina and nitric acid vapor which is recovered.

Impure alumina is subjected to a second decomposition at about $400^\circ C$ giving nitrogen oxides (N_2O_5) and pure alumina which is converted to α form by calcining at about $1100^\circ C$.

1.6. REDUCTION OF THE CONCENTRATION OF THE NITRATES OF IMPURITIES IN THE MOTHER LIQUOR.

In order to prevent the nitrate of impurities from concentrating and precipitating from the mother liquor, part of the latter is evaporated and concentrated, the concentrate is decomposed at $200^\circ C$ giving gaseous $N_2O_5 + HNO_3$ which are recovered.

1.7. ACID RECOVERY.

Nitric acid vapors from the various decomposers are condensed, the solutions are concentrated up to a 60 % HNO_3 concentration.

Gaseous N_2O_5 is recovered by absorption to form a 60 % nitric acid solution.

60 % nitric acid solutions are recycled to leaching.

A flowsheet is presented in figure 15.

A minipilot plant has been built and operated since 1975 at the Boulder City (Nevada) Research Laboratory [87] by U.S.B.M., kaolinitic clays are treated according to the nitric acid ion exchange process.

Ten major alumina-using companies in the U.S. and U.S.B.M. share the cost of the research project.

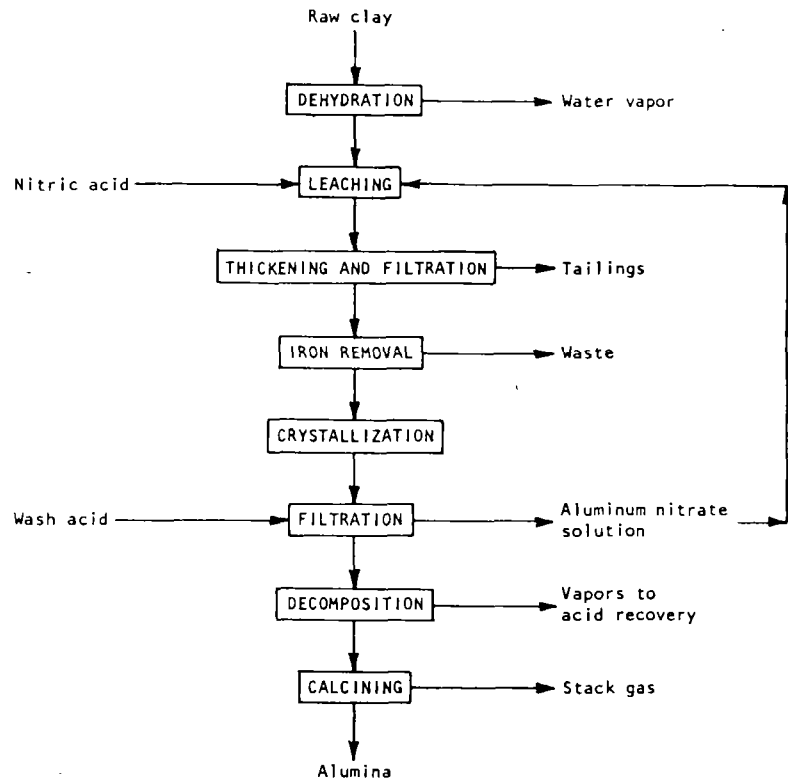


Figure 15 : Flowsheet of the nitric acid ion exchange process [86].

1.8. BASIC CONSUMPTION FIGURES FOR THE NITRIC ACID-ION EXCHANGE PROCESS [86].

(treatment of an hypothetical clay assaying : Al_2O_3 : 30 % - Fe_2O_3 : 3 % - SiO_2 : 50 % - L.o.I. : 15 %).

Alumina raw material requirement	t/t Al_2O_3	4.68
Hydrochloric acid consumption	kg/t Al_2O_3	19
Flocculant consumption	g/t Al_2O_3	100
Nitric acid consumption	kg/t Al_2O_3	93
Electric power	kW-hr/t Al_2O_3	163
Water requirements	m^3 /t Al_2O_3	171
Natural gas	{ t/t Al_2O_3	1.08
	{ Kcal/t Al_2O_3	12, 373, 200
Alumina recovery % (calculated)		71.23
Total energy consumption	Kcal/t Al_2O_3	12, 513, 400

2. HYDROCHLORIC ACID ION EXCHANGE PROCESS [86]

The process includes the following sequences :

2.1. CALCINATION OF THE CLAY.

The clay crushed at about 6.5 mm is dried and calcined at 700° C to remove constitution water and break the clay structure.

2.2. LEACHING WITH HYDROCHLORIC ACID.

The calcined clay is crushed at about 0.8 mm and digested in 20 % HCl solution for 1 hour at about 110° C.

87 % of the alumina passes into the solution as aluminium chloride, 87 % of the iron oxide interact with HCl to form ferric chloride, 20 % of the other impurities interact with HCl.

The slurry is thickened and the solid residue (Mainly silica) is washed counter currently.

2.3. IRON REMOVAL FROM CHLORIDE SOLUTION.

Ferric ions are extracted from chloride solution with an organic solvent which consists of a mixture of secondary amine, n-decyl alcohol, and kerosene.

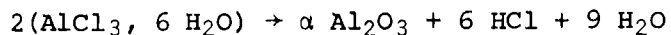
The raffinate is ready for crystallization, ferric chloride is recovered from the organic phase by contacting it with water. The regenerated solvent is recycled to the ion exchange operation.

The ferric chloride solution separated from the aluminium chloride can be decomposed by pyrohydrolysis.

2.4. CRYSTALLIZATION OF ALUMINIUM CHLORIDE HEXAHYDRATE.

Evaporation of iron free solutions of aluminium chloride leads to the removal of water, hydrogen chloride, and subsequent crystallization and precipitation of $\text{AlCl}_3 \cdot 6 \text{H}_2\text{O}$.

The crystals are decomposed at about 1100° C to produce alumina, according to the following reaction :



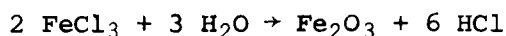
Hydrogen chloride can be recovered from the vapors.

Part of the mother liquors and washing effluents are recycled to the crystallization, while the remaining part is subjected to a further concentration so as to precipitate impurities that could build up in the recycled solutions.

2.5. RECOVERY OF THE HYDROCHLORIC ACID.

The separated mother liquor is evaporated to evolve hydrogen chloride resulting in crystallization of the residual aluminium chloride and impurities. The crystals are decomposed at 1100° C to recover hydrogen chloride.

The ferric chloride is subjected to pyrohydrolysis at 980°C (so as to recover hydrogen chloride and ferric oxide according to the reaction :



Acid vapors from the various crystallization and decomposition operations are mixed with the products of combustion in order to regenerate hydrochloric acid by passing the gas stream through a cooler absorber. The exhaust gas from the absorber is fed to packed tailings towers where residual hydrogen chloride is absorbed by water. The exhaust gas from the towers are free from hydrogen chloride.

The regenerated hydrochloric acid solutions are recycled to the leaching, crystal washing, and crystallization - decomposition stages.

A flowsheet is presented in figure 16.

U.S.B.M. is completing on 1976 the installation of a continuous mini-plant at Boulder City for treating kaolinitic clay according to the hydrochloric acid-ion exchange process [87].

