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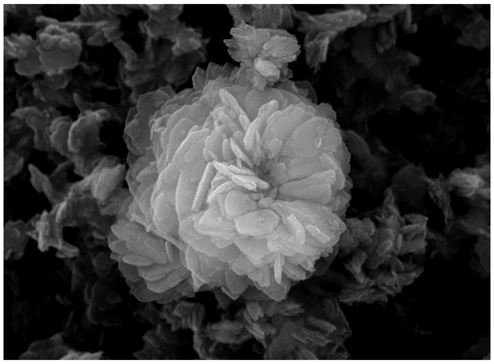

Prevention and Recycling in the Aluminum Anodizing Industry: Soda and Aluminum Recovery From Spent Etching Baths

(Extended Abstract)

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Prevention and Recycling in the Aluminum Anodizing Industry: Soda and Aluminum Recovery From Spent Etching Baths

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Abstract

This work fits in the philosophy of implementing preventive measures in industrial processes to reduce wastes and enhance enterprises' competitiveness. The aluminum anodizing industry is an important industrial sector that invariably produces great amounts of polluted effluents, which after treatment generate sludge. This brings environmental and economical concerns to the enterprises. Among the operations of an anodizing line, the etching/satinizing stage is responsible for the production of a huge quantity of wastewater neutralization sludge and for the bad use of caustic soda. "Caustic etch recovery" technology is claimed to drastically reduce the generation of neutralization sludge and the purchasing of fresh caustic soda by regenerating the exhausted etching/satinizing solution. Despite it, its use is very rare among European anodizers, a reason being the lack of well grounded data on its performances. The work assessed, by means of laboratorial scale tests, the capability of the technology to effectively regenerate the exhausted caustic solution, and investigated the parameters with major effect on the process yield, in order to optimize it. It was demonstrated that the technology effectively recovers the solution, increases its soda content and diminishes the dissolved aluminum content by precipitating it as gibbsite. Moreover the conditions that optimize the process are simple and inexpensive. After the treatment the solution has the properties to be recycled in the etching/satinizing operation. The gibbsite was structurally, dimensionally, and morphologically characterized, and thermally treated to produce a range of aluminas. It was seen that both the gibbsite and the aluminas owns the qualities to become attractive saleable byproducts of the "caustic etch recovery".

***Keywords**: Aluminum; Anodizing; Etching baths; NaOH regeneration; Anodizing sludge.*

1. Introduction

Industrial activities play a central role in the well-being of Europe, contributing to its economical growth and providing high quality jobs. Nevertheless, industrial activities also have a significant impact on the environment. Best way to deal with the problem, according to the "prevention strategy" set by the Council Directive 96/61/EC of the 24th September 1996 concerning Integrated Pollution Prevention and Control (IPPC), is to implement preventive techniques and technologies to optimize the use of resources and minimize losses, and in turn wastes. In waste management, prevention is the first priority in order to allow source reduction together with possible gain for the enterprises because of decreased environmental dues, and raw materials and energy saving. The aluminum anodizing industry is an important industrial sector that invariably produces great amounts of polluted effluents, which after treatment generate sludge. This brings environmental and economical concerns to the small and medium enterprises that act in the sector. Among the operations of an anodizing line, the etching/satinizing stage is responsible for the production of a huge quantity of wastewater neutralization sludge and for the bad use of caustic soda. "Caustic etch recovery" technology is claimed to drastically reduce the generation of neutralization sludge and the purchasing of fresh caustic soda by regenerating the exhausted etching/satinizing solution. This would reduce operational costs (for caustic soda purchase, for wastewater treatment, for sludge handling, transport, and disposal) and last but not least decrease the impact that anodizing industry has on the environment. Despite it, its use is very rare among European anodizers, a reason being the lack of well grounded data on its performances. This work stands in this scenario and is meant to contribute to the understanding of the "caustic etch recovery", for promoting its adoption by anodizing installations. The work assessed, by means of laboratorial scale tests, the capability of the technology to effectively regenerate the exhausted caustic solution, and investigated the parameters with major effect on the process yield, in order to maximize it. It further characterized and thermally treated the aluminum trihydroxide byproduct of the process, in order to understand if it can become a saleable material.

2. Aluminum and Aluminum Anodizing

Aluminum has become the predominant nonferrous metal in use. Its primary production has kept growing at an impressive rate since it was prepared for the first time. Lately, world primary production of this metal is growing at a slower but consistent rate, setting itself around 39.4 million metric tons in 2008. This data is not sufficient to draw the entire scenario of aluminum production and use, because they do not consider the fact that a big and increasing share of aluminum is recycled. Recycling contributes to 27% of the entire aluminum production.

