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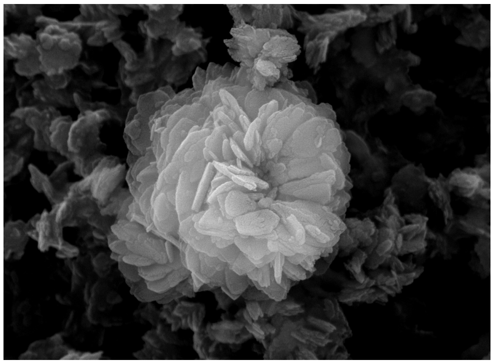

# Prevention and Recycling in the Aluminum Anodizing Industry: Soda and Aluminum Recovery From Spent Etching Baths

**Andrea Berto**

Dissertação para obtenção do Grau de Mestre em

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**Júri**

Presidente: Prof. António Jorge Gonçalves de Sousa

Orientadores: Prof$^a$ Fernanda Maria Ramos da Cruz Margarido

Prof. Carlos Alberto Gonçalves Nogueira

Vogal: Prof$^a$ Maria Joana Castelo B. de Assis T. Neiva Correia

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A mamma Mara
e papà Carlo

# RESUMO

A prevenção é a primeira prioridade na hierarquia política da gestão de resíduos. Tem como objectivo reduzir a geração na fonte bem como fomentar proveitos às empresas devido à diminuição das taxas ambientais, poupança de matérias-primas e energia. O trabalho realizado concentra-se nesta filosofia, pois estuda a implementação de tecnologias preventivas nos processos industriais, para reduzir os resíduos e aumentar a competitividade das empresas.

A indústria de anodização do alumínio é um sector importante, que produz grandes quantidades de efluentes, os quais após tratamento geram lamas que originam problemas económicos e ambientais graves nas empresas.

De acordo com a Directiva Europeia de Prevenção e Controlo Integrados da Poluição, a "estratégia de prevenção" consiste na implementação de medidas e tecnologias preventivas de optimização do uso de recursos e minimização de perdas, nomeadamente resíduos.

Entre as operações de uma linha de anodização, a etapa de satinagem é responsável pela produção de uma grande quantidade de lamas de neutralização de efluentes e pelo uso incorrecto da soda caústica.

A tecnologia de recuperação da soda tem por objectivo reduzir a geração de lamas de neutralização e o consumo de soda caústica fresca, através da regeneração dos banhos esgotados da solução de satinagem. A utilização desta via é muito rara entre os industriais de anodização, devido à falta de dados fiáveis relativos ao desempenho desta tecnologia.

O trabalho realizado assenta neste cenário, e pretende contribuir para a compreensão dos fenómenos de "recuperação da soda dos banhos de satinagem", promovendo a sua adopção nas instalações de anodização.

O trabalho realizado à escala laboratorial permitiu avaliar a aptidão da tecnologia para regenerar eficazmente a solução esgotada de soda, e investigar os parâmetros com maior efeito no rendimento do processo, de modo a optimizá-lo. Demonstrou-se que a tecnologia utilizada permite efectivamente recuperar a solução, aumentando o seu teor em soda e diminuindo o teor de alumínio dissolvido precipitando-o como gibsite. Além disso, o processo testado, nas condições optimizadas, prevê-se ser de fácil implementação, por ser simples e barato, apresentando a solução, após tratamento, as propriedades para ser reciclada na operação de satinagem. A gibsite produzida foi caracterizada estrutural, dimensional e morfologicamente. Foi efectuado o tratamento térmico da gibsite de modo a obter os principais tipos de aluminas existentes. A gibsite e as aluminas obtidas apresentam qualidade para serem vendidas como subprodutos da recuperação das soluções esgotadas de lavagem caustica.

**Palavras-Chave**: Alumínio; Anodização; Soluções de lavagem; Regeneração de NaOH; Lamas de anodização.

# ABSTRACT

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. This work fits in this philosophy: 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.

Best way to deal with the problem, according to the "prevention strategy" set by the European Directive on Integrated Pollution Prevention and Control, is to implement preventive techniques and technologies to optimize the use of resources and minimize losses, and in turn wastes.

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.

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 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 produced gibbsite was structurally, dimensionally, and morphologically characterized. A range of aluminas was also produced by thermal treatment of the gibbsite. 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.

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# INDEX

# INDEX OF FIGURES

# INDEX OF TABLES

# CHAPTER 1

# INTRODUCTION

## 1.1 General Remarks

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 [1].

Their outcomes on the natural means air, water and soil, represent a major share in the total impact man’s life has got on nature and which is placing several doubts regarding the sustainability of man’s life itself. Despite an increasing awareness among legislators, industrial actors and dwellers, and the consequent reactive actions which have been taken to face the problem, industrial undesirable effect has kept growing. It all happens as a result of the fact that the beneficial outcome of pollution managing measures is generally overcome by increasing industrial production. A feeling of urgency for stronger actions has risen along the years [2, 3].

Until 1996, the strategy for facing industrial pollution among European’s countries was grounded on an end-of-pipe approach: pollution was thought as an unavoidable effect industry had to take responsibility of, not without pain. This strategy, the so called “pollution control strategy” (reacting to pollution once it occurs), had been found to be non effective in reducing industrial emission for several reasons beside the one previously mentioned. Its fault was not to consider the environment as a whole, therefore generating a passage of pollution between different natural means, usually from water and air to the land (in the form of solid waste), thus not really solving the problem but just moving it. The results had been the spreading of industrial dumps and the partial return of pollution to its initial state, because of volatilization and liquid leaching. The fact that pollution control had been considered an heavy duty by the industry, for so long had drawn the idea that environment means cost, and worked against the strategy implementation itself [3 - 6].