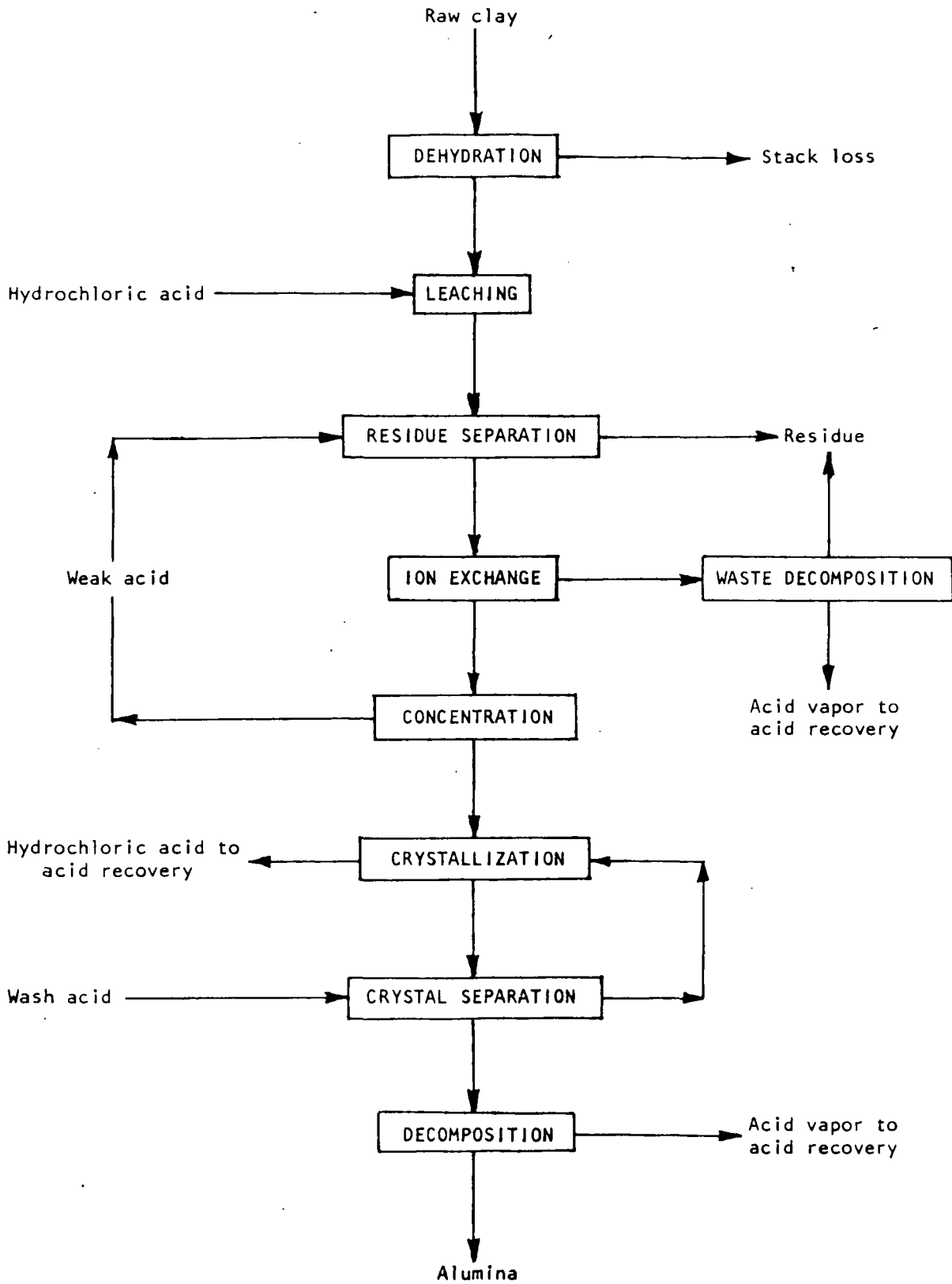


Figure 16 : Flowsheet of hydrochloric acid-ion exchange process [86].

2.6. BASIC CONSUMPTION FIGURES FOR THE HYDROCHLORIC ACID ION EXCHANGE PROCESS [86]

(treatment of an hypothetical clay assaying : Al_2O_3 : 30 % - Fe_2O_3 : 3 % - SiO_2 : 50 % - L.O.I. : 15 %).

Alumina raw material requirement	t/t Al_2O_3 :	5.92
Hydrochloric acid consumption	kg/t Al_2O_3 :	140
Organic solvent consumption	kg/t Al_2O_3 :	2
Electric power	kW-hr/t Al_2O_3 :	134
Water requirements	m^3 /t Al_2O_3 :	248
Natural gas	{ t /t Al_2O_3 :	0.83
	{ kcal/t Al_2O_3 :	9, 525, 600
Alumina recovery % (calculated)	:	66.40
Total energy consumption	Kcal/t Al_2O_3 :	9, 641, 000

3. THE H⁺ PROCESS

This process was devised for extracting alumina from low grade clayey materials (minimum alumina content 18-20 % [89]). Clays containing low alkalis, iron, and alkaline-earth oxides are the most suitable raw materials.

A flowsheet is presented in figure 17.

It consists of the following stages [90 to 93] .

3.1. CLAY PREPARATION.

- Crushing and grinding the ore,
- Calcination at about 700° C.

This latter operation is optional. Ores containing organic matter, carbonaceous products, pyrite, ferrous oxide have to be roasted in an oxidizing atmosphere so as to burn or oxidize the reducing elements.

The H⁺ process is applied to a material containing ferric iron and free from reducing agents *, before sulfuric acid digestion.

3.2. SULFURIC ACID DIGESTION.

Crude or calcined clay is leached for 1 to 4 hours at about 125-140° C and atmospheric pressure with H₂SO₄. Alumina is selectively solubilized as aluminium sulfate. Due to the H₂SO₄ concentration in the leach liquor (750 to 850 g/l) most of the impurities form low solubility sulfates, specially ferric iron and potassium oxide combine with SO₄⁻⁻⁻ to form the iron potassium double sulfate with low solubility in concentrated sulfuric solutions.

- titanium and iron combine with SO₄⁻⁻⁻ to form a low solubility double sulfate,
- sodium passes into the solution.

* reducing agents may reduce ferric iron and sulfuric acid (formation of SO₂).

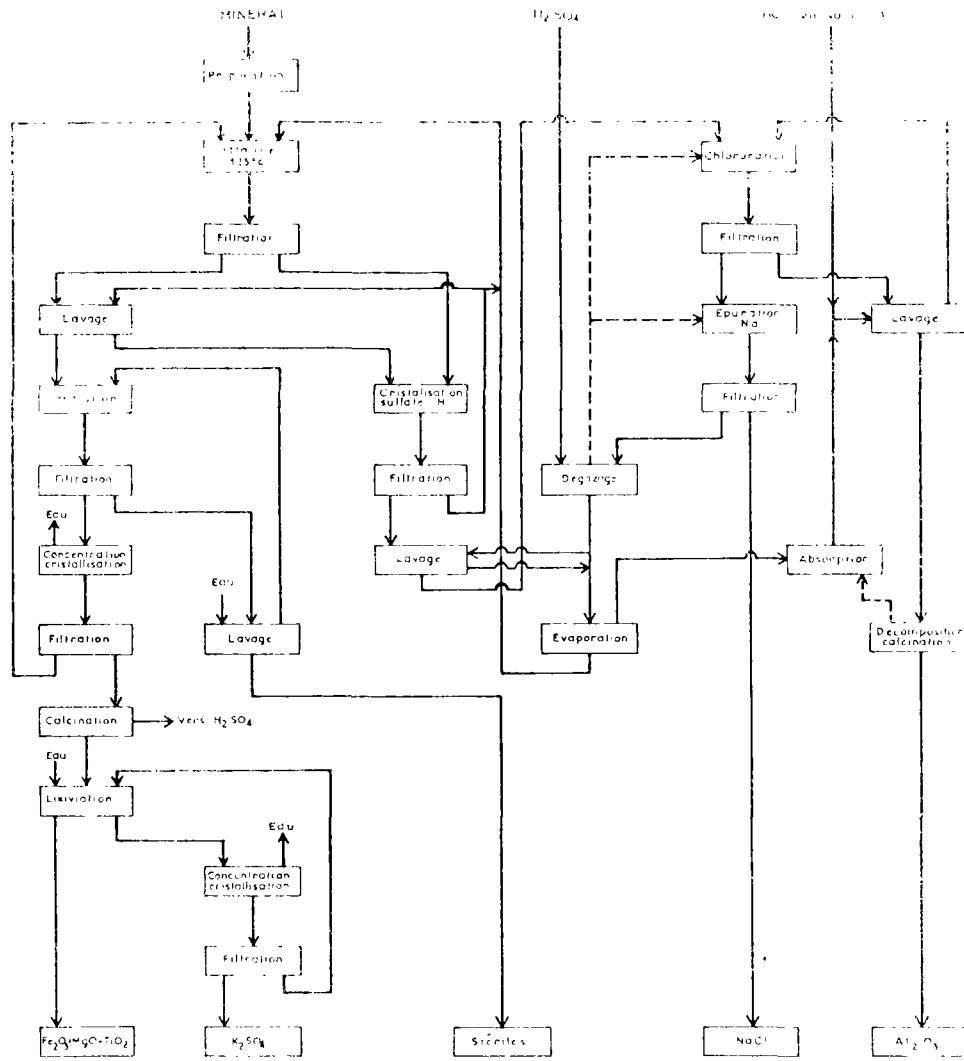


Figure 17 : Flowsheet of the H⁺ process [90].

3.3. PRIMARY LIQUID-SOLID SEPARATION.

The solid residue from the leaching stage containing silica, calcium and most of the impurities as sulfates : Fe-K-Mg, is recovered by filtration.

The filtrate mainly contains Al and Na as sulfates and a small proportion of the impurities : Mg-K-Fe.

3.4. COUNTER CURRENT WATER WASHING OF THE SOLID RESIDUE.

The sulfates of impurities that present a low solubility in concentrated sulfuric solution, are more soluble in diluted sulfuric solution. The solid residue from the digestion stage is washed counter currently with water so as to separate the soluble sulfates of Fe, K, Mg, from the insoluble compounds : silica, calcium sulfate ...

The washed solid residue is wasted.

3.5. RECOVERY AND SEPARATION OF THE IMPURITIES.

This operation aims at the regeneration of sulfuric acid from the iron and magnesium sulfates the decomposition of which occurs at low temperature. Potassium sulfate does not decompose, not allowing the sulfuric acid to be regenerated from it - however it can be used for manufacturing chemical fertilizers.

The liquid phase from the washed residue is evaporated and concentrated so as to precipitate Fe, K and Mg sulfates which are recovered by filtration.

The new solution containing residual sulfuric acid and few impurities is recycled to the leaching stage.

The precipitated sulfates are calcined at 1000-1100° C to decompose Fe and Mg-sulfates, SO₃ is recovered for regenerating concentrated sulfuric acid, which is recycled.

The solid residue from the calcination stage is water washed so as to separate K₂SO₄. The solid residue from this latter leaching stage consists of a mixture of Fe₂O₃ and MgO which can be used in iron metallurgy. It is worth while pointing out that iron sulfate decomposes at a lower temperature (about 500° C) than magnesium sulfate (about 1100° C) so that separa-

tion of Fe_2O_3 from MgO appears to be feasible.