Anodizing is a chief surface finishing treatments for aluminum, and it is mainly applied for transport and architectural aluminum made components. In 2000 only within Europe 640 thousand tons of aluminum had been anodized just for the architectural sector.

Aluminum is anodized in order to enhance corrosion resistance, surface hardness, to allow dyeing (coloring), to improve lubrication or adhesion, to obtain a specific aesthetic effect. Anodizing is an electrochemical treatment that increases the thickness of the natural aluminum oxide layer onto the metal surface. The name comes from the fact that the component to be treated is made anode (positive pole) of an electrochemical cell. The anodizing chain usually counts on some pre-treatment steps (brushing, degreasing, etching/satinizing, neutralization), a core treatment (anodizing), and one or more finishing steps (coloring, sealing). With the term "anodizing" one refers to both the whole finishing process and the core treatment from which it acquires its name.

3. Etching/Satinizing and Environmental Concerns

These two anodizing pretreatments are very similar, they can be executed singularly or sequentially, but they do pursuit two slightly different goals. They both are carried in an alkaline solution with similar chemical composition, made alkaline by the use of caustic soda NaOH. Their common goals are to complete the cleaning of the surface and to remove the natural oxide layer off of aluminum made items, in order to present a virgin surface to the following anodizing step (the presence of oxide would impede the proper passage of electrical current). Now, satinizing has an additional purpose, which is to give back a surface with specific aesthetical properties, overall called "satin finish". The final effect is a matte aspect, which reveals to be critical for the products final appearance. A typical formulation of both baths is shown hereafter:

- Free soda: 50 to 120 g/L
- Dissolved aluminum: 70 to 150 g/L
- Additives: 10 to 30 g/L
- Temperature: 50 to 70℃
- Dipping time: 1 to 25 min

The main phenomenon that takes place in the bath is the dissolution of the thin aluminum oxide layer together with a variable width of beneath aluminum, which passes in solution as sodium aluminate, as shown in equation *(1)*:

$$2Al_{(s)} + 2NaOH_{(aq)} + 2H_2O_{(l)} \rightarrow 2NaAlO_{2(aq)} + 3H_{2(g)} \qquad (1)$$

In order to run the bath properly and obtain the expected result from the treatment, the correct (dissolved aluminum)/(free soda) ratio has to be maintained. The best ratio is in the range 0.8 ÷ 1.0, because it prevents the hydrolysis of the sodium aluminate to aluminum trihydroxide, with the following formation of a very difficult to eliminate rocky precipitated at the bottom and the walls of the tank, and all over the components under treatment, according to reaction *(2)*:

$$NaAlO_{2(aq)} + 2H_2O_{(l)} \rightarrow Al(OH)_{3(s)} + NaOH_{(aq)} \qquad (2)$$

This is known as "Bayer reaction" and it is exploited in the production of aluminum from aluminum rich ores (bauxite). Being the etching/satinizing carried in a batch mode the leached aluminum accumulates in the solution as sodium aluminate while caustic soda runs out as the treatment goes by. This moves the (dissolved aluminum)/(free soda) ratio away from the proper range, creating the conditions for crystallization. Furthermore, the etching/satinizing rate slows down as NaOH concentration decreases, resulting in inacceptable variations in the final products appearance. To avoid all of this the continuous additions of caustic soda must be guaranteed, together with the control of the concentration of dissolved aluminum. Being dissolved aluminum conservative, the control can only be made by continuous and/or batch discharge of volumes of etching solution. This is mainly done by moving solution, together with the items under treatment, from the etching tank into the following rinsing tank, a phenomenon called drag-out. Rinsing water has then to be treated in an end-of-pipe plant and the treatment produces huge amounts of sludge (mostly made by sulphates and hydroxides of Al), that is expensive to handle, transport, and dispose. Even though recycling chances for the anodizing mud have been found, they can not absorb the whole production, and still the best solution would be not to produce it.

4. Caustic Etch Recovery

A technique to solve or reduce these problems has been known for several years and examples of its application can be found in North America and some European countries (France and Swiss). Caustic etch recovery consists in the regeneration of the etching/satinizing solution by its continue recirculation between the etching/satinizing tank and a crystallizer. Within this latter tank reaction *(2)* takes place and leads to the recovery of caustic soda and the contemporary crystallization of solid aluminum trihydroxide, which settles out in a clarification section. The solution enriched in caustic soda and with reduced aluminum flows back to the etching/satinizing tank, while aluminum trihydroxide is withdrawn from the bottom of the crystallizer, in a steady state process. The application of the technique is claimed to:

- reduce by 75 - 95% the caustic soda purchase;
- reduce by 70 - 80% the aluminum waste sludge generation;
- produce a saleable by-product (aluminum trihydroxide).