In 1996 a radical shift in the European Union’s strategy was brought by the Council Directive 96/61/EC of 24 September 1996 concerning integrated pollution prevention and control, named IPPC. The directive is considered a cornerstone of environmental legislation, sanctioning the changeover between pollution control and pollution prevention, in favor of the latter one. Its primary goal, as stated in Article 1, “*is to achieve integrated prevention and control of pollution in order to secure a high level of protection of the environment taken as a whole*” [7]. This means that no medium air, water and land will be compromised in an attempt to protect another. Instead of concentrating on preserving the quality of a singular natural mean, trying to emit a pollution up to a level which is thought to be the upper limit nature can handle by itself, it focuses on source control of pollution; so emissions from a facility will be preferentially prevented, reduced, recovered or recycled and otherwise, as a last chance, they will be treated using “end-of-pipe” technologies [8, 9].

Within this new strategy the connotation of the word “environment” drastically turns from “cost” to “opportunity”: pollution and wastes are seen as losses of raw materials which are consequence of imperfect production patterns and can be avoided by a continuous improvement, and by doing it the natural outcomes are production’s cost reduction, enhanced industry’s competitiveness and, of course, environmental benefits [1, 4, 5, 6, 10, 11].

The strategy set by the IPPC directive is established on the main concept of sustainability as defined by Gro Harlem Brundtland and his team: “*sustainability means meeting the needs of the present without compromising the ability of future generations to meet their own needs.*” [12, 13]. This definition describes sustainability as having three pillars: economic, social, and environmental, thus moving apart from the former idea of sustainability, totally centered on the environmental side (see *Figure 1.1*).

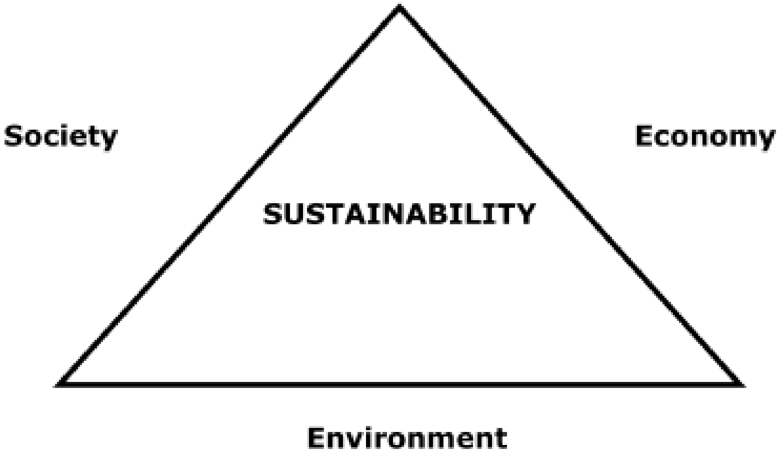


Figure 1.1 – The three pillars of sustainability [13]

The following text from the U.S. “Pollution Prevention Act” of 1990 is enlightening:

“*The United States of America annually produces millions of tons of pollution and spends tens of billions of dollars per year controlling this pollution … There are significant opportunities for industry to reduce or prevent pollution at the source through cost-effective changes in production, operation, and raw materials use. Such changes offer industry substantial savings in reduced raw material, pollution control, and liability costs as well as help protect the environment and reduce risks to worker health and safety … The opportunities for source reduction are often not realized because existing regulations, and the industrial resources they require for compliance, focus upon treatment and disposal, rather than source reduction; existing regulations do not emphasize multi-media management of pollution; and businesses need information and technical assistance to overcome institutional barriers to the adoption of source reduction practices … Source reduction is fundamentally different and more desirable than waste management and pollution control. The Environmental*

*Protection Agency seeks to address the historical lack of attention to source reduction … Congress declared it to be the national policy of the United States that pollution should be prevented or reduced at the source whenever feasible; pollution that cannot be prevented should be recycled in an environmentally safe manner, whenever feasible; pollution that cannot be prevented or recycled should be treated in an environmentally safe manner whenever feasible; and disposal or other release into the environment should be employed only as a last resort and should be conducted in an environmentally safe manner.*" [14].

The new environmental regulation on industrial emissions can be read as a "New-Deal" between the legislator, the industry and people, which pulls all the parties to face emerging concepts such as the industrial ecology's one, for making everybody better off.

Indeed, industrial ecology's beliefs surely influenced this new course. It considers none industrial system as apart from the rest, instead, it looks upon the industrial system as a whole, placed within the bigger environmental system, pursuing the optimizations of the links between industrial sub-systems, with the great goal of not generating losses, because each waste is seen as a resource for another branch of the integrated greed of industrial activities. Industrial ecology can be considered the productive part of the sustainable development [4, 15].

Industrial ecology's target is "zero-waste", which despite not being achievable because of thermodynamic second law, is the long term solution for sustainability. Zero waste is a philosophy that encourages the redesign of resource life cycles so that all substances are reused. Any residue sent to landfills is minimized. The process works similarly to the way nature work's in managing and reusing its resources. Inside industry this process involves creating commodities out of traditional waste products, essentially making old outputs new inputs for others industrial sectors [10].

The "zero-waste" idea helps defining a hierarchy within the industry on how to involve the environment in the development process, thus adopting an Environmental Management System (EMS). The hierarchy presented in order of preference and importance, counts on:

1. prevention: the use of materials, practices and techniques in order to eliminate or reduce the quantity and the danger of industrial emissions at the source;
2. reuse: the reintroduction of a substance in the production pattern, thus preventing it from becoming a loss;
3. recycling: the reprocessing of a waste in order for it to recover its initial properties and use or to become functional for others uses;
4. treat: the mandatory treatment for those emissions which can't be avoided, done with end-of-pipe techniques and carried to reduce their volume and their toxicity;
5. dispose: the choice for end-of-life residues, which has to be the best one in order to not place harms to the environment and people.

