DEVELOPMENT OF ALUMINA AND SILICA BASED PRODUCTS IN HUNGARY

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Abstract

HUNGALU Ajka Aluminiumindustrial Ltd. has two more or less independent alumina plants with a half million t/year capacity.
Quality of metallurgical grade alumina has been improved during the latest several years. Especially chemical impurities were decreased such as iron, soda and silica content of alumina produced.

An alumina hydrate product family has been developed as well in HUNGALU Ajka Aluminiumindustrial Ltd.
A special fine alumina hydrate production process is described by the authors which is being used to produce alumina hydrate with less than /um particle size (d_{50}).
The central unit of this plant technological system is a 300 m^3 precipitation tank.
Reflecting environmental concerns some types of synthetic zeolites and silica based products (Na-A; Na-X; Na-Y etc.) have also been developed on the basis of spent liquor of the Bayer process in different for several purposes. The essence of this development work has been summarized in this study.

Introduction

HUNGALU Ajka Aluminiumindustrial Ltd. has two alumina plants. According to its strategic plan one of them is to produce a good quality of metallurgical grade alumina and another one is to be transformed into production lines for nonmetallurgical alumina and silica based products.
This study shows two types of development process: firstly improvement of metallurgical grade alumina produced in so called "new plant" and secondly the few alumina and silica based products as aluminium trihydrates with fine particle size distribution and some types of synthetic zeolites (NaA; NaX; NaY) as well as silica based filling materials.
These newly developed metarials are environment friendly and used in detergent and cosmetic industry.

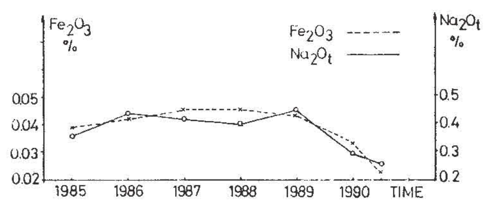
1. Improving the quality of smelter grade alumina produced in Ajka Alumina Plant.

HUNGALU Ajka Aluminiumindustrial Ltd. has two alumina plants connected to each other. The "new" alumina plant was established in 1973 based on HUNGALU ALUTERV-FKI design with 3oo kt/y capacity. It was a typical floury alumina technology using hungarian bauxite as raw material to produce alumina with a better quality regarding chemical contaminations and particle size distribution.

1.1. Decreasing the level of chemical impruities

As it is known the most important impurities of alumina are iron (Fe_2O_3) and soda (Na_2O_t). That is way they have been in the focus of different development processes (1,2,3). Figure 1. shows the trend of iron and soda content of alumina between 1985 and 1991 in Ajka Alumina Plant.

Figure 1.
Iron and soda content of alumina in Ajka Alumina Plant



In 1989 a very effective control filtration technology was launched applying LVAZS type press filters. This control filtration technology and system is based on calcium aluminat additive metarial which is created from burnt lime using spent liquor. This calcium aluminat slurry is used as filling material to form an effective additive filter cake on the surface of press filters after an aging process.
The main parameters of this control filtration process are shown in Table 1., comparing to the traditional $Ca(OH)_2$ control filtration method used in Ajka Alumina Plant.

Table 1.
The main parameters of calcium aluminate and calcium hydroxide control filtration process

Name of parameters	calcium aluminate	calcium hydroxide
	control filtration	
quantity of lime /kgCaO/m^3 liquor/	o,1	o,35
efficiency of filtration, /%/ **x**	64	5o-6o
Fe_2O_3 content in aluminat liquor after filtration, /mg/l/	8-1o	8-1o
Capacity of filter /m^3/m^2h/	1.6	1.2
periodic time /h/	4-5	4

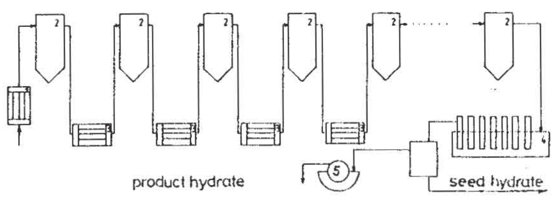
x = it is determined by following phrase:

$$\text{efficiency of filtrat.} = \frac{Fe_2O_3\ (b.f.) - Fe_2O_3\ (after\ f.)}{Fe_2O_3\ \text{before filtration}\ (b.f.)} \times 100$$

This calcium aluminate control filtration method has a great advantage: after filtration period the filter cake can be used in caustification section of Bayer process,thus the lime is used for two purposes, firstly as an additive filter material and secondly as a caustification reagent.