The basic caustic etch recovery layout is shown in *Figure 1*.

5. Caustic Etch Recovery: Laboratory Tests

Caustic etch recovery adoption by anodizing installations passes also through a better understanding of this technology and its optimization. Industrial managers need sure and well grounded data to justify the initial investment. This work is meant to partially fill the hole and contribute to the spreading of knowledge on the caustic etch recovery.

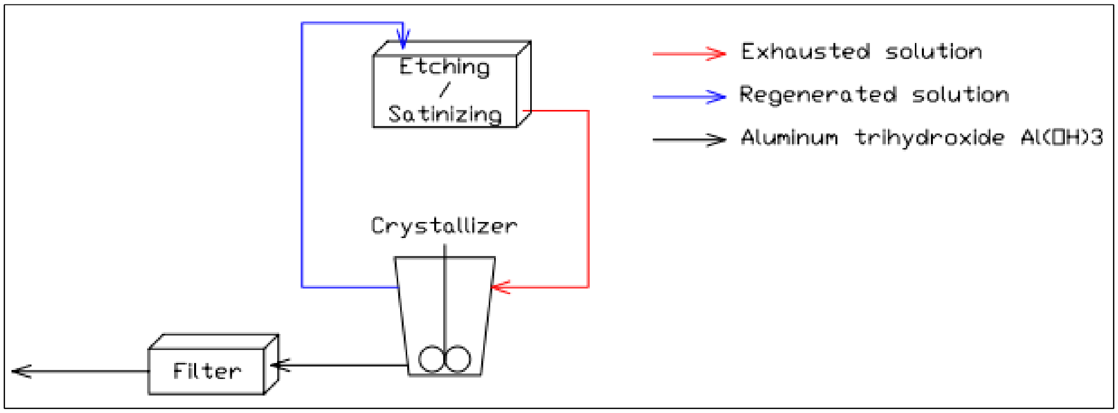

Figure 1 – Basic caustic etch recovery layout

5.1. Materials and Methods

A 10 L representative sample of caustic sodium aluminate solution resulting from the satinizing of aluminum was collected from the anodizing line of the Hydro Alumínio Portalex S.A. facility located in S. Carlos – 2726-901 Mem Martins (Portugal). The sample was stored in a PVC tank and periodically withdrawn for the trials.

Declared goals of the work were:

- finding the factors affecting the “caustic etch recovery” process course in the perspective of optimizing the caustic soda and aluminum recovery yields;
- characterizing (structurally, dimensionally and morphologically) the aluminum trihydroxide byproduct in order to find its possible applications.

Laboratorial tests consisted in the simulation of the more basic configuration of the caustic etch recovery, that is a crystallizer tank that works in batch mode (see *Figure 2*). System parameters which were thought to affect the process were set on different levels, according with the author experience and the literature review. Several series of trails were carried and each was planned according with the feedback of the previous ones.

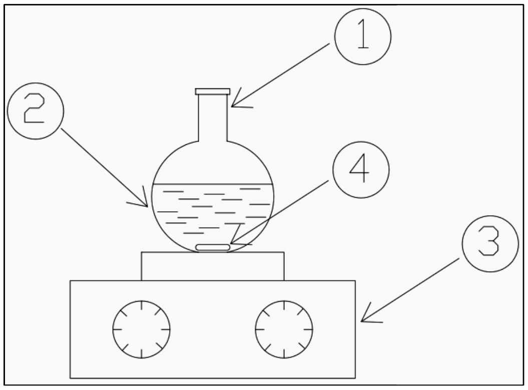

Figure 2 – Basic layout used in the caustic etch recovery laboratory tests, being: 1) Flat-bottom flask; 2) Caustic etch solution; 3) Magnetic stirrer; 4) Stir bar (flea).

Every series of tests was made by a number of this basic system configuration, each configuration with a different set of control parameters. Factors effect was first studied by drawing the temporal evolution of aluminum and caustic soda concentrations, and the byproduct particles size distribution progression with time. Dissolved aluminum and caustic soda concentrations were measured at certain time intervals by titration. Particles size distribution was measured by means of a laser diffraction instrument, the CILAS 920.

5.2. Results and Discussion

The effect of three parameters was studied: water addition, seed concentration, and stirring intensity. Three series of tests were executed.