Certainly, industrial concepts, such like those ranked above, won't allow mankind to reach his life's sustainability just by themselves. Sustainable development depends from a number of factors such as: world population's growth, people habits and lifestyles (which involves their power to choose as consumers), natural resources management and economical development among the others. Nevertheless, they are steps in the staircase that leads to sustainable development, and if one of them is missing then the whole climb would be compromised, and the target missed (see *Figure 1.2*).

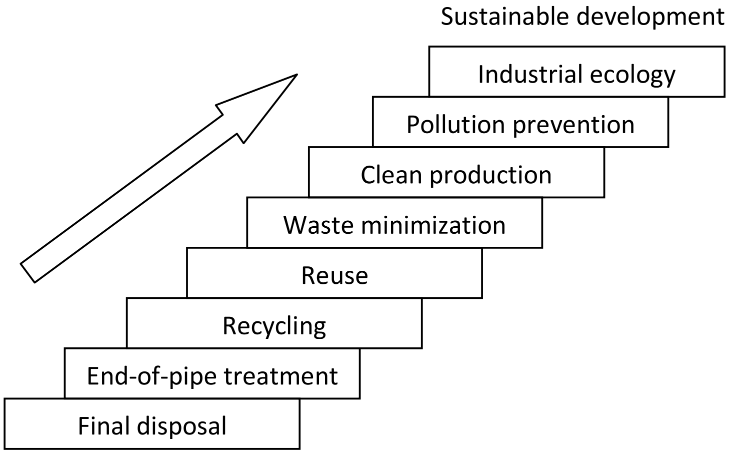


Figure 1.2 - Environmental management levels

The European Community aims to implement the IPPC legislation and thus to attain the expected results in terms of sustainable development by the use of two main devices, among the others:

- the principle of the polluter-pays: is enacted to make the party responsible for producing the emission, also responsible for paying for the damage done to the natural environment;
- the implementation, by the industry, of the Best Available Techniques (BATs), which according to the IPPC Directive "means the most effective and advanced stage in the development of activities and their methods of operation which indicate the practical suitability of particular techniques for providing, in principle, the basis for emission limit values designed to prevent and, where that's not practicable, generally to reduce emissions and the impact on the environment as a whole". In particular it is stressed that:
    a) " *"techniques" shall include both the technology used and the way in which the installation is designed, built, maintained, operated and decommissioned*";
    b) " *"available techniques" means those developed on a scale which allows implementation in the relevant industrial sector, under economically and technically viable conditions, taking into consideration the costs and advantages, whether or not the techniques are used or produced inside the Member State in question, as long as they are reasonably accessible to the operator*";

c) “ *“best” means most effective in achieving a high general level of protection of the environment as a whole*”.

Article 16(2) of the IPPC Directive requires the Commission to organize “*an exchange of information between Member States and the industries concerned on best available techniques, associated monitoring and developments in them*”, and to publish the results of the exchange. Recital (25) explains that “*the development and exchange of information at Community level about best available techniques will help to redress the technological imbalances in the Community, will promote the worldwide dissemination of limit values and techniques used in the Community and will help the Member States in the efficient implementation of this Directive*”. The participation of the industries and the general availability of the published results should stimulate the uptake of cleaner production techniques. The results of the information exchange take the form of BATs reference documents (BREFs) which are published for each singular industrial sector under the Directive.

## 1.2 Problem Overview

The surface treatment of metals and plastics (STM) collects a wide range of industrial processes that alter the surface of metallic and plastic manufactured items to achieve a certain property. STM processes may be applied with many different goals such as: improve appearance, reflectivity, wettability, weldability, corrosion resistance, wear resistance, hardness, modify electrical conductivity, remove burrs and flaws, and control the surface friction [2, 9, 16].

In order to find the first historical traces of STM one has to go back to early man using gold decoratively before 4000 B.C… Gold and silver plating was well-known by the 13th century A.D., and tin plating of iron was carried out in Bohemia in 1200 A.D… In the mid-19th century, the electrodeposition of metals was discovered enabling new possibilities, which are still being extended [16].

Currently the STM main areas of application are: automotive 22%, construction 9%, food and drink containers 8%, electrical industry 7%, electronics 7%, steel semis (components for other assemblies) 7%, industrial equipment 5%, aerospace 5%, others 30%. The range of components treated varies from small ironmongery’s items such as screws, nuts and bolts, jewelry and ornaments, components for automotive and other industries to steel rolls up to 32 tons and over 2 meters wide for pressing automotive bodies, food and drink containers, etc. Two further commercial areas of application have stand out since the 1960’s: microelectronics, where high conductivity is achieved by applying precious metal plating over a cheaper surface, and printing, where aluminum is usually the choice for lithographic plates [16].

The surface treatment of metals and plastics is carried out in more than 18,300 European plants. Around 55% are specialist sub-contractors (known as jobs or jobbing shops) while the rest provide the service within another installation. Larger plants are owned by major multinational companies although the vast majority are small or medium enterprises (SMEs), typically employing 10 to 80 people. The whole industry for the surface treatment of metals and plastics employs about 440,000 people in Europe. There's not a typical installation, and although there are of course strong similarities between sites committed in the same activities, no two sites will be identical. Surface treatments create no products, they change the surface of previously formed objects for subsequent use. Thus the STM sector does not itself form a distinct vertical industry sector as it provides a service to a wide range of different industries. Therefore gathering statistics for the whole sector or for specific surface treatments, whenever possible, is quite a challenge, because of its horizontality and intrinsic variability also, and because being sometimes secondary activities carried out in manufacturing industries, their outcomes are legally classified according to the industry manufacture. While no overall figures exist for European production, in 2000 the large scale steel coil through put was about 10.5 million tons and about 640,000 tons of architectural components were anodized. Indications of the industry size and importance are that a car contains over 4,000 surface treated components, including body panels, and an Airbus aircraft contains over two million [9, 16, 17].