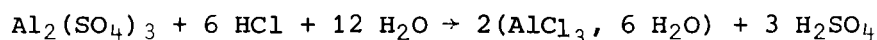
3.6. SEPARATION AND PURIFICATION OF THE ALUMINA.

361. Crystallization of aluminium sulfate.

The sulfuric solution separated from the primary solid residue is cooled so as to precipitate alumina as a crystallized sulfate containing most of the sodium. These sulfates are separated by filtration, the filtrate containing most of the sulfuric acid and a small proportion of the soluble impurities, is recycled to the leaching stage.

362. Crystallization of the aluminium chloride hexahydrate.

The sulfate crystals are dissolved in a hydrochloric acid solution. Alumina is selectively precipitated as aluminium chloride hexahydrate while cooling ($40-45^\circ \text{C}$) the solution saturated with hydrogen chloride ; sulfuric acid is regenerated according to the following reaction :



The primary aluminium chloride hexahydrate crystals can be subjected to a further purification stage including :

- dissolution of the crystals in a hydrochloric acid solution,
- precipitation of purer crystals while saturating the solution with hydrogen chloride.

The crystals are washed, the hydrochloric acid solutions are recycled to the first chlorination stage.

3.7. RECOVERY OF THE ACIDS.

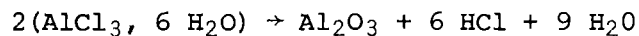
The filtrate separated from the primary aluminium chloride crystals mainly contains H_2SO_4 - HCl and NaCl . Cooling the solution down to $35-40^\circ \text{C}$ while saturating with hydrogen chloride gives rise to NaCl precipitation which is recovered by filtration - so that sodium is eliminated from the acid solution to be recycled.

The remaining solution is heated so as to recover gaseous HCl (anhydrous). The residual liquor is concentrated by heating, a hydrochloric acid solution is obtained by distillation. HCl , (gaseous HCl and hydrochloric acid) is recycled to precipitation stage or purification stage of the aluminium chlorides.

The residual liquid from the distillation stage mainly contains H_2SO_4 which is recycled to the leaching stage.

3.8. RECOVERY OF ALUMINA AND HYDROGEN CHLORIDE.

$AlCl_3, 6 H_2O$ crystals are subjected to pyrohydrolysis at $600-1100^\circ C$. Alumina is produced along with gaseous HCl which is recycled to the chlorination stage



3.9. MAIN FEATURES OF THE H^+ PROCESS.

391. Hot sulfuric acid digestion allows solubilization of the alumina at atmospheric pressure without preliminary calcination of the clay.

392. Sulfuric acid is recycled from the sulfates through decomposition at high temperature and conversion of the $SO_2 + SO_3$ mixture to H_2SO_4 , in a catalytic unit.

The recovery of alumina as an aluminium chloride allows a direct recovery of HCl .

393. The selective precipitation of $AlCl_3, 6 H_2O$, under controlled temperature conditions, from chlorhydric solutions, saturated with gaseous HCl , allows separation and purification of alumina while using a simple process, the other metallic chlorides remain in the solution.

394. The acids H_2SO_4 and HCl are recycled through the thermal decomposition of the salts in which they were bound as anions : iron and magnesium sulfates, aluminium chloride.

The liquors containing free acids are sufficiently purified to be directly recycled, under continuous stable working conditions.

395. Silica, calcium compounds remain insoluble in the sulfuric leaching liquor. Titanium dioxide, ferric iron and potassium, form low solubility double sulfates (titanium-iron sulfate and potassium-iron sulfate), magnesium sulfate is also a low solubility compound.

These latter compounds are soluble in diluted acid solution, allowing their corresponding sulfates to be recovered from the leach residue by water leaching so as to :

- regenerate H_2SO_4 through thermal decomposition of $Fe_2(SO_4)_3$ and $MgSO_4$,
- separate K_2SO_4 (stable compound) as a valuable component for fertilizer production.

It is worth while noting that this latter salt is an important by-product from the alunite processing.

Under the conditions used while leaching and recycling the acid solutions, Al and Na remain in the sulfuric solutions.

396. The sodium concentration in the recycled liquors is kept constant, in stable working conditions, by precipitating sodium chloride from the chloride solutions saturated with hydrogen chloride under controlled temperature conditions, so that, any major impurity is concentrated on account of time in the recycled solutions, that is essential for a continuous process.

397. The acids are recycled. The losses are represented by the anions combined to CaO, K_2O and Na_2O ($CaSO_4 - K_2SO_4 - NaCl$).

3.10. RELATIONS BETWEEN THE RAW-MATERIAL CHARACTERISTICS AND THE H^+ PROCESS.

On an economic point of view, the minimum alumina grade must be higher than 18-20 % [89] however the suitability of a raw material depends on the nature of its impurities :

- SiO_2 (free or combined) is insoluble the silica does not affect recycling of the acids,
- CaO forms a low value sulfate which cannot be decomposed (decomposition is possible when using high temperature and a reducer), CaO found in various forms in clays : carbonates, feldspars, micas, exchangeable cations, represents the major impurity (gypsum or anhydrite are not acid consuming impurities),
- Fe_2O_3 , MgO, K_2O can be separated from the siliceous solid residue, Fe and Mg sulfates are easily decomposed (specially $Fe_2(SO_4)_3$) that allows SO_3 combined to the corresponding oxides, to be recovered. Fe and Mg do not give rise to acid losses

the high temperature decomposition of the sulfates and the subsequent conversion of the $\text{SO}_2 + \text{SO}_3$ mixture in H_2SO_4 are the main troublesome problems encountered when treating high iron or high magnesium containing raw materials. These inconveniences might be offset by using Fe_2O_3 and MgO in iron metallurgy [93],

- K_2SO_4 cannot be easily decomposed, K_2O is an acid consuming oxide. The sulfate can be used in fertilizer manufacture [93].
- Na_2SO_4 cannot be decomposed. Na is separated as a low value NaCl which cannot be decomposed. Na_2O is a major impurity because high Na_2O content result in large hydrochloric acid losses,
- P_2O_5 can be considered as an impurity P_2O_5 is known to exert an unfavourable influence on the quality of the alumina,
- Ferrous compounds or clay containing Fe^{2+} in their crystal lattice (glaucosite, sometimes smectites and illites) are major impurities. Ferrous ions are not fully insolubilized in the sulfuric acid leaching solution. It is necessary to roast the clay at 700°C , in order to "break" the clay structure and oxidize ferrous iron.

Alumina raw materials, containing reducing agents or ferrous iron, like carbon, organic compounds, pyrites, magnetite and certain clay minerals, have to be roasted, increasing thermal requirements.

However, it is likely, that breaking the clay structure may improve the leaching kinetics.

- "Acid" raw materials, with low CaO , MgO and Na_2O contents, assaying more than 20 % Al_2O_3 are suitable for the H^+ process. High Fe_2O_3 and K_2O contents are not critical on a technical point of view.

3.11. DEVELOPMENT OF THE H^+ PROCESS AT THE PECHINEY COMPANY.

The whole of the proved reserves : $17 \cdot 10^9$ tons, of high quality bauxites assaying - 40 to 60 % Al_2O_3 and less than 10 % SiO_2 , suitable for the Bayer process, represents 50 years of supply, taking into account the present level in Al production : 15×10^6 t/year and its rate of growth of about 6 to 8 % per year [92, 41].

Taking into account the location of the main deposits, the political and economical contingencies related to bauxite supplies, the progressive depletion in bauxite reserves, the Pechiney Company studied for about ten years, basic and acid alumina extraction processes from clays, feldspars and feldspathoids. The abundance of the clay reserves throughout the world, the average alumina grade, usually higher for clays than other non bauxite ores, the regularity in composition, the cheap clay mining and preparation, were sufficient arguments for Pechiney Company to develop alumina extraction processes from clays.

On 1967, at the end of a laboratory research program, the H^+ process was patented [93].

A continuous minipilot plant (200-250 kg of alumina per day) has been operated by the Company at Gardanne since 1971, allowing to define the best technical and economical conditions for using the process.

Alumina extraction yields (recovery) range between 85 and 95 % and are usually greater than 90 % [90]. By-products recoveries range between 80 and 85 % [91]. Acid consumptions (H_2SO_4 and HCl) depend on CaO , K_2O and Na_2O contents of the clays.

The calcined alumina produced according to the H^+ process is purer than the Bayer alumina : 99.7 to 99.8 % Al_2O_3 for the H^+ process, 99.5 % Al_2O_3 maximum, for the Bayer process.

The content in minor impurities is low [90] :

	Na_2O ppm	CaO ppm	Si ppm	Fe ppm	V ppm	Ti ppm	P ppm	Zn ppm
H^+ process	< 100	150-200	60	< 50	< 5	20-25		< 5
Bayer	4000-7000	300-500	60-100	100-250	5-10	15-25	5	30-100

The particle size distribution of the α alumina produced according to the H^+ process would be more favourable than that of the usual Bayer alumina, for aluminium reduction by the Hall-Heroult process, a slightly lower energy consumption is expected.

Pechiney (5th World producer of Al) associated to Aluminium of Canada (ALCAN : 2nd World producer of Al) for developing the H^+ process.