First series is called “exploratory”. Samples of 250 mL of satinizing solution were treated at T_{amb} and with the conditions presented in *Table 1*:

Table 1 - Experimental conditions of the exploratory tests series

Test ID	Added water	Seed concentration	Stirring intensity
	[%]	[g/L of solution]	
S1	60	20	Very low
S2	80	20	Very low
S3	100	20	Very low
S4	120	20	Very low

The only configuration that resulted in the caustic soda recovery and the precipitation of a white and sandy byproduct was S1. Being all the control parameters equals beside water addition, a first hypothesis arises: water addition is a negative factor in the process development with an upper limit above which the normal course of the reaction is not being fastened. This upper limit should set in the 60 - 80 % range. Temporal evolution of chemicals recovery yields is shown in *Figure 3*. It is observed a changeover of the system behavior between 101h and 166h. It corresponds to an external action on the system: at 101h, because the process was not developing, the stirring intensity was increased for an hour at a high level, and then set to a level called “low”. A second hypothesis arises: stirring intensity is a factor that affects the process and it has a lower limit underneath which the normal course of the reaction is not fasten.

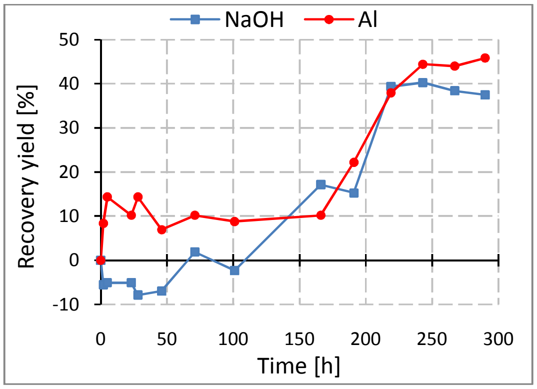

Figure 3 - Temporal evolution of chemicals recovery yields in test S1

The changeover is confirmed by looking at the particles size distribution histograms created by CILAS 920, as shown in *Figure 4*:

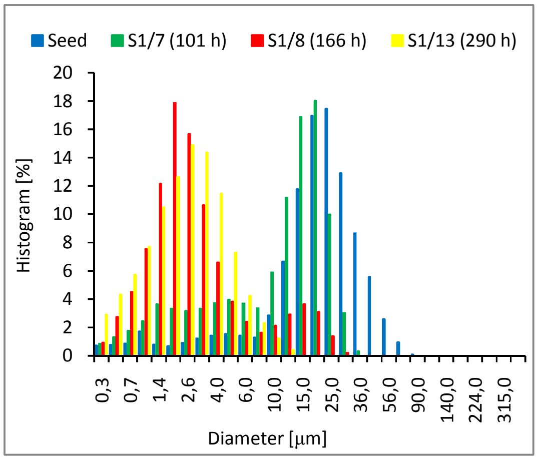

Figure 4 - Particles size distribution histograms for test S1

It can be seen that between 101 h and 166 h the histogram shifts left. This is due to the appearance and growth of a particles population with ≈ 2 µm of average diameter, which rapidly becomes the main one, substituting itself to the seed's one. Since 166 h no substantial further evolution can be revealed. The fact that it exists a lower limit for the stirring intensity is an indication that diffusion phenomenon are critical for the process.

A second series of tests was therefore performed, to study the influence of seed concentration and further study the water addition's one. Samples of 130 mL of satinizing solution were treated at T_{amb} with the conditions reported in *Table 2*:

Table 2 - Experimental conditions of the second series of tests

Test ID	Added water [%]	Seed concentration [g/L of solution]	Stirring intensity
S5	0	60	Low
S6	30	60	Low
S7	60	60	Low
S8	30	20	Low
S9	30	100	Low

Results from the past series were taken into account by setting the stirring intensity as "low" (the reader should notice that despite being called "low" this is the stirring intensity that led to the activation of the process in the former series) and by scanning the 0 - 60 % range of water addition. Seed concentration effect was studied by setting it on three different levels (20, 60 and 100 g/L) while water addition was kept constant at 30 % of the caustic solution volume (tests S6, S8, and S9). First consideration is that, in contrast with the exploratory series, the recovery process took place in all these tests. This is a first confirmation of the hypotheses about water addition and stirring intensity derived above. An additional confirmation of the hypothesis that water addition effect is detrimental for the process progression comes from the analysis of the results, placed in *Figures 5* and *6*.