As it can be seen in Figure 1. soda content of alumina has been decrasing effectively. The main reason of it that the precipitation technology has been transformed. The newly supplemented precipitation process is seen in Figure 2.

Figure 2.
The precipitation technology of Ajka Alumina Plant

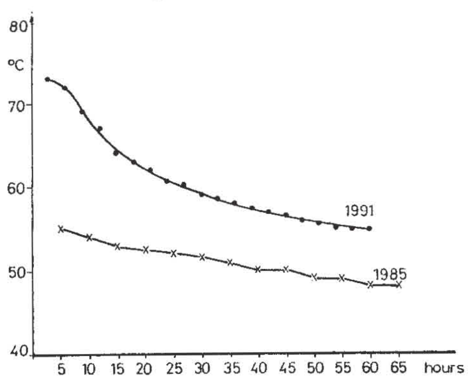


(1): aluminate liquor coolers
(2): precipitation tanks
(3): interstage slurry coolers
(4): disc filters for seed hydrate
(5): drum filters for product hydrate

As this figure shows four additional interstage coolers have been intstalled providing easy temperature control in the precipitation line.

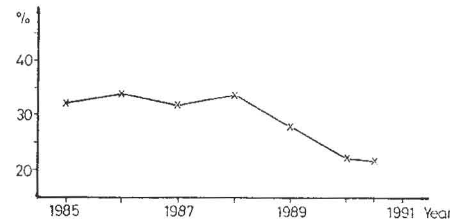
Recently the temperature regime has been modified according to the diagram depicted in Figure 3.

Figure 3.
The precipitation temperature regime in Ajka Alumina Plant



This temperature regime facilitates increasing precipitation yield, but the main role is to increase of the particle size of aluminium hydrate.
The quantity of seed hydrate has been increased as well and several another measures have been taken (4,5,6).
Measure like surveying number of particles on continous basis assuring the adjustment of main technical parameters and resulting in precise control of particle distribution.
Changing the precipitation technology the particle size distribution has continously been changed and -45 μ fraction has been being decreased as it is depicted in Figure 4.

Figure 4.
The trend of -45 μ fraction of alumina produced in Ajka Alumina Plant



Analysing the situation of other impurities of alumina shown in Table 2. the following can be stated:

- P_2O_5 content is unchanged
- SiO_2, TiO_2, ZnO, have been decreasing in harmony of the effect of control filtration
- CaO content has increased because of using lime in control filtration

Table 2.
Impurities of alumina produced in Ajka Alumina Plant (in percentage)

	1985.	1986.	1987.	1988.	1989.	1990.	1991.I. halfyear
Al_2O_3	99,29	99,16	99,19	99,23	99,36	99,31	99,40
SiO_2	0,016	0,019	0,019	0,018	0,016	0,017	0,013
TiO_2	0,006	0,006	0,005	0,006	0,006	0,005	0,004
Fe_2O_3	0,039	0,042	0,045	0,045	0,043	0,033	0,022
P_2O_5	0,001	0,001	0,001	0,001	0,001	0,001	0,001
Na_2O_t	0,36	0,44	0,42	0,40	0,45	0,29	0,25
CaO	0,008	0,009	0,009	0,007	0,011	0,014	0,016
-45 μm	31,9	33,7	31,7	33,5	27,7	22,2	21,4
ZnO	0,015	0,018	0,016	0,013	0,013	0,015	0,010
slope grad.	33	31	32	33	33,5	32	32

1.2. Increasing whiteness of aluminium trihydrate

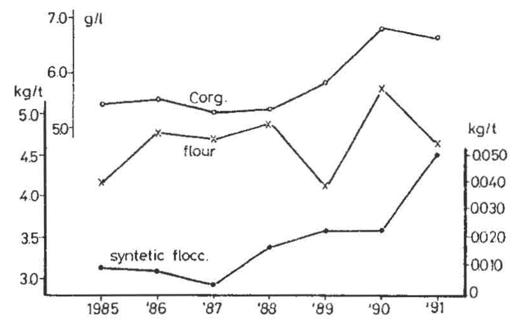
Using aluminium trihydrate for nonmetallurgical purposes generally claims a high value of whiteness (plastic and cosmetic industrial filling material, etc.).
As it has been shown above the general level of impurities of alumina has been decreased in Ajka Alumina Plant.Especially iron content of alumina has decreased sharply, but unfortunately whiteness of alumina has not changed parallel. Aluminium trihydrate produced in Ajka Alumina Plant has a slight pink colour despite the several experiments to eliminate it.