Another measure of the importance of the STM sector is available, although quite undesirable: it is one of the six industrial sectors under the first IPPC Directive. Section 2.6 of Annex 1 of the Directive states that, besides other kinds of industrial activities (energy production and transformation, production and processing of metals, petroleum product processing, chemicals manufacture, food and agricultural activities and waste treatment), "installations for the surface treatment of metals and plastics using an electrolytic or chemical process where the volume of the treatment vats exceeds 30 $m^3$", are covered by the Law. Although practice and infrastructure in this industry has improved in the last decades, it is still responsible for a relevant number of environmental accidents and the hazard of unplanned discharges and their impacts is considered to be high. The STM sector is therefore officially recognized as a highly polluting industry, with a significant harmful potential for man's life, wildlife and nature as a whole, and has an intervention priority within the terms of the IPPC Directive [16].

The main environmental concerns this industry arises are related to energy, water and raw materials consumption, emissions to surface and groundwater, solid and liquid wastes and the site condition on cessation of activities. The STM industry is not a major source of pollution to air, although some emissions may be locally dangerous. Emissions into the water mean and production of hazardous solid wastes are the main undesired outcomes of this industrial activity; heavy metals rank first among the most dangerous water polluters discharged and about 300,000 tons of hazardous solid waste are produced per year, by the STM's activity itself and the end-of-pipe processes for wastewater treatment within its installations [16, 18].

The STM sector can be seen as the paradigm of the "pollution treatment strategy" failure: its processes are usually water-intensive, thus leading to a high contamination of this natural mean, and by applying an end-of-pipe kind of treatment the result is simply a shift of pollution to the land in the form of solid waste, which is hazardous in many cases. Of course, the shift is advantageous in term of environmental protection, being solid pollution easier to deal with if compared to a liquid one. Nevertheless, hazardous solid waste requires specific and authorized disposal landfills and particular care along the years, and they never really stop placing environmental problems, because of the formation of toxic leachate and the volatilization of organic compounds.

It all means costs for the STM industry, accordingly with the principle of the “polluter-pays”, costs for the extra inputs to overcome the losses, for the end-of-pipe treatment systems (which are usually oversized and more complicated than it is strictly necessary, because of the absence of emissions prevention), for the solid waste transport, treatment and disposal, costs which are increasing year by year and are impacting the economical viability of most of the SMEs that make the industry’s backbone [5].

It is not currently feasible to achieve a zero discharge of pollutants for the metals and plastics surface treatment sector. However, significant reductions in the harmful potential and volume of emissions from most finishing operations are possible by applying the best available techniques in a perspective of a “pollution prevention strategy”, which has been shown to reduce costs as well as emissions through source reduction and recycling/reuse. Because of the costs rising and the changeover in environmental regulation within European’s borders, STM sector’s management and production personnel may be more willing to consider the opportunities brought by the introduction of cost-effective BATs in their productive context.

As a result of the foregoing the singular STM supplier will do the following [4, 5, 19]:

- decrease costs for raw materials, energy consumption, and waste treatment/disposal;
- improve the working environment, thus decreasing costs associated with workers health;
- acquire the favorable image of a company that protects the environment;
- create a competitive advantage.

The limited use of BATs within the STM sector, in spite of their significant potential for emissions minimization and cost saving, has a number of causes [4, 5]:

1. a former legislative and regulatory regime that did not assign priority to emissions prevention;
2. the memory in manager’s minds of a recent investment for an end-of-pipe system;
3. the low priority of surface finishing steps within the manufactory chain, which leads to insufficient attention to comply with latest specifications and lack of investment (with some important exceptions);
4. the intrinsic adversity toward changes, caused by the fear of losing customers, in a sector which is oversaturated in finishing suppliers;
5. confusion over the difference between “emissions prevention” and “pollution control”;
6. the lack of comprehensive information about new technologies and their performances;

7. a lack of human resources at the plant level to install and maintain techniques and technologies;
8. the slow rate of new investment among SMEs, which lowers the rate of diffusion of new technologies;
9. the low monetary margin within which the STM's small and medium enterprises operate, that do not enable long-term planning;
10. lack of visibility to the final customer, namely the consumer who buys the final product, that cancels any image advantage because of environmental caring.

Considering these assumptions, the legislator has made the first step toward a cleaner production with the changeover in environmental legislation. He has also defined the next step to be taken, namely the sharing and spreading of information among the industry's actors in order to cover the lack of knowledge on BATs, step that could unleash all the emission prevention potentials within the STM sector.

This information spreading goes in the direction pointed by the IPPC legislation, as stated in its article 16(2) and recital (25), and reaches its maximum with the "Reference Document on Best Available Techniques for the Surface Treatment of Metals and Plastics", which was published in the August 2006 by the European Commission.

Being the STM sector a broad one, its BREF document comes out as being certainly useful tool but in some instances also an imprecise one. By using the words of the team who wrote the report "*Details of data problems are given: primarily a lack of consistent quantitative information. The consumptions and emissions data given are predominantly for groups of techniques, rather than individual ones. This has resulted in some BAT being general, or no conclusions being reached, where specific conclusions would be helpful to the industry and regulators*" [16].

Therefore, there is still work that has to be done in the direction of covering the gap of knowledge on BATs within the surface treatment industry. This work has to bring precise economical and technical data on specific BATs to the attention of industry's managers and it has to be supported by academic researches and real industrial trials.