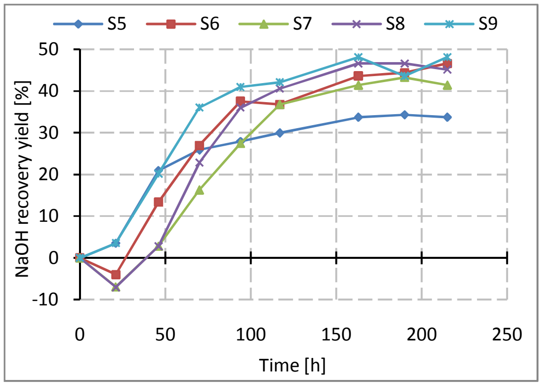

Figure 5 - Temporal evolution of caustic soda recovery yield in the second series of tests

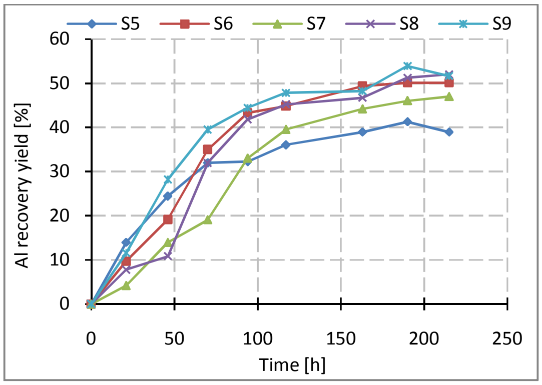

Figure 6 - Temporal evolution of aluminum recovery yield in the second series of tests

It is qualitatively seen that the more water it is added, the slower it is the reaction at the beginning. Test S7, with 60 % water addition, is the slower system to develop up to 80 – 100 h, while tests S6, S8, and S9, with 30 % water addition, are a little slower than test S5, that has no water addition, in the first 46 h. The water addition effect is also revealed by comparing the temporal evolution of the particles size distribution of S5 (0 % water addition) and S7 (60 % water addition). They are indeed very similar, but after 21 h the parameter d_{50} is 3.19 μm for S5 while it is 11.71 μm for S7, suggesting that nucleation phenomenon is faster with S5 conditions. About the seed concentration, by looking at the recovery yields progressions of S6, S8, and S9, it seems that this parameter has no significant effect on the system.

The third and last series of tests was meant to statistically quantify the influence of singular factors and their interactions on the system response. Factorial design was the experimental method selected to achieve the goal, while ANOVA has been implemented for the statistical analysis.

The factorial program used is a 2^3, it studies the influence of three factors and their interaction, on a two levels basis. Number of required tests is eight. The factors are water addition (W), seed concentration (S9, and stirring intensity (I). The factorial program is presented in *Table 3*, together with those tests (SI, SII, SIII, SIV) for applying the central point method to estimate the experimental error. Natural and coded values are attributed to the variables. Levels were chosen according with the former series of tests, in order to understand if the previously obtained results own statistical relevance, and with the specific goals of investigating the existence of a lower limit for seed concentration

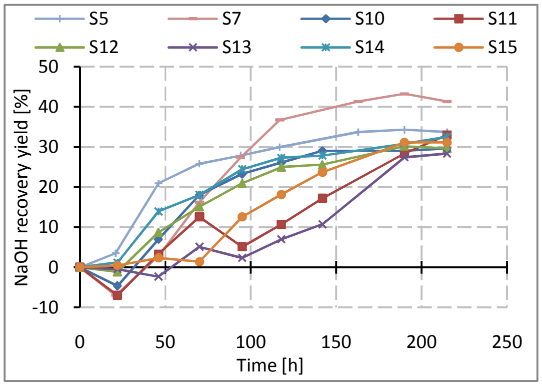

Figure 7 - Temporal evolution of caustic soda recovery yield in the factorial program's tests

Table 3 - Factorial program

Test ID	Natural variables			Coded factors						
	Water addition (W)	Seed concentration (S)	Stirring intensity (I)	W	S	I	W·S	W·I	S·I	W·S·I
	[%]	[g/L of solution]								
S10	0	10	Low	-1	-1	-1	+1	+1	+1	-1
S11	60	10	Low	+1	-1	-1	-1	-1	+1	+1
S5	0	60	Low	-1	+1	-1	-1	+1	-1	+1
S7	60	60	Low	+1	+1	-1	+1	-1	-1	-1
S12	0	10	High	-1	-1	+1	+1	-1	-1	+1
S13	60	10	High	+1	-1	+1	-1	+1	-1	-1
S14	0	60	High	-1	+1	+1	-1	-1	+1	-1
S15	60	60	High	+1	+1	+1	+1	+1	+1	+1
SI	30	35	Medium	0	0	0	0	0	0	0
SII	30	35	Medium	0	0	0	0	0	0	0
SIII	30	35	Medium	0	0	0	0	0	0	0
SIV	30	35	Medium	0	0	0	0	0	0	0

and the effect of stirring intensity. Results are reported in *Figures 7* and *8* and further analyzed by ANOVA.