A continuous pilot plant of 20 tons alumina per day was to be put in operation at Lestaque (near Marseille) on May/June 1976 [90].

3.12. EVALUATION OF AVAILABLE RAW MATERIALS IN SAUDI ARABIA ON ACCOUNT OF THE H^+ PROCESS.

Under economically favourable conditions the average production of an aluminium producing plant ranges between 150-200,000 tons/year [91] corresponding to an alumina consumption of about 300 to 400,000 tons/year.

Taking into account an average alumina recovery of 85 %, a minimum mining duration of 50 years, the alumina reserves in the considered ore deposits must be in the range 18 to 24 x 10⁶ tons.

In Saudi Arabia, the Dhurma Shales deposit appears to be suitable for the H^+ process both on a quantitative and qualitative point of view. Estimated reserves amounted at more than 100 x 10⁶ tons (on 1975). The raw clay containing kaolinite-illite-quartz-smectite-iron oxides as main components, assays about 27 % Al_2O_3 (based on analysis carried out on 1974-1975).

34 samples were analysed at the Jeddah laboratory :

Average Al_2O_3 content (Al_2O_3) : 27 %

- 27 samples assaying $Al_2O_3 \geq 25$ % (Al_2O_3 : 28.2 %)

- 7 samples assaying $20 \leq Al_2O_3 < 25$ % (Al_2O_3 : 22.4 %)

Complete chemical analysis carried out on 14 samples gave the following results :

9 samples assaying $Al_2O_3 \geq 25$ %

SiO_2 : 43.33 % - Al_2O_3 : 28.39 % - CaO : 0.6 % - MgO : 1.15 % -

Fe_2O_3 : 7.70 % - FeO : 0.06 % - K_2O : 2.07 % - Na_2O : 0.77 % -

L.o.I. : 14.51 % - CO_2 : $\sim < 0.5$ % .

5 samples assaying $Al_2O_3 < 25$ %

SiO_2 : 48.10 % - Al_2O_3 : 21.96 % - CaO : 1.16 % - MgO : 1.28 % -

Fe_2O_3 : 8.22 % - FeO : 0.05 % - K_2O : 1.90 % - Na_2O : 1.0 % -

L.o.I. : 14.74 % - CO_2 : ~ 0.5 % .

These results are favourable for the H^+ process, CaO and Na_2O contents are low. MgO and K_2O contents do not reach critical levels. Iron content is rather high, but this impurity does not affect the acid consumption.

First investigations revealed the clay deposit to be sufficiently homogeneous for large scale mining. The limestone overburden is not very thick. The fine grained shale presents low free silica and water contents, these features are quite favourable for low cost mining and raw material preparation before leaching.

3.13. ROUGH EVALUATION OF THE H^+ PROCESS.

A rough evaluation of the H^+ process applied to Dhurma shales was computed from published data and information obtained from private communications [90, 91].

Raw clay consumption t/t Al_2O_3 produced : 4.12, acid requirements calculated to combine

CaO, K_2O to SO_4^{--} , and Na_2O to Cl^-

(acids cannot be regenerated from $CaSO_4$, K_2SO_4 and

NaCl)

H_2SO_4 kg/t Al_2O_3 : about 150

HCl kg/t Al_2O_3 : about 45

Energy consumption including thermal and

electric power requirements

6,500,000
kcal/t Al_2O_3 : to
9,500,000

Water requirements (used mainly for

cooling)

m^3 /t Al_2O_3 : about 25

Valuable by-products

Fe_2O_3 kg/t Al_2O_3 : about 260

K_2SO_4 kg/t Al_2O_3 : about 120

Alumina recovery (estimated from reference [90]) : 90 %

4. COMPARISON OF VARIOUS ACID PROCESSES

Energy consumption or energy cost as well as the total operating cost of different acid processes are presented in references [90, 94 and 79 to 88].

	Total energy consumptions (including thermal and electric power consumptions) expressed in Kcal/t Al_2O_3 [90]
H ⁺ process applied to clays or shales *	6,500,000 - 9,500,000
Nitric acid process applied to kaolin	11,500,000 - 12,500,000
Hydrochloric acid process applied to kaolin	12,000,000 - 12,500,000
Sulfurous acid process applied to kaolin	10,000,000 - 11,000,000

The following diagram [94] presented in figure 18 gives the total production cost expressed in Swedish Kronor per ton of produced alumina. Capital, power and operating costs in Sweden on 1975 have been taken into account for the computation of the total costs.

The shaded area of the diagram indicates the energy costs.

* Bayer process : 4,000,000 - 5,000,000 Kcal/t Al_2O_3 .

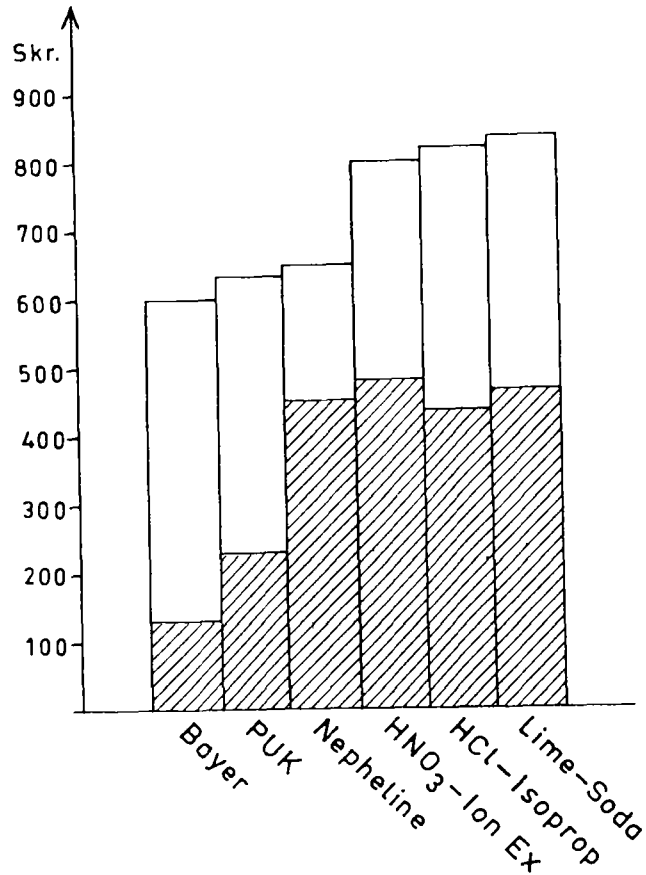


Figure 18 : Comparison of the production costs of alumina with various processes [94]. (Costs expressed in Swedish Kronor)
 P.U.K. = H⁺ process from Pechiney Ugine Kulhman.

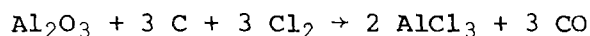
5. THE TOTH PROCESS [95, 96]

The Applied Aluminium Research Corporation (A.A.R.C.) developed a chlorination process so as to recover aluminium from clay, bauxite or other alumina bearing material.

This process can be subdivided into four stages.

5.1. STAGE 1.

Reduction and chlorination of the calcined clay in the presence of a reducer to form aluminium-chloride, according to the reaction :



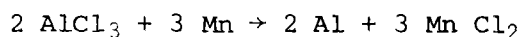
Addition of SiCl_4 impedes further chlorination of the silica, 90 % of the alumina, 93 % of the iron oxide, about 100 % of the titanium and alkalis oxides are chlorinated.

FeCl_3 is condensed and oxidized so as to separate Fe_2O_3 and regenerate Cl_2 .

SiCl_4 and TiCl_4 are condensed and then separated by distillation. A final epuration of the aluminium trichloride is obtained by contacting with Al particles : $\text{FeCl}_3 + \text{Al} \rightarrow \text{AlCl}_3 + \text{Fe}$.

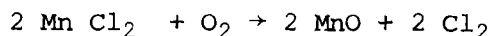
5.2. STAGE 2.

Pure aluminium trichloride liquid is reacted with solid manganese metal to form aluminium metal and manganese dichloride according to the reaction :



5.3. STAGE 3.

Manganese dichloride is oxidized with oxygen to form manganous oxide and regenerate chlorine gas according to the reaction:



5.4. STAGE 4.

Reduction of manganous oxide by carbon so as to regenerate manganese metal according to the reaction :



Aluminium metal is directly produced from alumina bearing materials, without separating alumina. A.A.R.C. claimed that the production cost of aluminium would be reduced by 50 %.

High chlorination temperatures involve corrosion problems which will be difficult to solve.

A flowsheet is presented in figure 19.

This process will have to be proved feasible at a pilot plant scale before considering its application.