1.2.1. Organic level in Ajka Alumina Plant

It is generally known that organic content of Bayer liquor /especially the so called colouring organic compounds/ has an effect on whiteness of hydrate.

The general level of organic impurities has been increasing recently in Ajka Alumina Plant as it is depicted in Figure 5. The quantity of flour and synthetic flocculants are described in this figure as well.

Figure 5.
The organic level and quantity of flour and synthetic floculants used in Ajka Alumina Plant



The general mass balance of organic material has a small shortage as it is described in Figure 6. The reason of it may be the spontaneaus transformation and the increase in organic level of Bayer liquor.

Figure 6.
The general mass balance of organic material in Ajka Alumina Plant
/kgCorg/t Al_2O_3/

INPUT — OUTPUT

bauxit: 1.52 → | 0.62 Δ | → red mud solid: 2.2
flour : 1.6 → | | → red mud liquid : 0.27
synt.flocc: 0.02 → | | → hydrate: 0.2
water : 0.15 →

Input total: 3.23 — Output total: 2.67

The organic level of Ajka Alumina Plant is not a general problem: the organic content of hungarian bauxit used is low. But in respect of hydrate colour is to be further investigated.

1.2.2. <u>Experimental results in increasing whiteness of hydrate</u>

There are several methods for decreasing organic level of Bayer process. Some of them are also effective in respect of hydrate colour as well (7).
The quantity of colouring organic compounds in Ajka Alumina Plant is about 6 %, and only a very well method can be used for its removal.
The main point of this development work was to avoid the huge investment cost during the intruduction to plant process.
A laboratory test system has been established which is appropriate to examine the effects of different additiv materials. Photoextinction measurement method was applied to determine the results using VARIAN 300 AAS type photometer.
Three types of additiv materials have been used: calcium hydroxide, MAGNAFLOC 369 and NALCO 81o3. By the use of calcium hydroxide an additive filter cake has been created with a thickness of 15 mm. Three parallel samples have been filtered in this laboratory equipment. The results are summarised in Table 3.

Table 3.
The effect of calcium hydroxide control filtration on colour of aluminate liquor

No.	Aluminate liquor Al_2O_3 g/l	Na_2O g/l	Fe_2O_3 mg/l	Corg g/l	Extinction –	Extinction percentage
Base	135.2	124.0	15.0	3.48	0.480	–
1.	137.2	126.5	7.0	–	0.450	6.25
2.	137.2	124.0	7.0	–	0.440	8.33
3.	138.2	124.0	6.0	4.14	0.450	6.25

In the second phase MAGNOFLOC 369 has been used creating additional filter cake in the way mentioned above.
Different quantities of additive materials and different temperatures have been investigated as they are described in Table 4.

Table 4.
The effect of MAGNAFLOC 369 on colour of aluminate liquor in control filtration

No.	quantity of M.369 /ppm/	temperature /C°	Aluminate liquor Al_2O_3 g/l	Na_2O g/l	Fe_2O_3 mg/l	Corg g/l	Extinction –	Extinction percentage
Base	–	–	127.5	117.8	17.0	4.20	0.523	
1.	200	90	129.3	119.0	5.0	3.84	0.355	32.1
2.	200	80	130.1	117.8	5.0	–	0.335	35.9
3.	200	70	129.5	117.8	5.0	3.48	0.320	38.8
4.	300	90	129.5	117.8	5.0	–	0.325	37.8
5.	300	80	128.0	117.8	4.0	–	0.310	40.7
6.	300	70	128.3	117.7	5.0	3.84	0.310	40.7

In the third phase NALCO-8103 has been used in the same way mentioned above (8). Different quantities of additive materials have been used as they are shown in Table 5.