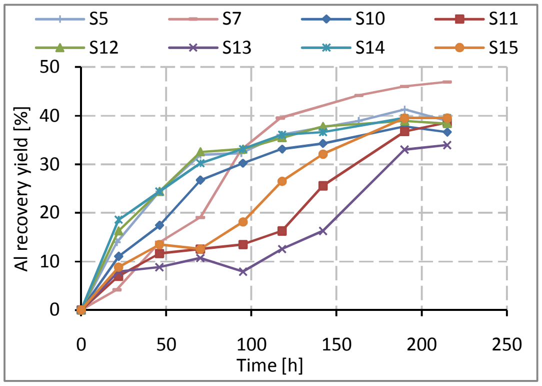

Figure 8 - Temporal evolution of aluminum recovery yield in the factorial program's tests

An important qualitative result is referred here: while by acting on the system the reaction time is reduced to the temporal scale of a week, the normal course of the process would take about 2 months to develop, as it has been observed to happen in the mother solution container.

Particles diameters evolutions are not reported, only the final (215 h) particles parameters are presented for each test of the factorial program in *Table 4*, together with the parameters average, in order to dimensionally characterize the solid final product of the process.

Table 4 - Characteristic particles' diameters. 215h.

Test ID	d_{10}	d_{50}	d_{90}
	[μm]	[μm]	[μm]
S5	0.99	2.59	6.26
S7	0.63	2.11	5.59
S10	0.79	3.04	6.80
S11	0.58	2.29	5.35
S12	0.85	2.70	7.21
S13	0.61	2.14	5.26
S14	0.81	3.06	8.83
S15	0.50	2.53	11.40
Average	0.72	2.56	7.09

Crystallization conditions do not significantly modify the final solid byproduct dimensions, which is seen to be very fine and characterized by a d_{10} = 0.72 μm, a d_{50} = 2.56 μm, and a d_{90} = 7.09 μm on average.

ANOVA was implemented on the factorial program's results at three different time's intervals, in order to study the effects of the factors and their interactions on the recovery yields, and the effects' possible variation along time. The three times are evenly distributed along the total reaction period, one at the beginning (46h), one in the middle (95h), and one at the end (215h). The main outcomes of the variance analysis are:

- water addition has got a marked detrimental effect, on recovery yields of both aluminum and caustic soda, with at least significant confidence in the first half of the process (46h and 95h of reaction time);
- seed concentration has got a significant marked positive effect at halftime (95h of reaction time);
- interactions effects are neither relevant nor significant;
- water addition and seed concentration effects tend to lose importance and significance with time (215h of reaction time).

6. Structural and Morphological Characterization of Aluminum Trihydroxide

It is claimed in various papers that "caustic etch recovery" success is intimately linked with the selling of its byproduct, aluminum trihydroxide. In fact, its commercialization leads to a consistent cut off of the investment amortizing time and make this cleaner technology more desirable at the eyes of anodizers. In order to enter a well established market such as the aluminum oxides and hydroxides one, this byproduct must firstly be well characterized. Structural and morphological studies had been carried on the solid produced in the laboratorial tests reported in *chapter 5.*.

6.1. Materials and Methods

After 215h of treatment the caustic etch solutions were filtered on a Whatman "42 ashless" filter paper for fine crystalline retention and the solid fractions were firstly washed with about 1 L of demineralized water and then naturally dried at a temperature of 25°C for about a week. At this point no mechanical grinding was implemented on the solid, only a manual shaking of the containing flasks which revealed to be enough to obtain a manageable powder. Structural characterization was performed by means of a Philips PW 1830 X-Ray diffractometer, with a Copper X-Ray source. For the data collection and analysis X' Pert Quantify and X'Pert Highscore software were used. The morphological investigation was carried by means of an Oxford FEG-SEM JEOL JSM-7001F with EDS (Energy Dispersion System).

6.2. Results and Discussion

XRD patterns are not reported in this context. Analyzing them it is clear that they all belong to the same compound, therefore the different conditions of reaction did not alter the structure of the crystallizing solid. The experimental patterns were compared with the sample patterns in the software's database in an iterative screening process, in which every screen was more accurate than the former one. It was determined that the experimental X-Ray diffraction patterns are generated by the diffraction grating of gibbsite, $\gamma\text{-Al(OH)}_3$, and not by other polymorphs. A sort of expected result is obtained: by seeding the caustic solution with gibbsite seed, the solid that crystallizes is gibbsite as well, no matter which the reaction conditions are. By SEM it is relieved that the basic crystallized morphologies are thin circular plates with irregular edges. The major grain dimension is variable but in any case it is less than 1 μm and the minor one sets in the nanometric scale. Crystals do form clusters of various sizes and shapes, usually rounded and similar to the sandy conformation called "desert rose". One of them is shown in *Figure 9*.