## 1.3 Scope of the Work

This research work stands in the scenario depicted in the previous points. It is meant as a contribution for the improving and spreading of knowledge on BATs within the metals and plastics surface treatment industrial sector.

In particular, it is meant as a contribution in the understanding of a specific technology recognized as a BAT, in a specific context such as the aluminum anodizing industry (a subsector of the STM one).

Anodizing is an electrolytic passivation process that increases the thickness of the natural oxide layer on the surface of metal items. Results are increased corrosion protection, wear resistance, and surface hardness, better adhesion for paint primers and glues than bare metal. Anodic films can also be used for a number of decorative effects. Moreover, anodizing is used to prevent galling of threaded components and to make dielectric films for electrolytic capacitors. Anodic films are usually applied to protect aluminum alloys, though processes also exist for titanium, zinc, magnesium, niobium, and tantalum.

The specific technology under consideration is named “caustic etch recovery” in the surface treatment sector’s BREF. Its purpose is to recover the reagent caustic soda, NaOH, from the exhausted caustic solution of the etching step in the aluminum anodizing line, generating aluminum trihydroxide, $Al(OH)_3$, as a byproduct. This is done by a simple crystallization reaction, better known as the “Bayer reaction”. Caustic soda can be reused in the process, while aluminum trihydroxide is a commercial product with plenty of uses which could find its own way into the market.

This could lead to several economical, technical and environmental advantages, namely:

- cost saving because of a minor use of reagents;
- cost saving because of the decreased production of solid wastes in the end-of-pipe treatment processes, which means decreasing handling, transport and disposal costs;
- cost saving because of minor performance requirement from the end-of-pipe treatment system (in the case of a new installation this could also mean an investment cost saving because of a smaller treatment plant required);
- monetary income from the potential commercialization of the aluminum trihydroxide;
- better control of the etching step, which could operate in a steady state mode;
- decreased impact of the anodizing industry on land, because of the reduction in solid wastes it produces;
- decreased environmental impacts of the caustic soda and aluminum trihydroxide primary production industry, because of the reuse and recycling within the anodizing industry.

The study began with the specific goals of exploring and optimizing the Bayer reaction within the specific aluminum etching conditions (anodizing line), and of characterizing the reaction byproduct (aluminum trihydroxide), up to the point allowed by available time and means.

The initial work plan is presented in the *Figure 1.3* and it has been carried out to the letter.

The work can be ideally divided in two temporary consecutive parts:

- During the first one the parameters which govern the Bayer reaction had been investigated and optimized in the perspective of maximizing the caustic soda and aluminum recovery yields. The solid byproduct of the reaction had also been dimensionally characterized with its particles' size distribution.

- During the second one the reaction's byproduct had been thermally treated, and the starting material together with the treatment products had been structurally and morphologically characterized by means of X-Ray diffraction and Scanning Electron Microscopy analysis. So much interest in the byproduct is justified by the critical importance of its commercialization in the successful spreading of this particular BAT, as it is explained in the following chapters.