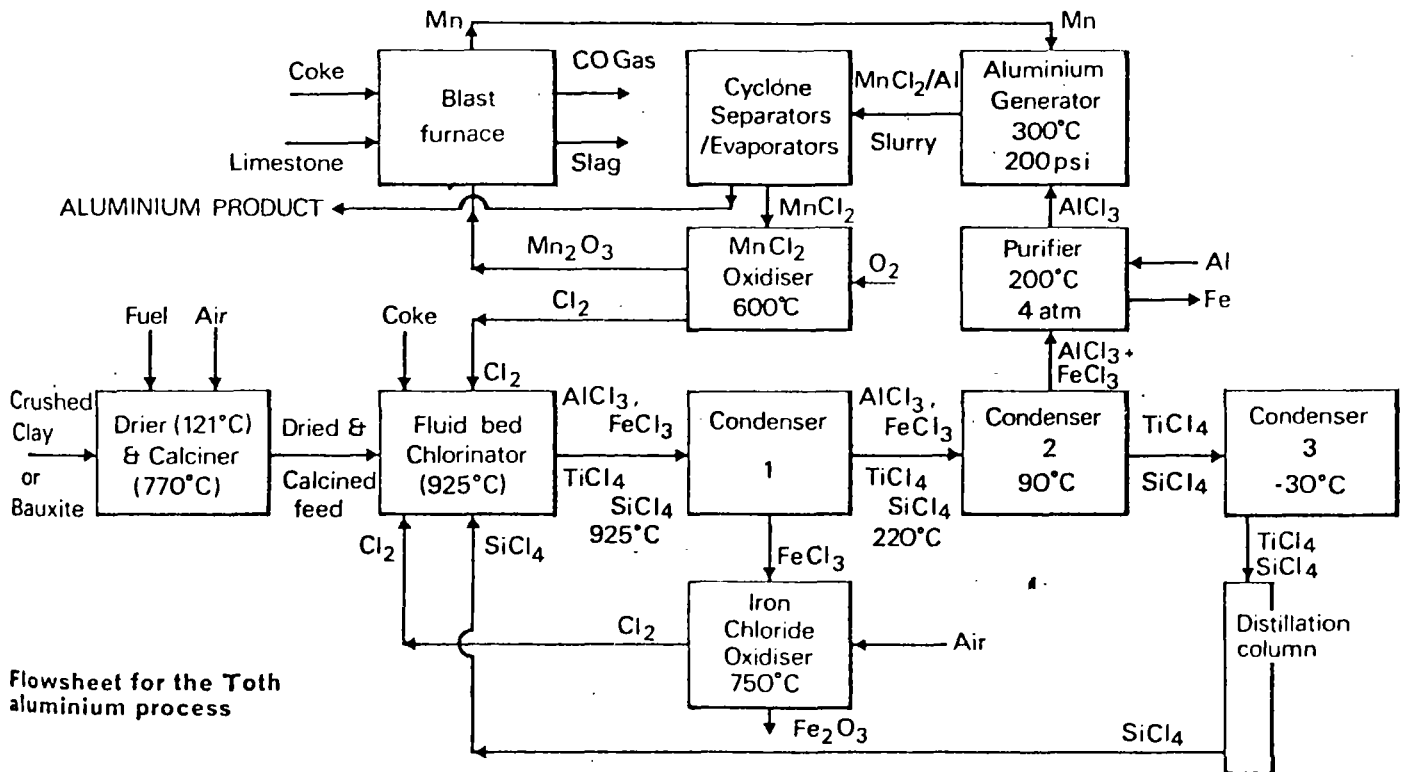


Figure 19 : Flowsheet for the Toth aluminium process [95].

C O N C L U S I O N

This documentary study accounts for alumina extraction processes which have been developed beyond the laboratory trials and can be carried into industrial practice in a short period of time.

Processes related to alumina extraction from alumino silicates are only considered in this study in the absence of known large alunite deposit in Saudi Arabia.

The minimum amount of aluminium to be produced under economical conditions from a plant can be estimated at 150,000 - 200,000 tons per year, that implies a production of 300,000 - 400,000 tons of alumina per year. Two huge deposits of alumino silicate rocks :

- Shales from Dhurma assaying 25 - 27 % Al_2O_3 ,
- Anorthosites from Yanbu area assaying about 22 % Al_2O_3 represent sufficient alumina reserves for providing such a quantity of processed alumina for more than 50 years.

In the present state of knowledge related to the alumina content and extension of these deposits, Dhurma shales appear to be the most suitable material as a source of alumina. Low compacity, water and free silica contents, fine particle size and good homogeneity of this clayey ore are quite favourable for large scale mining and material preparation at low cost.

Alumina extraction processes, from alumino silicate rocks, which are available at present time or that will be for the near future can be subdivided in two groups :

- acid processes involving treatment of "acid" alumina bearing raw materials such as clays or shales,
- basic processes. These processes are suitable for both "acid" and "basic" alumina bearing raw materials, including for the latter, feldspars containing materials such as anorthosite.

Among the acid processes developed in U.S.A. and France, three processes present the lowest estimated energy requirements and operating costs :

- nitric acid-ion exchange process,
- hydrochloric acid-ion exchange process.

These two latter acid processes are studied in U.S.A. by the United States Bureau of Mines. A continuous minipilot plant evaluation of the Nitric acid process has begun at the Boulder City (Nevada) Research Laboratory since 1975. The hydrochloric acid process evaluation is under development, a minipilot plant operation is planned for 1976-1977.

The H⁺ process from the Pechiney-Ugine Kuhlman Company.

This process is revealed as the most economic and feasible alumina extraction process from clays, shales, oil or coal shales and clayey industrial wastes, according to published technical data and cost estimates.

The technical and economic evaluations of this process are the most advanced among the corresponding evaluations of the acid processes considered so far. It was proved feasible at a pilot plant scale. A pilot plant producing 200-250 kg of calcined alumina per day is operated at Gardanne since 1971 and treated a large variety of alumina raw materials. A larger pilot plant with a capacity of 20 t per day had to be put in operation at Marseille on May/June 1976.

For this latter operation, Aluminium of Canada (ALCAN) the second World producer of aluminium, joined Pechiney to share the cost of the process development.

According to analysis carried out on 1974-1975, the Dhurma clay assays :
 27 % Al₂O₃ - 7.7 - 8.2 % Fe₂O₃ - 1.15 - 1.28 % MgO - 1.90 - 2.10 % K₂O - 0.8 - 1.0 % Na₂O - 0.6 - 1.2 % CaO - < 0.5 % CO₂ - 14.5 % L.o.I. This chemical composition is suitable for the H⁺ Process.

A rough evaluation of the H⁺ process applied to Dhurma clays was computed from published data :

- Raw clay consumption t/t Al₂O₃ 4.12
 (assuming an average Al₂O₃ recovery of 90 %)
- Theoretical acid requirements (calculated to combine
 CaO, K₂O to SO₄⁻⁻⁻ and Na₂O to Cl⁻ - acids cannot be
 regenerated from CaSO₄ - K₂SO₄ and NaCl)

H ₂ SO ₄ kg/t Al ₂ O ₃ :	about 150
HCl kg/t Al ₂ O ₃ :	about 45

- Energy consumption including thermal and electric power requirements

Kcal/t Al_2O_3	{	6,500,000
	}	to
	{	9,500,000

- Water requirements (used mainly for cooling) $m^3/t Al_2O_3$: about 25

- Valuable by-products :

Fe_2O_3 kg/t Al_2O_3 :	about 260
K_2SO_4 kg/t Al_2O_3 :	about 120

It is worth while pointing out that alumina recoveries, for the H^+ Process, determined under laboratory and pilot plant conditions (85 to 95 % - most frequently a 90 % recovery is claimed by Pechiney) constitute the highest alumina yields quoted in the literature.

The basic processes can be subdivided in four groups :

- 1) processes involving sintering of the alumina bearing material with :
 - limestone
 - limestone + carbon
 - limestone + soda ash
 - limestone + soda ash + carbon.

- 2) hydrometallurgical processes.

- 3) Bayer sintering sequential method and combined hydrochemical treatments.

- 4) Processes involving smelting of the alumina raw material with limestone, carbon and optionally with an aluminous iron ore.

Hydrometallurgical processes are under development in U.S.S.R., few details related to technical evaluation and operating cost are available, so that these processes cannot be considered for the treatment of the potential ores in Saudi Arabia.

Group n° 3 processes involve complex treatments applied to low grade bauxites (high silica, high iron containing bauxites) large deposits of which have not been found in Saudi Arabia).

Group n° 4 processes are suitable for treating high iron containing raw materials or mixtures containing iron ore. Energy requirements are very high. Cast iron and Portland cement which are or can be produced along with alumina, have to be commercialized to make the process economically feasible. It seems unrealizable to bind three major industries in a single combine.

The basic processes involving sintering of the alumina raw material with limestone or limestone + soda ash (and optionally carbon to reduce iron in high iron containing raw materials) are derivatives from the lime sinter process which is extensively used in the U.S.S.R., where about 2 million tons of alumina per year are estimated to be produced from nepheline.

A large pilot plant is operated for several years in Poland (at Groszowice since 1954) treating coal shales with the lime sinter process.

These processes were also tested at a pilot plant scale :

IN FRANCE : by SEAILLES - Ciments Français at Guerville and Aubervilliers between 1935 and 1955.

IN U.S.A. : by the Tennessee Valley Authority
by the Ancor Corporation at Harleyville (South Carolina)
during second World War (lime sinter process applied
to clays)
by the United States Bureau of Mines at Laramie (Wyoming)
between 1945-1952. (lime soda sinter process applied to
clays and anorthosite).

Research projects are planned in Norway to treat anorthosite and in Italy to treat leucite.

Alumina and aluminium were produced at an industrial scale (about 5,000 t Al_2O_3 /year) during the second World War in Hungary, Rumania (Tornaverni) and Germany (Stremberg), according to the SEAILLES processes (lime-sinter process).