7. Gibbsite Dehydration and Calcinations: Production of Activated and Calcined Aluminas

A number of marketable aluminas can be produced by dehydration and calcinations of gibbsite, at various temperatures and conditions. In the present study the gibbsite produced by caustic etch recovery is thermally treated and the effects of temperature, time, and starting material on the final product are investigated.

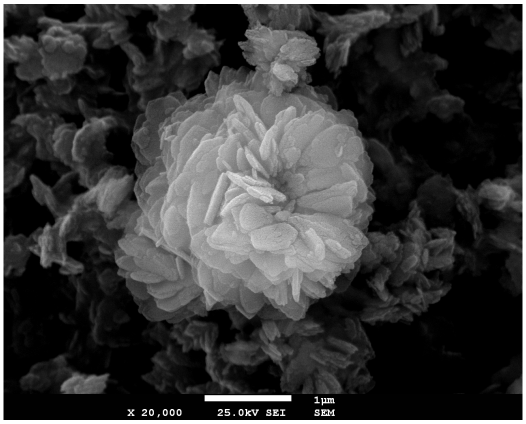

Figure 9 – Cluster of crystals (x20,000).

7.1. Materials and Methods

Samples of gibbsite were calcined in silica crucibles using two types of equipment: for heating up to 1000℃ it was used a muffle furnace with embedded heating elements (Carbolite AAF 1100 6.99 kW), while for calcinations over 1000ºC a muffle furnace with open-coiled heating elements (Termolab, 6.5 kW) was adopted. Final product was characterized by X-Ray diffraction, Scanning Electron Microscopy and laser diffraction.

7.2. Influence of Temperature and Time

Samples of the gibbsite crystallized in test S7 were heated at various temperatures and for different times in order to understand the influence of these two factors on the final product. The reader should notice that all the samples belong to the same experimental test for not introducing another possible source of variability that is the crystallization conditions of the starting material. Test S7 was chosen randomly among the others of the factorial program. Samples preparation conditions are:

- Temperatures: 450℃, 600℃, 1000℃, 1200℃
- Times: 30 min, 3 hours, 7 hours

The calcined samples were characterized by X-Ray diffraction in order to identify the phases formed. It is seen that by heating the gibbsite at 450℃ and for 30 minutes, the main produced phase is a hexagonal χ-Al_2O_3. Still, the dehydration process is not complete and a residual orthorhombic phase with chemical formula AlO(OH) can be distinguished. For higher heating times this latter phase disappear but no further evolution in the material structure is revealed by X-Ray analysis. A significant change happens when the temperature is risen at 1000℃: a cubic γ-Al_2O_3 becomes the main phase, no matter which the heating time is. At 1200℃ a radical change is clearly seen as the material converts its structure in the rhombohedric α-Al_2O_3, the final stage in the gibbsite dehydration and calcinations pattern. χ-Al_2O_3 and γ-Al_2O_3 are generally classified as activated aluminas. α-Al_2O_3 is classified as calcined alumina. The calcined S7 samples were also studied by means of SEM. No morphology evolution can be detected between the starting material and the various calcined samples, except for the case of the one heated at 1200℃ for 7 h. With these conditions new crystals with a globular shape appear among the original plate-like ones (*Figure 10*).

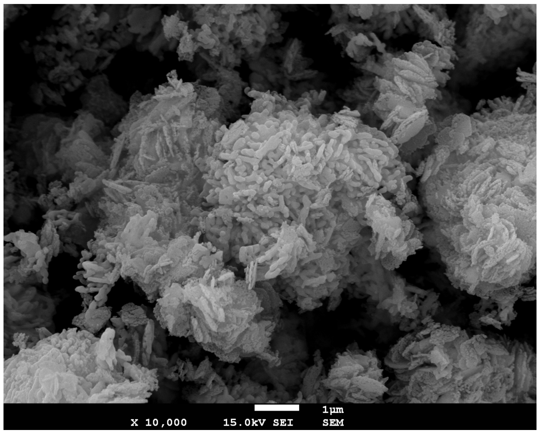

Figure 10 – α-Al_2O_3 globular-like crystals (x10,000)

7.3. Influence of the Starting Material

Starting material influence was investigated by thermally treating with equal conditions of temperature, time, and heating profile, one sample of gibbsite for each of the tests that belong to the factorial program. Conditions of temperature and time were selected randomly, and are 1000℃ and 7h. The final material was studied by XRD and SEM. From X-Ray patterns it is clearly seen that the different crystallization conditions have no significant effect on the final alumina structure. A cubic γ-Al_2O_3 is evenly identified in each pattern. By SEM analysis it is also seen that they have no influence on the final alumina morphology, which keeps being as the starting gibbsite one.