Table 5.
The effect of NALCO 8103 on colour of aluminate liquor in control filtration

No.	quantity of N-8103 /mg/l/	Aluminate liquor Al_2O_3 /g/l/	Na_2O /g/l/	Fe_2O_3	C_{humat} /g/l/	Extincition –	Extincition percentage
Base*1	–	153.4	140.0	25	0.11	0.95o	
Base**2	–	153.9	139.3	9	0.10	0.931	6.9
1.	40	156.3	139.9	12	0.09	0.82o	13.7
2.	60	154.8	139.9	12	0.07	0.878	7.6
3.	80	153.2	140.7	11	0.07	0.738	22.3
4.	100	153.8	139.7	12	0.06	0.714	24.8

* without filtration
** after $Ca(OH)_2$ filtration without NALCO-8103

Summarising the results of this experimental work the following findings can be stated:

- the calcium hydroxide additive filter cake has only little effect on the colour of aluminate liquor,
- both MAGNAFLOC 369 and NALCO 8103 can be used as additive material to increase whiteness of hydrate,

- using MAGNAFLOC 369 additive material it has been found that the lower the temperature the higher the effect on the colour of aluminate liquor.

The experimental work is to be continued: further experiments are to be made in laboratory and industrial plant tests are needed.

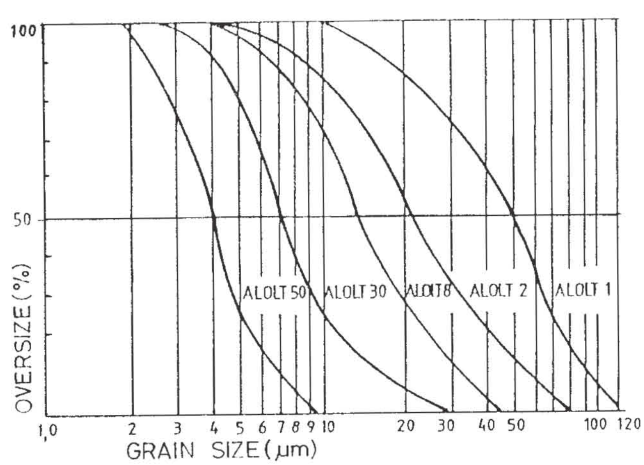
2. Production of ultra fine aluminium trihydrate

As it has been presented in (9) an aluminium trihydrate product family was developed in HUNGALU Ajka Aluminiumindustrial Ltd. The main parameters of this ALOLT family are summarised in Table 6. and their physical characteristics (grain size distribution) are depicted in Figure 7.

Table 6.
Parameters of the ALOLT product family

		ALOLT1	ALOLT2	ALOLT8	ALOLT30	ALOLT50
$Al(OH)_3$	(%)	99,5	99,5	99,5	99,5	99,5
SiO_2	(%)	0,015	0,015	0,015	0,015	0,009
Fe_2O_3	(%)	0,017	0,017	0,017	0,017	0,010
Na_2O_{total}	(%)	0,30	0,30	0,30	0,30	0,25
$Na_2O_{soluble}$	(%)	0,03	0,03	0,03	0,03	0,03
Moisture	(%)	0,2	0,2	0,2	0,2	0,2
L.O.I.	(%)	34,5	34,5	34,5	34,5	34,5
Bulk density (loose)	(kg/m^3)	1200	600	400	300	250
d_{50}	(μm)	40-60	40-60	20-25	5-10	2-5
Specific surface area	(m^2/g)	0,01	0,2-1	1-2	2-4	3-5

Figure 7.
Grain size distribution curves of the ALOLT product family



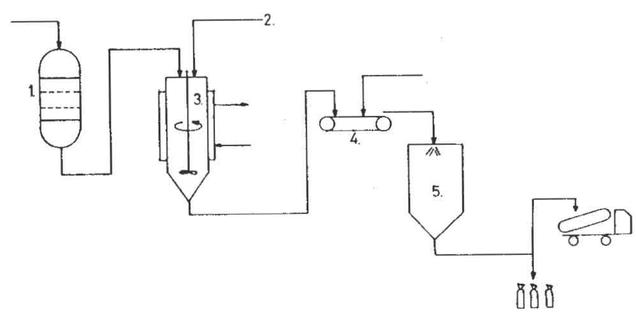
In the study mentioned above (9) the different production process of the ALOLT family have been presented. In this study an industrial production process of the ALOLT 90F product is to be shown.