The dicalcium silicate residue produced along with alumina, when using basic processes on clays or anorthosites, can be used to manufacture Portland cement, the characteristics of which (low heat of hydration and salt resistance) are suitable for local conditions of utilization in Saudi Arabia.

The shales from Dhurma are potential ores for basic processes, large limestone deposits are known in the vicinity of the shale deposit.

A rough evaluation of the lime sinter process applied to clays or shales assaying 30 % Al_2O_3 was obtained from published data :

raw clay consumption t/t Al_2O_3 produced	:	4.2	
limestone consumption for sinterization t/t Al_2O_3	:	10.1	
limestone consumption for clinkerisation of the calcium silicate residue t/t Al_2O_3	:	about 4.5	
Soda ash consumption : kg/t Al_2O_3 :	:	165 ***	
Natural gas consumption :			
(8000 Kcal/N m^3 - specific weight 0.7 kg/N m^3)			
for sinterization t/t Al_2O_3	:	1.45	
for alumina calcination t/t Al_2O_3	:	0.1	
for Portland cement production * t/t Al_2O_3	:	1.49	
Steam consumption: t/t Al_2O_3	:	4.0	
Total electric power KW-hr	:	about 2,000	
for alumina production	:	about 1,100	
for cement production	:	about 900	
Portland cement production : t/t Al_2O_3	:	11.8	
Total energy consumption expressed in Kcal for producing 1 t Al_2O_3 and 11.8 t of Portland cement	Kcal	:	
		:	39,250,000
Total energy consumption Kcal/t Al_2O_3	:	21,450,000	
Total energy consumption Kcal/t Portland cement	:	1,508,500	
Water requirements : m^3 /t Al_2O_3	:	50 to 65	

High iron content of Dhurma clays might require the addition of carbon, before sintering, so as to improve alumina recovery, in that case the amount of carbon to be used can be roughly estimated at 150 kg/t Al_2O_3 (carbon consumption

* wet processing

*** This figure represents a maximum because Dhurma shales contain about 3 % alkalis

will be slightly offset by a reduction of the fuel consumption for sintering).

High energy and raw material consumptions for producing alumina alone make the process unfeasible. For producing both alumina and Portland cement the total energy and raw material consumptions are quite favourable. One must point out that ^alarge increase in Portland cement production (10 million tons) is planned in Saudi Arabia.

It can be estimated that the lime-soda sinter process applied to a shale like Dhurma shale would involve energy and raw material requirements of the same order of magnitude as with the lime sinter process.

With current prices (ex. works in France) of calcined alumina (148 \$/t) and Portland cement (30 \$/t bagged), about 4.5 tons of clay and 15 tons of limestone represent a value of about 500 \$ when they are beneficiated according to a basic process.

Detailed informations related to basic processes and evaluation of the suitability of the alumina raw materials (anorthosite and clays) for these processes can be obtained from :

SOUTHWIRE CORPORATION IN U.S.A. :

This company is the sole agent in the U.S.A. (and probably in the Western World) of Licenzentorg the Russian licensing agency. Southwire had chosen the Soviet technology for treating alunite from a large deposit located near Cedar City (Utah).

The technologies related to nepheline process and other derived basic alumina extraction processes operated in U.S.S.R., can be obtained through Southwire. It is important to emphasize the 25 years of industrial experience of Russian companies about basic processes, the related patents and know how, might be turned rapidly to account for an industrial project.

It is also worth while pointing out that Southwire is engaged in a feasibility study for the construction of an aluminium plant with a capacity of 225,000 t/year, near Djubail in Saudi Arabia.

UNITED STATES BUREAU OF MINES :

(Lime-sinter and lime-soda sinter processes applied to anorthosites and clays).

POLSERVICE AT VARSAW (POLAND) :

(lime-sinter process applied to shales).

SOCIETE DES CEMENTS FRANCAIS :

This company disposes of the know how related to alumina and cement technologies and may act as a consultant or project supervisor.

REFERENCES

- [1] V. Ya ABRAMOV - Iz PEVZNER
"Analyses of the operation of rotary sintering furnaces in alumina production" .
Tsvetnye Metally - vol. 6 n° 2 - p. 57-61 - 1965
- [2] S.M. ROYAK - L.A. KROICHUK
"Rational conditions for using nepheline slime in cement production" .
Tsvetnye Metally - vol.10 n° 4 - p. 69-70 - 1969
- [3] I.I. BELYAEV
"Automation of nephelinite and limestone grinding at the Volkhov aluminium works" .
Tsvetnye Metally - vol. 3 n° 1 - p. 52-57 - 1962
- [4] ARLYUK - M.N. SMIRNOV - S.M. ERMOLAEVA - KIRILLOVA
"Improving the control over alumina-sinter quality"
Tsvetnye Metally - vol. 10 n° 7 - p. 61-63 - 1969
- [5] GERMAN - GALKINA - ZLOKAZOVA and alii
"Using hydrocyclones in combination with thickeners to separate solids when leaching alumina-bearing sinter".
Tsvetnye Metally - vol. 2, n° 1 - 1961 - p. 54-56
- [6] V.M. POLYANSKII - A.F. KARFIDOV - V.V. PETROVSKII
"Control algorithms for the leaching process in the hydrometallurgy shop at the Achinsk alumina combine" .
Tsvetnye Metally - vol. 4 n° 11 - 1963 - p. 43-45
- [7] ABRAMOV and alii
"Basic rules governing the leaching of nepheline sinters".
Tsvetnye Metally - vol. 12 n° 11 - p. 39-40 - 1971

- [8] M.N. SMIRNOV
"Decomposition of dicalcium silicate and silica passage to solution when leaching fine-ground aluminate sinters".
Tsvetnye Metally - vol. 7 n° 1 - 1966 -
p. 56-64
- [9] M.F. MALYSHEV
"On the interaction of β -2 CaO, SiO₂ with caustic soda solution".
Tsvetnye Metally - vol. 6 n° 2 - 1965 -
p. 62-64
- [10] N.S. MAL'TS - Z.D. ZIRKEVICH - O.I. ARAKELYAN
"Effect of sinter leaching conditions on the degree of β 2 CaO, SiO₂ decomposition, the relationship of the formed phases and the composition of hydrogarnets".
Tsvetnye Metally - vol. 16 n° 1 - 1976 -
p. 40-43
- [11] G.A. ARKSEL'RUD - V.Y. ABRAMOV and Alii
"Theoretical principles underlying calculations of secondary alumina losses incurred when leaching alumina sinters".
Tsvetnye Metally - vol. 12 n° 2 - 1971 -
p. 36-39
- [12] I.B. FIRFAROVA - I.G. GORELIK and Alii
"An examination of α' 2 CaO, SiO₂ stabilization conditions when sintering alkali alumina-containing charges".
Tsvetnye Metally - vol. 16 n° 2 - 1975 -
p. 26-28
- [13] T.I. AVDEEVA - A.A. NOVOLODSKAYA
"Effect of salts on desilicification of sodium aluminate solutions".
Tsvetnye Metally - vol. 10 n° 10 - 1969 -
p. 45-48
- [14] N.S. VOLKOVA and Alii
"Role of impurities during desiliconization of aluminate solutions".
Tsvetnye Metally - vol. 12 n° 11 - 1971 -
p. 33-35

- [15] B.K. SHVARTSMAN - N.S. VOLKOVA
"Influence of potassium on the desilicification of aluminate solutions" .
Tsvetnye Metally - vol. 3 n° 6 - 1962 -
p. 82-84
- [16] T.I. AVDEEVA - A.A. NOVOLADSKAYA
"Composition and thermographic characteristics of some potassium hydroaluminosilicates" .
Tsvetnye Metally - vol. 5 n° 7 - 1964 -
p. 62-67
- [17] A.I. LAINER - M.A. KOLENKOVA - L.U. KOTIEVA
"White slime as an activating addition for the process of aluminate solution desilicification" .
Tsvetnye Metally - vol. 3 n° 10 - 1962 -
p. 49-54
- [18] M.F. MALYSHEV
"Comparative chemical activity of β 2 CaO, SiO₂ and CaO, SiO₂ H₂O" .
Tsvetnye Metally - vol. 5 n° 11 - 1964 -
p. 60-63
- [19] A.I. LAINER and MAI-KI
"Desilicification capacity of lime in view of data obtained from the system Na₂O - Al₂O₃ - CaO - CO₂ - SiO₂ - H₂O" .
Tsvetnye Metally - Vol. 7 n° 9 - 1966 -
- [20] M.G. LEITEIZEN and M.S. BELETSKII
"Thorough desilicification of aluminate solutions in the presence of lime" .
Tsvetnye Metally - vol. 4 n° 9 - 1963 -
p. 52-56
- [21] B.K. SHVARTSMAN - N.S. VOLKOVA
"An examination of the effect of adding CaO and MgO on the desiliconization of aluminate solutions" .
Tsvetnye Metally - vol. 8 n° 8 - 1967 -
p. 79-82