8. Conclucions

“Caustic etch recovery” technology was studied at a laboratorial level. Its more basic configuration, a crystallizer tank working in batch mode, was used in various series of tests. Samples of an exhausted satinizing solution with 155 g/L of dissolved aluminum and 91 g/L of caustic soda were treated in order to fasten the Bayer reaction that is intrinsically slow to develop. The system behavior was studied by acting on a number of parameters (% of added water, seed concentration, stirring intensity) that were thought to affect the process. Qualitative and statistical analysis of the experimental results allows stating that:

- % of water addition owns a marked detrimental effect on reaction speed. Its influence is stronger at the beginning but loses significance in time, being zero after 215h. Water addition has no effect on the Al and NaOH recovery yields after 215h.
- Seed concentration has a very low inferior limit, quantified in 10 g/L of caustic solution in this work. Higher concentrations’ effect is positive but tends to tail off in time.
- Stirring intensity has to be higher than a threshold for the process to develop, but above it has no effect on the Al and NaOH recovery yields.
- The treatment effectively reduces the natural time for the process to develop. Recovery yields ranging from 30 to 40 % (for both Al and NaOH) were obtained after 215h of treatment, while the process took about two months to start by itself in a resting caustic etch solution.
- Reaction conditions affect the particles’ size distribution only at the beginning of the process, according with the reaction rate they impose. After 215h no

significant effect on particles' diameter is relieved, the crystallized particles are very fine and characterized by a d_{10} = 0.72 μm, a d_{50} = 2.56 μm, and a d_{90} = 7.09 μm (on average).

On these basis, it can be guessed that caustic etch recovery can be an effective technique to be introduced in an anodizing line in order to cut down the costs for reagents purchasing and wastewater neutralization sludge handling and disposal, without introducing new operational costs. In fact best conditions for the process to work are by chance also simple and inexpensive. No water addition is required, so that fresh water cost is saved and the recovered caustic solution is so concentrated in NaOH (160 to 170 g/L after 215h of reaction time) that can be directly reused in the etching/satinizing stages, avoiding the use of costly evaporators and of a great amount of thermal energy. Furthermore, in these conditions, an hypothetic steady-state recovery system would not drastically diminishes the Al concentration in the etching/satinizing bath, being the Al concentration in the recycled solution (from 90 to 100 g/L after 215h of reaction time) still within the treatment best range (70 – 150 g/L). This is advantageous because the bath's Al concentration is considered a critical parameter for the final product aesthetic, which would therefore not vary so drastically (quality issue is fundamental in the spreading of the caustic etch recovery). Being the (crystallized solid)/(seed concentration) ratio very high it is possible to imagine a continuous system that requires external seeding only in the start-up and that internally recycles a small share of the byproduct for the rest of the operational time. The rest of the solid mass produced would be withdrawn and subject of further processing. Moreover the system can be optimized in order to minimize the expenditure for shaft energy, being stirring intensity only to be higher than a threshold.

Further laboratorial work should confirm these results by scaling up the batch experimental configuration. Then with solid basis it would be possible to pass to a continuous configuration. Last step would be a pilot test in a real industrial situation. This pilot test should be optimized in order to achieve the best possible chemicals recovery yields without drastically changing the chemicals concentration inside the etching/satinizing bath, and in turn the quality of the final products.

On a second phase of this study the solid byproduct of caustic etch recovery was structurally and morphologically characterized in order to realize whether it can find applications or not. The settled powder has a flour-like consistency and its color is bright white. The structural study found that gibbsite (γ-$Al(OH)_3$) is what crystallizes during the process when gibbsite seed is used, and that crystallization conditions do not alter the structure of the solid. The morphological study shown that the powder is generally made by crystals clusters. Each cluster is formed by a number of thin plate-like crystals cemented together. The small dimension and the irregular morphology of the powder's particles confer a high surface area to the product. This could favor it in a number of applications in which a high reactivity is desirable, such as flame-retardant fillers in polymers and rubbers, reagents for aluminum chemicals production, and base material for activated and calcined aluminas production.

The gibbsite produced by caustic etch recovery then went through a thermal treatment of dehydration/calcination. A number of marketable activated and calcined aluminas were produced. They range from the porous and high-surface χ and γ phases, suited for adsorbents and catalysts purposes, to the hard and inert α phase, used in the ceramic, refractory, and abrasive industries. After the thermal treatment they conserved the fineness, the bright white color, and the morphology of the original gibbsite.

On this basis it can be said that the caustic etch recovery byproduct owns specific qualities that could make it attractive in the market, as it is or after thermal treatment. Of course further characterization would be required before it could enter a well established sector such as the gibbsite and aluminas one.