2.1 Production process and technology

The essence of the production process of ALOLT 90F product is a special precipitation technology in the presence of $Al_2(SO_4)_3$ additive. The kinetic parameters which have been presented in (9) show that some 1.0 to 4.0 % $Al_2(SO_4)_3$ is to be applied relative to the amount of pregnant liquor.

The production scheme of this industrial technology is shown in Figure 8. The central units of this process are the two 300 m^3 precipitators which determine the capacity level at about 5000 t/y.

Figure 8.
Flowsheet of the production technology of ultra fine aluminium trihydrate



1. Kelly type filter
2. additive material feeder
3. precipitation tank
4. belt filter
5. spray drier

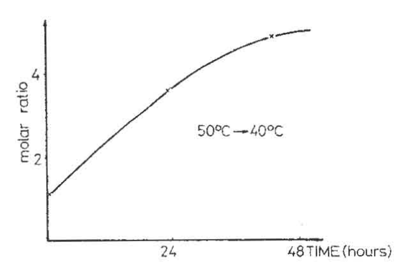
As it can be seen the pregnant liquor goes to a control filtration station (including Kelly filters) to decrease the iron content below 4-6 mg/l expressed in Fe_2O_3. In the first step of precipitation process the additive material is to be added. The precipitation time is about 50-70 hours, using mechanical agitated tanks. After precipitation aluminium trihydrate can be separated in belt filter and can be dried in a spray drier.

2.2 Results and parameters of the product

Aluminate liquor of the Bayer process was used as raw material. After the control filtration the iron content was below 5 mg/l (expressed in Fe_2O_3). The relative amount of $Al_2(SO_4)_3$ was 4-5 % regarding to the aluminate liquor.

The parameters of this batch precipitation are depicted in Figure 9.

Figure 9.
Parameters of precipitation process of ultra fine aluminium trihydrate technology



aluminium trihydrate produced in this process resulted a very high value of whiteness with very low value of impurities as summarised in Table 7.

Table 7.
Parameters of ultra fine aluminium trihydrate

Na_2O_t	0,49	%
SiO_2	0,009-0,014	%
Fe_2O_3	0,006-0,01	%
TiO_2	0,001	%
V_2O_5	0,001	%
P_2O_5	0,0004-0,0005	%
CaO	0,007-0,009	%
ZnO	0,008-0,011	%
SO_3	0	
$C_{org.}$	0,02-0,027	%
whiteness	97,3-99,5	%
d_{50}	1,0	μm
conductivity	30-40	μS
BET surface	8-15	m^2/g
+ 45 μm screen rest	max. 0,1	%

Grain size distribution curve is shown in Figure 10. and electron micrograph in Figure 11.

Figure 10.
Grain size distribution curve of ultra fine aluminium trihydrate

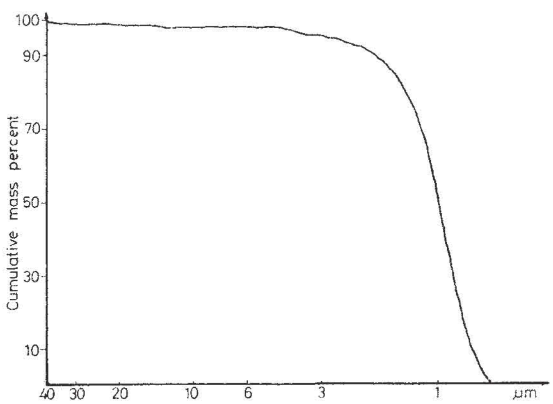
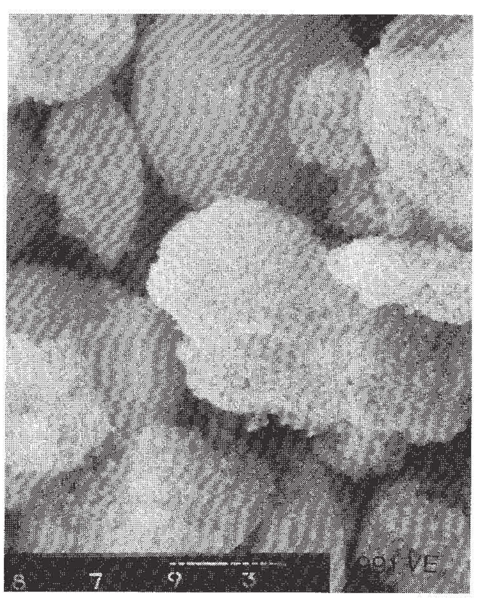