- [22] T.I. AVDEEVA and A.A. NOVOLODSKAYA
"Employing gray mud as a desilicifying addition" .
Tsvetnye Metally - vol. 8 n° 5 - 1967 -
p. 67-70
- [23] A.I. LAINER and MAI-KI
"Two stages desilicification of pure potassium aluminate solutions, at atmospheric pressure" .
Tsvetnye Metally - vol. 5 n° 9 - 1964 -
p. 55-57
- [24] M.G. MANVELYAN and Alii
"Effect of recentrifuging autoclave pulp on the results of aluminate solution desilicification" .
Tsvetnye Metally - vol. 5 n° 5 - 1964 -
p. 45-47
- [25] A.I. LAINER and L.U. KOTIEVA
"Laboratory and pilot studies on the desilicification of aluminate solutions at atmospheric pressure and with a large amount of white mud" .
Tsvetnye Metally - vol. 4 n° 8 - 1963 -
p. 53-58
- [26] I.Z. PEVZNER - A.I. LAINDER and Alii
"Testing the method of alumina solution desiliconizing, without digestion in autoclaves" .
Tsvetnye Metally - vol. 8 n° 2 - 1967 -
p. 61-69
- [27] B.I. ARLYUK - V.A. MAREL - E.I. KHODOROV
"Kinetics of sintering nepheline charges" .
Tsvetnye Metally - vol. 8 n° 2 - 1967 -
p. 54-60
- [28] J.B. ALLEN - T.J. CHARLESLEY
"Nepheline - syenite and phonolite" .
Institute of geological sciences - Mineral division - London Her majesty's stationary office -
1968

- [29] M.G. MANVELYAN and Alii
"Using white mud as an active additive in the desilicification of predominantly potassium aluminate solutions" .
Tsvetnye Metally - vol. 5 n° 9 - 1964 -
p. 47-49
- [30] M.G. MANVELYAN and Alii
"Desilicification of pure potassium aluminate solutions in the presence of chemical additives" .
Tsvetnye Metally - vol. 3 n° 11 - 1962 -
p. 66-73
- [31] B.K. SHVARTSMAN and Alii
"Influence of silica on the forming of crystals when carbonating solutions obtained in the process of treating nepheline raw material" .
Tsvetnye Metally - vol. 5 n° 4 - 1964 -
p. 39-44
- [32] R.M. BERLIN - R.V. BEREZIN
"A method of continuously controlling the thoroughness of the process of aluminate solution carbonation" .
Tsvetnye Metally - vol. 6 n° 7 - 1965 -
p. 58-60
- [33] M.V. NISHANINA and Alii
"Formation of sodium hydro-alumino carbonate when aluminium hydroxyde interacts with soda solutions" .
Tsvetnye metally - vol. 12 n° 9 - 1971 -
p. 35-38
- [34] A.I. LAINER
"Behavior of silica during carbonation of aluminate solutions"
Tsvetnye metally - vol. 6 n° 7 - 1965 -
p. 61-65
- [35] B.K. SHVARTSMAN and Alii
"Industrial tests on methods of producing high-grade alumina from nepheline raw material" .
Tsvetnye metally - vol. 3 n° 7 - 1962 -
p. 39-42

- [36] A.N. LYAPUROV and Alii
"Employing $Al(OH)_3$ seeding to carbonate an aluminate solution"
Tsvetnye Metally - vol. 12 n° 2 - 1971 -
p. 40-42
- [37] S.I. KUZNETSOV and R.A. ABANIN
"Kinetics of decomposing aluminate solutions in increased concentrations" .
Tsvetnye Metally -
- [38] N.I. EREMIN and Alii
"An examination of the true solubility of sodium hydroaluminosilicate in aluminate solutions" .
Tsvetnye Metally - vol. 9 n° 7 - 1968 -
p. 63-66
- [39] S.S. NURKEEV and Alii
"Effect of heating and cooling conditions on Al_2O_3 and Na_2O extraction during sintering of red mud" .
Tsvetnye Metally - vol. 9 n° 6 - 1968 -
p. 76-78
- [40] B.K. SHVARTSMAN - N.S. VOLKOVAR
"Obtaining high-quality alumina when heating bauxites by sintering" .
Tsvetnye Metally - vol. 1 n° 4 - 1960 -
p. 60-63
- [41] G.A. BAUDART
"Alumine sans bauxite" .
Revue de l'Aluminium - Février 1975 - n° 437 -
p. 57-61
- [42] G.P. MEDVEDEV and Alii
"Extraction of aluminium oxide, alkali and silica when treating high silicon bauxites" .
Tsvetnye Metally - vol. 16 n° 2 - 1975 -
p. 34-36

- [43] V. Ya ABRAMOV and Alii
"Increasing the efficiency of flow-type leaching for bauxite sinter-cakes" .
 Tsvetnye Metally - vol. 13 n° 4 - 1972 -
 p. 35-37
- [44] P.W. JOHNSON and F.A. PETERS
"Methods for producing alumina from anorthosite. An evaluation of a lime-soda sinter process" .
 U.S.B.M. - R.I. 7068 - January 1968
- [45] F.A. PETERS and Alii
"Methods for producing alumina from clay. An evaluation of a lime-soda sinter process" .
 U.S.B.M. - R.I. 6927 - 1967
- [46] T.I. LITVINOVA - T.A. BEKUZAROVA
"An examination of the effect of a calcium oxide dosage on the nature of the silicate phases in bauxite sinters".
 Tsvetnye Metally - vol. 2 n° 4 - 1961 -
 p. 45-49
- [47] M. BROFMAN and Alii
"An examination of the bauxite sintering process in rotary furnaces" .
 Tsvetnye Metally - vol. 10 n° 3 - 1969 -
 p. 65-71
- [48] A.I. LAINER and Alii
"An examination of equilibrium states in system $Na_2O \cdot Al_2O_3 - Na_2O \cdot Fe_2O_3 - 3 CaO \cdot MgO \cdot 2 SiO_2$ at $1200^\circ C$ " .
 Tsvetnye Metally - vol. 10 n° 8 - 1969 -
 p. 49-51
- [49] R.V. LUNDQUIST - D.D. BLUE
"Role of alumina to silica mole ratio in the lime-soda sinter process" .
 U.S.B.M. - R.I. 7434 - September 1970
- [50] R.V. LUNDQUIST - E.L. SINGLETON
"Some characteristics of iron in the lime soda sinter process for recovering alumina from anorthosite" .
 U.S.B.M. - R.I. 6090 - 1962

- [51] J.J. HENN and Alii
"Methods for producing alumina from clay. An evaluation of two lime sinter processes" .
U.S.B.M. - R.I. 7299 - September 1969
- [52] *"Metodo para la produccion de oxido aluminico con produccion simultanea de cemento Portland"* .
Cemento - Hormigon n° 416 - Novembre 1968 -
p. 1027-1041
- [53] V.A. MAZEL
"Some technological and economic aspects of converting kaolin clay, and other aluminosilicates to alumina and cement" .
Tsvetnye Metally - vol. 5 n° 10 - 1964 -
p. 42-46
- [54] V.A. MAZEL and V.P. MEL'NIKOVA
"Use of dolomitized limestone in the production of aluminium oxide from aluminosilicates by sintering with limestone" .
Tsvetnye Metally - Vol. 6 n° 4 - 1965 -
p. 53-55
- [55] Marcel VON EUW
"Etude physico-chimique des laitiers alumineux autopulvérisants dans le système $SiO_2 - Al_2O_3 - CaO$ " .
Thèse C.N.A.M. - 12 juillet 1949 published in
"Silicates Industriels" - October 1950 to
March 1951
- [56] D.S. MUKIMOV - N.I. EREMIN - V.A. MAZEL
"Ferric oxide reduction when roasting a bauxite limestone carbon charge" .
Tsvetnye Metally - March 1968 - vol. 9 n° 3 -
p. 59-61
- [57] R.G. ROZENSTRETER and Alii
"Producing alumina by sintering aluminosilicates with limestone, soda and reducer" .
Tsvetnye Metally - vol. 4 n° 7 - 1963 -
p. 41-46

- [58] V.A. DEREVYANKIN and Alii
"Converting sideritic bauxites to alumina" .
Tsvetnye Metally - vol. 16 n° 2 - 1975 -
p. 29-30
- [59] M.G. MANVELYAN and Alii
"A method of decomposing the alkali-calcium deposits obtained when treating nephelines hydrochemically" .
Tsvetnye Metally - vol. 2 n° 2 - 1961 -
p. 57-62
- [60] S.B. MUJAHED - A.P. PRUSSER - O. MELGREN
"Mechanism of NaOH - Ca(OH)₂ leaching process for extraction of alumina from aluminosilicate minerals" .
Transactions of the I.M.M. - December 1974 -
p. C 241 - C 249
- [61] V.D. PONOMAREV - L.P. NI - V.S. SAZHIN
"Combined method for complex treatment of high silica and high iron bauxites containing titanium" .
Tsvetnye Metally - vol. 1 n° 5 - 1960 -
p. 44-48
- [62] M.G. MANVELYAN and Alii
"Method of decomposing and alkali-calcium deposit obtained in the hydrochemical processing of nephelites" .
Tsvetnye Metally - vol. 3 n° 4 - 1962 -
p. 47-49
- [63] U.I. ISAKOV and Alii
"Joint treatment of aluminosilicate slags with nephelite" .
Tsvetnye Metally -
- [64] A.S. GERMAN - GALKINA - O.I. ARAKELYAN
"The nature of chemical losses of alumina when treating hydroargillite bauxite mud by the hydrochemical method" .
Tsvetnye Metally - vol. 4 n° 11 - 1963 -
p. 55-60