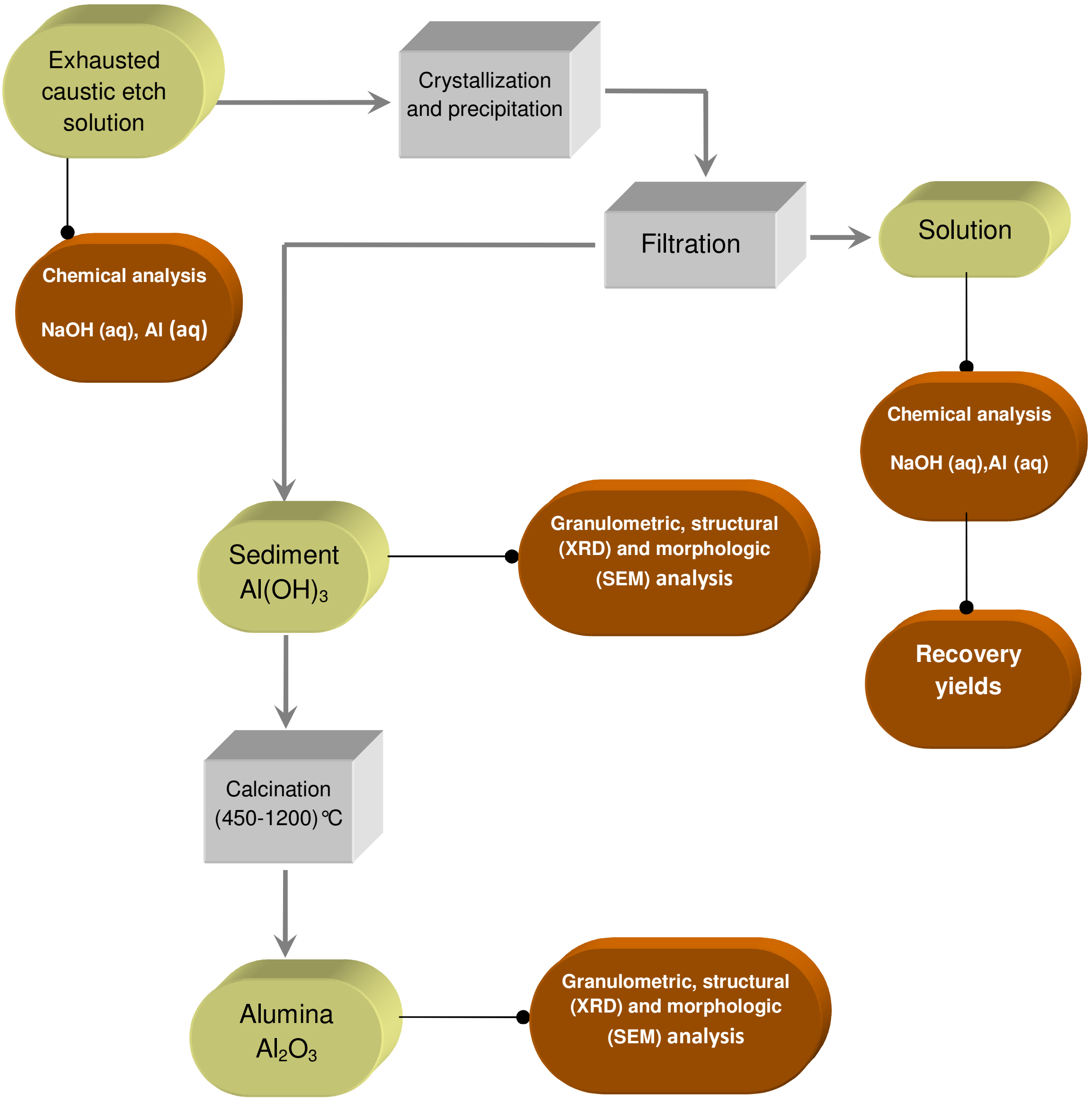


Figure 1.3 – Initial work plan

This research work had been carried out inside Instituto Superior Técnico's structures (IST, Lisboa, Portugal), together with the help of "Unidade de Produção-Consumo Sustentável" from "Laboratório Nacional de Energia e Geologia" (LNEG), in partnership with the Hydro Alumínio Portalex S.A. facility located in S. Carlos – 2726-901 Mem Martins (Portugal), which provided the exhausted caustic etch solution to be treated.

Resuming, *Chapter 1* was meant to set the scenario within which this work stands, to present the questions placed by the STM industry, and to introduce the reader to the job that had been carried out and its goals.

In *Chapter 2,* after a first introductory subchapter that highlights the relevance of this work by showing data on the aluminum and aluminum anodizing industries, it is presented the state of the art of the aluminum anodizing.

*Chapter 3* relates the state of the art of the "caustic etch recovery" technology. A subchapter on aluminum oxides and hydroxides, their properties and possible commercial applications is also present.

*Chapter 4* is committed to the presentation of the first part of the work, that is the investigation of the caustic etch recovery, together with the discussion of its results.

*Chapters 5* and *6* refer the second part of the work, that is the characterization of the caustic etch recovery byproduct.

*Chapter 7* contains the study's conclusions and some insights for a possible future continuation of this work.

# CHAPTER 2

## ALUMINUM AND ALUMINUM ANODIZING INDUSTRY

### 2.1 Aluminum: Overview and Relevance of its Market

Aluminum is the most abundant metallic element in the Earth's crust, and the third most copious element therein, after oxygen and silicon. It makes up about 8% of the Earth solid surface's weight. It is very reactive and normally it is found combined with other elements, and occurs rarely, if at all, in its pure state. It appears in a wide variety of minerals together with oxygen, silicon, the alkali and alkaline-earths, fluorine, and as hydroxides, sulfates, and phosphates [20].

Aluminum has become the predominant nonferrous metal in use, yet it is one of the newest of the common metals. Its primary production has kept growing at an impressive rate since 1854 (see *Figure 2.1*), when it was first prepared electrolytically by a method discovered independently by Deville in France and Bunsen in Germany (with primary production it is meant the one which begins with the extraction of bauxite, an aluminum compounds rich ores). 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. Its main producers (with an output above 1 million metric tons each) are in order: the People's Republic of China, Russia, Canada, the United States, Australia, Brazil, Norway and India (see *Figure 2.2*) [21].

Europe as a whole is a top producer with its 5.5 million metric tons in 2008 [22].

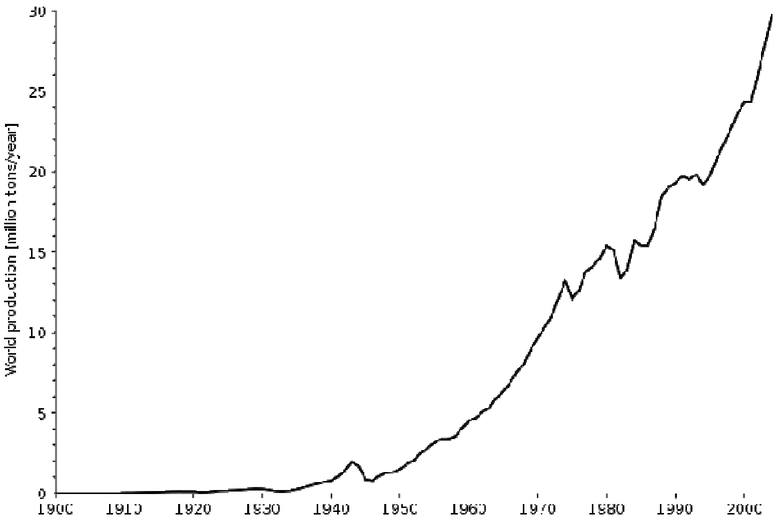


Figure 2.1 – Aluminum World Production Trend [http://www.usgs.gov].