Figure 11.
Electron micrograph of ultra fine aluminium trihydrate



1 cm = 3 μm

This aluminium trihydrate is to be used in plastics and cable industries as filling material and it has been tested in cosmetic and ceramic industries as well.

3. Development of alumina and silica based product fitting to the Bayer process

Crystalline aluminium hydrosilicates (zeolites) occur in large quantities in the nature. However, their industrial users demand an increased purity and well-determined composition, therefore more and more of them are manufactured by synthesis. The end product and by-products of the Bayer process can be used as raw material in these processes. Obviously the water glass and the hydroxide (or carbonate) of the relevant alkali metal are to be used as basic materials, together with some additional compounds.
Zeolites are important materials ofthe modern chemical industry and environmental protection and innumerable zeolite structure compounds have been developed (10).

HUNGALU Ajka Aluminiumindustrial Ltd. strives to diversify its activity in developing and introduceing new, "easy to sell" products.

3.1 Development of synthetic zeolites

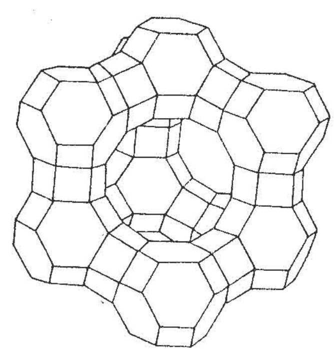
Zeolites have special adsorption and ion-changing properties provided by their special molecular structure:

$$M2/nO.Al_2O_3.xSiO_2.yH_2O$$

M: positive ion with "n" valencies

The three-dimensional picture of "x" type zeolite is depicted in Figure 12. There is not possibility to analyse this structure deeply but it can be seen that there are different size channels in it.

Figure 12.
Three dimensional picture of "X" type zeolit structure

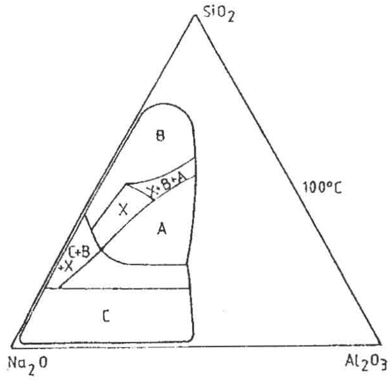


The size of these channels can be varied by changing M positive ion (Na,K,Ca,etc.) or transforming this structure (changing Al_2O_3/SiO_2 molecular ratio). Both methods are used.
If M is a Na ion, this structure is a so called 4A type (diameter of one channel is 3.6 angstrom), if Al_2O_3/SiO_2 molecular ratio is betwen 2 and 3 the structure is X type and if this figure is betwen 3 and 5 the structure is Y type. The diameter of the channel in case of NaX is 7.4 angstrom.

The zeolite structure can adsorb different molecules according to their channel diameter in are reversible way.
In the (9) study the principle, the production technology and an 1500 t/y pilot plant have been presented to produce 4A type zeolite for detergent and adsorbent purposes.

Recently a new X type zeolite production technology has been developed in HUNGALU Ajka Aluminiumindustrial Ltd. The essence of this process is to be analysed in this study.
The Na_2O-SiO_2-Al_2O_3-H_2O system can be analysed in Figure 13.

Figure 13.
Na_2O-SiO_2-Al_2O_3-H_2O system phase diagram



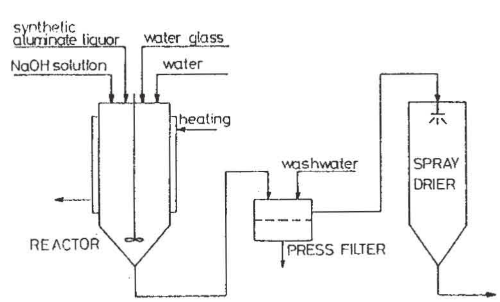
It is stated that "X" type zeolite can only be crystallized in the following molar ratio:

$$8\ SiO_2 \times Al_2O_3 \times 3\ Na_2O \times 120\ H_2O$$

The crystallisation process consists of two parts: in the first one the Bayer process spent liquor and water glass are mixed and NaOH is used to provide the appropriate molar ratio mentioned above. A well-determined gel form is to be created which is used in the second step to crystallize zeolit-structure.