- [65] M.G. MANVELYAN and Alii
"Desilicification of pure potassium aluminate solutions" .
Tsvetnye Metally - vol. 3 n° 7 - 1962 -
p. 43 - 47
- [66] N.W. BLISS
"Alternatives to imported minerals. Non bauxite sources of alumina. A survey of canadian potential" .
C.I.M. Bulletin - October 1976 -
p. 75-85
- [67] M. VON EUW
Private communication - October 1976
- [68] E.I. KHAZANOV and Alii
"Combined complex treatment of high-iron containing alumina and alkaline aluminosilicate rocks" .
Tsvetnye Metally - vol. 6 n° 7 - 1965 -
p. 66-70
- [69] B.Z. KUDINOV and Alii
"Pilot tests on a system of metallurgical treatment of red muds in rotary furnaces" .
Tsvetnye Metally - vol. 8 n° 1 - 1967 -
p. 73-76
- [70] A.S. V'YUKHINA - L.P. DMITRIEVA
"Effectiveness of complex treatment of red mud in rotary furnaces" .
Tsvetnye Metally - vol.6 n° 10 - 1965 -
p. 53-57
- [71] A.I. BYCHIN - B.Z. KUDINOV
"Prospects for complex metallurgical treatment of red mud" .
Tsvetnye Metally - vol. 4 n° 10 - 1963 -
p. 49-52
- [72] MILLER JAN - IRGENS - AAKE
"Alumina production by the Pedersen Process history and future" .
Light Metals Proc. 103rd AIME Annual Meeting
1974 - 3 - 789-99 - Cited in Chemical Abstracts -
54 Extractive Metallurgy - vol. 81 - 1974 -
n° 156520 C

- [73] P.J. BARAT - J. COURSIER - A. DAURAT - H. MERCIER - L. SEIGNEURIN
"Metallurgie extractive de l'aluminium" .
Techniques de l'ingénieur
- [74] FABRIZIA LANDI - MARIA
"Alumina production from leucite alkali sinter process in pilot plant" .
Alluminio 1975 - 44 (4) - p. 225-30 -
cited in Chemical Abstracts - 49 Industrial Inorganics - vol. 84 - 1976 -
n° 46 640 w
- [75] *"Southwire starts test of Soviet process to produce alumina from alunite"* .
Engineering and Mining Journal - March
1976 - p. 26
- [76] *"Soviet alternatives for alumina production said to be cheap, clean, easy"* .
Engineering and Mining Journal - June 1976 -
p. 35
- [77] J. NIONCEL
"Les promesses du Moyen-Orient : les investissements en pétro-dollars ont-ils servi ou desservi notre industrie ?" .
Revue de l'aluminium - Juillet-Août 1976 -
p. 339-344
- [78] M. VON EUW
"Fabrications liées en cimenterie - procédés SEAILLES - Ciments français - fonte, alumine, ciment" .
Note Société des Ciments Français -
Octobre 1976 .
- [79] F.A. PETERS - P.W. JOHNSON - R.C. KIRBY
"Methods for producing alumina from clay. An evaluation of the sulfuric acid caustic purification process" .
U.S.B.M. - R.I. 5997 - 1962
- [80] F.A. PETERS and Alii
"Methods for producing alumina from clay. An evaluation of five hydrochloric acid processes" .
U.S.B.M. - R.I. 6133 - 1962

- [81] F.A. PETERS and Alii
"Methods for producing alumina from clay. An evaluation of a potassium alum. process" .
U.S.B.M. - R.I. 6290 - 1963
- [82] F. A. PETERS and Alii
"Methods for producing alumina from clay. An evaluation of three sulfuric acid processes" .
U.S.B.M. - R.I. 6299 - 1963
- [83] F. A. PETERS and Alii
"Methods for producing alumina from clay. An evaluation of a nitric acid process" .
U.S.B.M. - R.I. 6431 - 1964
- [84] F. A. PETERS and Alii
"Methods for producing alumina from clay. An evaluation of two ammonium alum processes" .
U.S.B.M. - R.I. 6573 - 1965
- [85] F. A. PETERS and Alii
"Methods for producing alumina from clay. An evaluation of a sulfurous acid sulfuric acid process" .
U.S.B.M. - R.I. 7758 - 1973
- [86] F. A. PETERS and Alii
"Revised and updated cost estimates for producing alumina from domestic raw materials" .
U.S.B.M. - I.C. 8648 - 1974
- [87] D. H. BAKER Jr
"Using non bauxitic raw materials for alumina production" .
Bureau of Mines - Research 75 - p. 22-24
- [88] J. A. BARCLAY - F. A. PETERS
"New sources of alumina" .
Mining Congress Journal - June 1976 -
p. 29-32

- [89] *"Alumina producers look to alternate raw materials"* .
Chemical Engineering - April 29, 1974 -
p. 98-99
- [90] J. COHEN - H. MERCIER
*"Traitement acide des minerais non bauxitiques pour la
production d'aluminium : le procédé H⁺"* .
Annales des Mines - Mai 1976 - p. 49-56
- [91] *"Note sur le procédé H⁺"* .
Note intérieure BRGM - SGN/MIN/N° 328
du 16 avril 1975 .
- [92] *"Production d'alumine par le procédé H⁺ Aluminium Pechiney"* .
Documentation Aluminium Pechiney
- [93] *"Procédé de préparation d'alumine par attaque acide des
minerais"* .
Brevet français n° 1.558.347 du 25.10.67
- [94] N. A. SHAIKH
"Non bauxite sources of alumina in Scandinavia and Finland" .
Paper presented at the 2nd Industrial
Minerals - International Congress -
Munich 1976
- [95] *"Aluminium process shows metallurgical trends"* .
Mining Magazine - September 1973 -
p. 203-204 .
- [96] *"Nouvelles méthodes de traitement des minerais pauvres
d'aluminium"* .
C.I.A.M. Dossier B-9 - Ministère de l'Indus-
trie et de la Recherche.

A P P E N D I X

List of patents related to alumina extraction processes
from non bauxite ores

British	982,098	Anaconda Co Feb. 3 1965
Canadian	688,565	Anaconda Co June 9 1964
Russian	172,047	V.S. Sazhin, et al. Nov. 1965
U.S.	3,436,176	Kennecott Copper Corp. Apr. 1 1969
Canadian	791,612	Anaconda Co Aug. 6 1968
U.S.	3,387,921	Allied Chem. Corp. June 11 1968
U.S.	3,415,618	Allied Chem. Corp. Dec. 10 1968
Canadian	777,052	Allied Chem. Corp.
Canadian	800,944	Anaconda Corp. Dec. 10 1968
U.S.	3,503,705	Marathon Oil Corp. Mar. 31 1970
U.S.	3,510,255	Oil Shale Corp. May 5, 1970
U.S.	3,489,514	Timax Associates Jan. 13 1970
U.S.	3,507,629	U.S. Secretary of the Interior Apr. 21, 1970
British	1,229,278	} A.A.R.C. Apr. 21, 1971
U.S.	3,615,359	
U.S.	3,594,122	E.C. Fornes July 20, 1971
British	1,257,521	Allied Chem. Corp. Dec. 22, 1971
Canadian	888,089	} Pechiney, Dec. 14, 1971
U.S.	3,620,671	
British	1,223,095	Allied Chem. Corp. Feb. 24, 1971
U.S.	3,647,373	Arthur D. Little Inc. March 7, 1972
British	1,264,672	Allied Chemical Corp. Feb. 23, 1972
U.S.	3,647,372	Eleusis Bauxite Mines Mining Industrial and Shipping Inc. Mar. 7, 1972
U.S.	3,642,433	U.S. Secretary of the Interior Feb. 15, 1972
U.S.	3,642,437	Stauffer-Chemical Corp. Feb. 15, 1972
U.S.	3,652,208	TRW Inc. Mar. 28, 1972
U.S.	3,664,809	TRW Inc. May, 23, 1972

British	1,302,431	A.A.A.R.C. Jan. 10, 1973
U.S.	3,758,289	Ethyl Corp. Sept. 11, 1973
Canadian	951,872	Arthur D. Little Inc. July 30, 1974
U.S.	3,821,353	Superior Oil Corp. June 28, 1974
British	1,375,808	Oil Shale Corp. Nov. 27, 1974
U.S.	3,816,590	Arthur D. Little Inc. June 11, 1974
U.S.	3,793,003	D.F. Othmer Feb, 19, 1974
U.S.	3,856,508	D.F. Othmer Dec, 24, 1974
U.S.	3,853,541	D.F. Othmer Dec, 10, 1974
U.S.	3,843,351	Boeing Co Oct. 22, 1974
U.S.	3,832,164	Tatabanyai } Szenbanyak } Aug. 27, 1974
U.S.	3,929,975	Alcoa Dec., 30, 1975
U.S.	3,937,786	A.A.A.R.C. Feb. 10, 1976
German Offen.	2,535,659	Freeport Minerals Mar. 4, 1976
German Offen.	2,440,929	Lowenstein July 17, 1975
France demande	2,261,344	Anaconda Co Sept., 12, 1975
Hungary Teljes	9,834	Nemec 2 and al, May 28, 1975
German Offen.	2,416,407	Chemokomptex Vegyipari Oct. 16, 1975
East Germany	112,745	Reisner and al. May 5, 1975
U.S.	3,935,297	A.A.A.R.C. Jan. 27, 1976