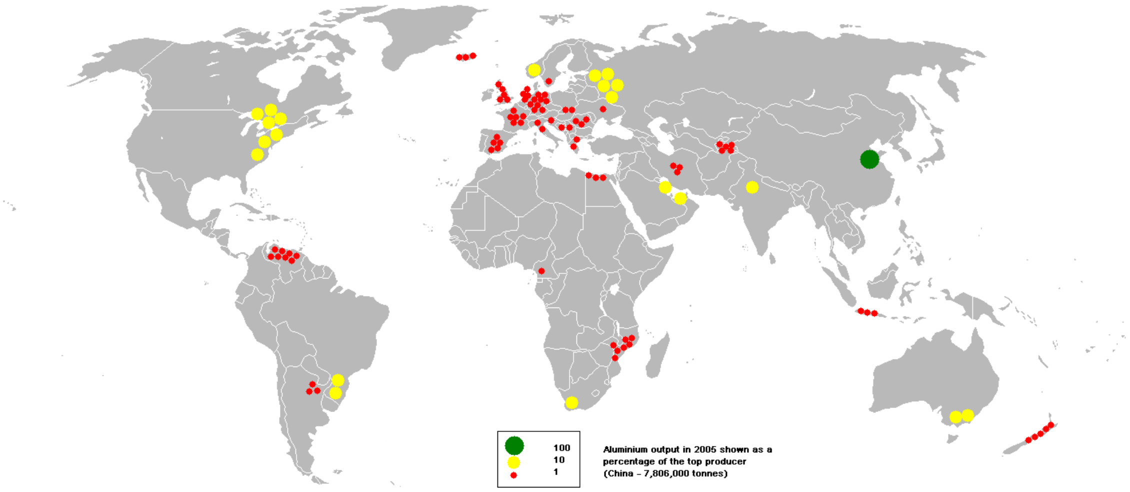


Figure 2.2 – Aluminum output in 2005 shown as a percentage of the top producer (China – 7.806 million tons) [http://www.bgs.ac.uk accessed on 29th May 2007].

These data are 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 [21]. The European aluminum recycling industry accounted for 40% of Europe's aluminum supply in 2009 [22]. Recycled aluminum is named "secondary aluminum" in order to be distinguished from the primary one, but it conserves all its former properties (aluminum can be recycled indefinitely) [23].

What makes this metal so remarkable is its low density, high electrical and thermal conductivities, high reflexivity, weldability, and its outstanding ability to resist corrosion.

It owes its stability to the phenomenon of passivation, which indicates the rapid growth of a thin but protective oxide layer (thickness of 3 nm for pure aluminum and 5-15 nm for aluminum alloys, both under normal conditions of temperature and humidity) over an aluminum item's surface as soon as this is exposed to atmospheric oxygen, water or other oxidants. The aluminum oxide layer can protect the bulk even in strongly oxidizing and acid environments. However, this oxide film dissolves in strong alkaline solutions; corrosion is rapid, producing soluble alkali-metal aluminate and hydrogen as shown in equation *(2.1)* [20]:

$$2Al + 2OH^{-} + 6H_2O \rightarrow 2[Al(OH)_4]^{-} + 3H_{2(g)} \tag{2.1}$$

The alumina extraction from bauxite ores and every finishing process of aluminum made items that requires an etching phase takes advantage of this last phenomenon.

Passivation phenomenon is exploited by the anodizing process, which aims to increase the thickness of the natural oxide layer for enhancing its performances.

Pure aluminum is soft and shows low strength, nevertheless it can be alloyed with many other elements (such as copper, zinc, magnesium, manganese and silicon) and treated by thermomechanical processes to increase its strength and impart a number of useful properties. Aluminum alloys are light, strong, readily formable, machined or casted and accept a wide variety of finishes.

Components made from aluminum and its alloys are vital to the transport industry, and are as well crucial in the building and packaging ones (see *Figure 2.3*). Its reactive nature makes it also useful as a catalyst or additive in chemical mixtures.

Some of the many uses of aluminum metal happen in:

- transportation (cars, aircraft, trucks, railway cars, marine vessels, bicycles, etc.);
- packaging (cans, foil, etc.);
- construction (windows, doors, siding, building wire, etc.);
- a wide range of household items;
- electronics (super pure aluminum: 99.980% to 99.999% of Al);
- transistors and CPUs (heat sinks);
- paints and pyrotechnics (solid rocket fuels).

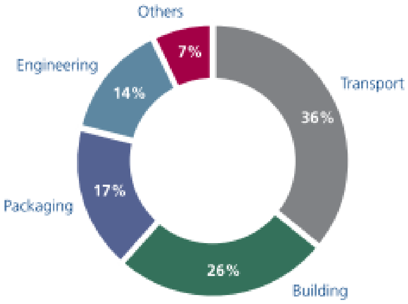


Figure 2.3 – Main end-uses for aluminum products in Europe (2008) [22].

Nowadays the only relevant industrial process known for the production of commercial grade aluminum is the Hall-Héroult electrochemical process, which implies the electrochemical reduction of the metal oxide, the alumina ($Al_2O_3$).

Alumina is in turn produced from bauxite ores in an economical feasible way by a single process, the Bayer one.

Bauxite is the richest ore in aluminum on Earth (after corundum from which aluminum can't be extracted with industrial methods). It is a hard, reddish, clay-like material. Chemically speaking it is a mix of aluminum hydroxide, iron oxide and hydroxide, titanium dioxide, aluminumsilicate minerals, with a relevant percentage of water and a variable quantity of organic impurities. Its chemical reference formula is $Al_2O_3 \cdot nH_2O$, therefore a hydrated alumina. The main minerals that makes up the bauxite are the aluminum hydroxide gibbsite Al(OH)$_3$, and the aluminum oxide hydroxides boehmite and diaspore, both AlO(OH), but characterized by different crystal parameters [20, 24, 25].

The World's bauxite top miners are Australia, Brazil, China, Indonesia, Guinea, India and Jamaica (see *Figure 2.4*). Total extraction for year 2008 had been 212 million metric tons [21].