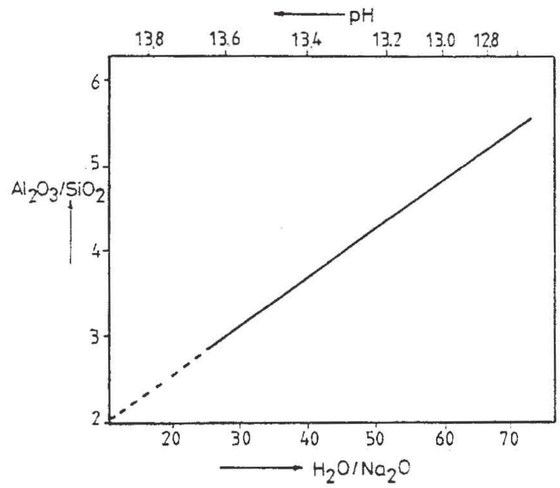
The flowsheet of this experimental system is depicted in Figure 14. The central unit is a 300 l mechanically agitated reactor with gel formator.

Figure 14.
Flowshet of "X" type zeolit crystallization



During the experiments the effect of pH and H_2O/Na_2O molar ratio were examined on the Al_2O_3/SiO_2 molar ratio and crystallinity of the zeolite product. The other parameters for example mode and ratio of feeding of reactants, temperature and length of gel-formation were fixed. The experimental data are depicted in Figure 15.

Figure 15.
Experimental data of "X" type zeolite crystallization

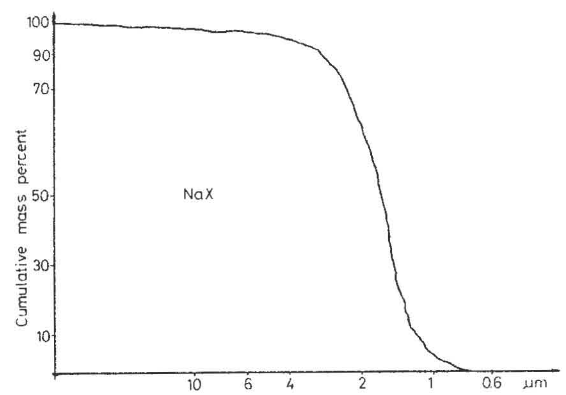


Chemical parameters of the product zeolite are summarized in Table 8. and the grain size distribution of it can be seen in Figure 16.

Table 8.
Chemical parameters of "X" type zeolit

Al_2O_3	27 – 29 %
SiO_2	54 – 56 %
Na_2O_t	16 – 18 %
BET surface	9 – 13 m^2/g
Ion exc.cap.	120 mg CaO/g zeolit
d_{50}	1,2-2,0 /um

Figure 16.
Grain size distribution of "X" type zeolite

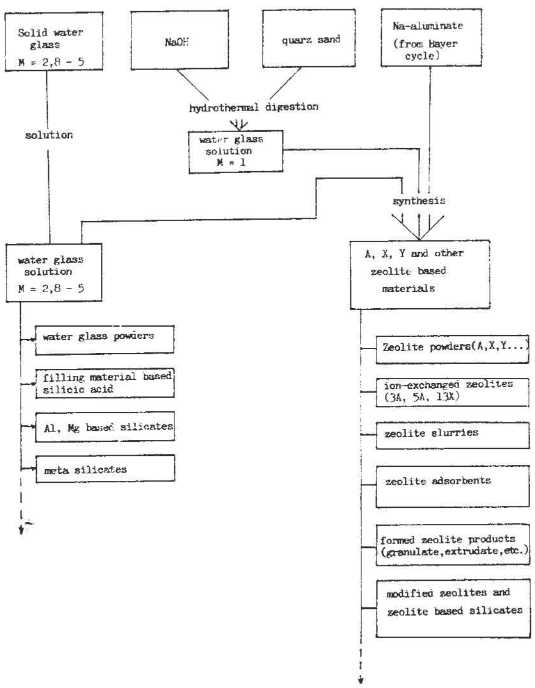


This zeolit production technology fitted to the Bayer process has the following advantages:
- it does not decrease the capacity of the Bayer process because of using spent liquor as raw material (in traditional method aluminium trihydrate is used)
- it enables the investors to reduce the investment cost by 10-20 %
- the production cost of zeolite is lower by 20-30 % than it is in traditional method.

3.2 Development of other silica based products

Several silica based products can be produced using water glass and aluminate or pregnant liquor as it can be seen in Figure 17.

Figure 17.
Silica based products



There is a real possibility to produce different kinds of silicate and SiO_2 based filling materials.

A new hydrated SiO_2 filling material production technology has been developed in HUNGALU Ajka Aluminiumindustrial Ltd.

This hydrated SiO_2 so called amorphous silica without crystallic water and it does not have silica's special X-Ray picture. Water content of it is less than 14 %. Generally this material is produced from water glass using H_2SO_4 or HCl to precipitate it.

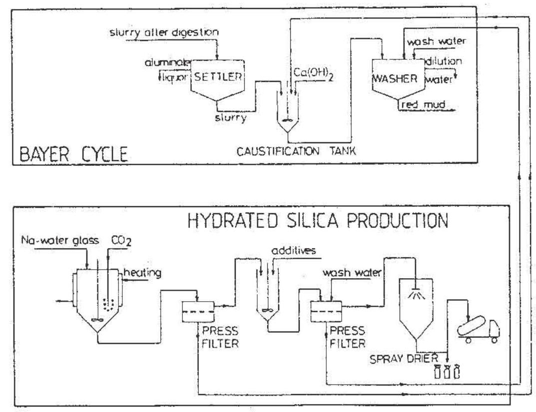
This new process uses gasouos CO_2 which creates Na_2CO_3 in the reaction mixture. Na_2CO_3 can be handled in the Bayer process so this production process can be fitted to it very easily.

During the caustification process Na_2CO_3 is transformed into NaOH using $Ca(OH)_2$ thus the production cost and the investment expenditure of hydrated SiO_2 can be reduced.

The flowsheet of production process shows (see Figure 18.) that water glass is fed into the reactor and gaseous CO_2 reacts with it:

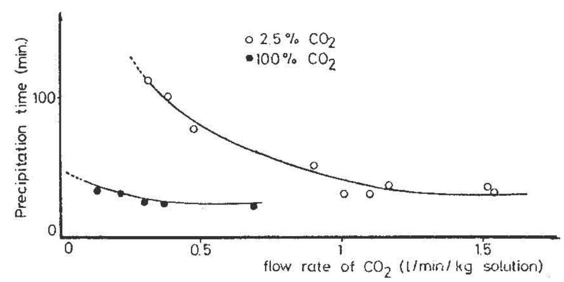
$$Na_2SiO_3 + H_2CO_3 \longrightarrow H_2SiO_3 + Na_2CO_3$$

Figure 18.
Flowsheet of production process of hydrated SiO_2



During this experimental work the effect of flow rate of carbonising CO_2 on the time of precipitation has been investigated. The results are summarized in Figure 19.; the higher the speed of CO_2 the lower the precipitation time.

Figure 19.
The effect of flow rate of CO_2 on the precipitation time in hydrated SiO_2 production process



Different kinds of silica based filling materials can be produced by changing the parameters of production. Table 9. shows two types of them (ATASIL1; ATASIL2) whichdiffer first of all in their BET surface value.

Table 9.
The main characteristics of ATASIL1 and ATASIL2

		ATASIL1	ATASIL2
SiO_2	(%)	85–88	85–88
Fe_2O_3	(%)	0.06	0.06
Na_2O	(%)	1.0	1.0
SO_4^{2-}	(%)	0.5	0.5
L.O.I.		5.0–8.0	5.0–8.0
BET surface	(m^2/g)	100–160	160–230
DBP	(ml/100g)	240–260	240–290
alkalinity		8.5–9.5	8.5–9.5

These products are to be used mainly in plastics and rubber industry as filling materials.

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