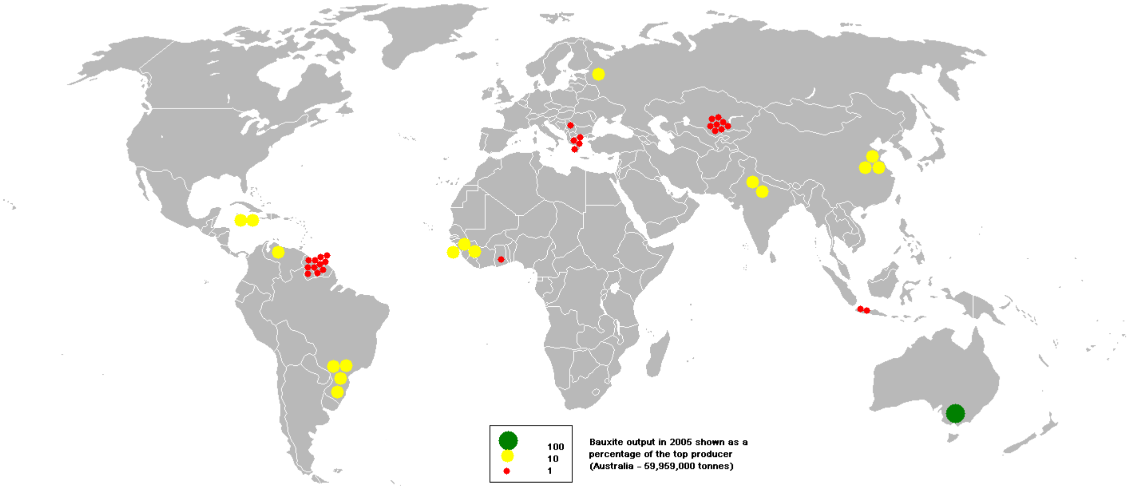


Figure 2.4 – Bauxite output in 2005 shown as a percentage of the top producer (Australia – 59.959 million metric tons) [http://www.bgs.ac.uk accessed on March 2008].

The Bayer process takes advantage of the amphoteric nature of aluminum compounds by the use of a concentration mechanism in an alkaline mean. The bauxite is firstly grinded and exsiccated at around 450°C for enhancing its reactivity and eliminating the organic impurities. The aluminum hydroxide and oxide hydroxides contained in this "bauxite flour" are then selectively leached from the other substances in an alkaline solution within a digester, according to equations *(2.2)* and *(2.3)*.

$$Al(OH)_3 + NaOH \rightarrow Al(OH)_4{}^- + Na^+ \tag{2.2}$$

$$AlO(OH) + NaOH + H_2O \rightarrow Al(OH)_4{}^- + Na^+ \tag{2.3}$$

Caustic soda and lime are the main reactants in a process which takes place in autoclaves at high pressure and temperature (between 100 and 350°C). After the extraction stage the insoluble bauxite residue must be separated from the sodium aluminate liquor. The solution is then filtered to remove the so-called red mud (the red color is due to the high concentration of iron oxides and hydroxides). Crystalline aluminum trihydroxide (gibbsite) is precipitated from the sodium aluminate liquor by cooling it and adding gibbsite seeds:

$$Al(OH)_{4-} + Na^+ \rightarrow Al(OH)_3 + NaOH \tag{2.4}$$

Reaction *(2.4)* is basically the reverse of reactions *(2.2)* and *(2.3)*, and it is named "Bayer reaction". The permanence time of the liquor inside the precipitation tanks is around 100 hours. The aluminum hydroxide is then calcined in rotary or fluidized-bed furnaces, at about 1100°C.

$$2Al(OH)_3 \rightarrow Al_2O_3 + 3H_2O \tag{2.5}$$

The end-product, aluminum oxide, is a white granular material [20, 24, 25, 26]. The entire Bayer process is shown in *Figure 2.5*.

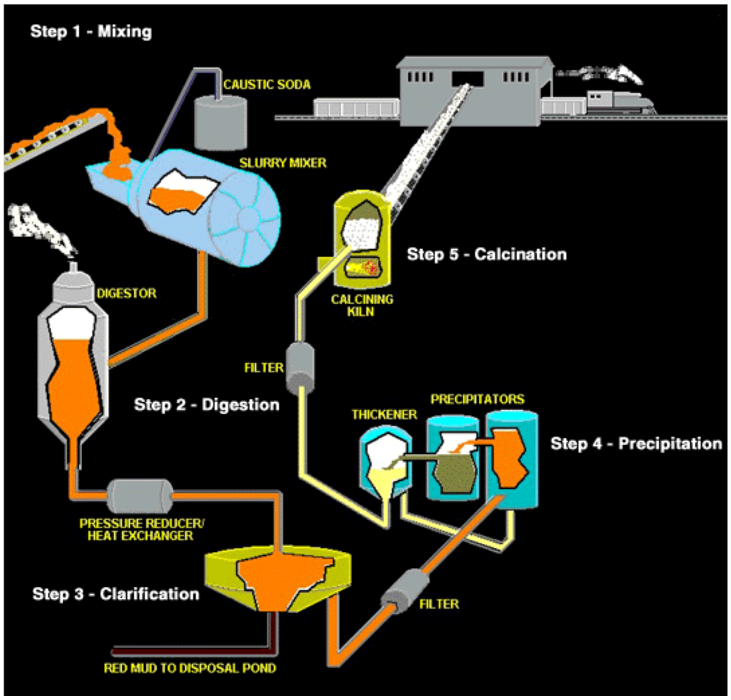


Figure 2.5 – Bayer process layout [http://lq.sherwinalumina.com/ accessed on 12th September 2010].

At this point alumina is separated in metallurgical grade (approximately 90%) and chemical grade, accordingly with its quality. The metallurgical one will be used in the Hell-Héroult process for manufacturing aluminum, while the chemical one will assume a number of different uses that will be shown later in this chapter. World's alumina production for year 2008 had been 82.3 million metric tons [21].Main alumina producers are shown in *Figure 2.6*.

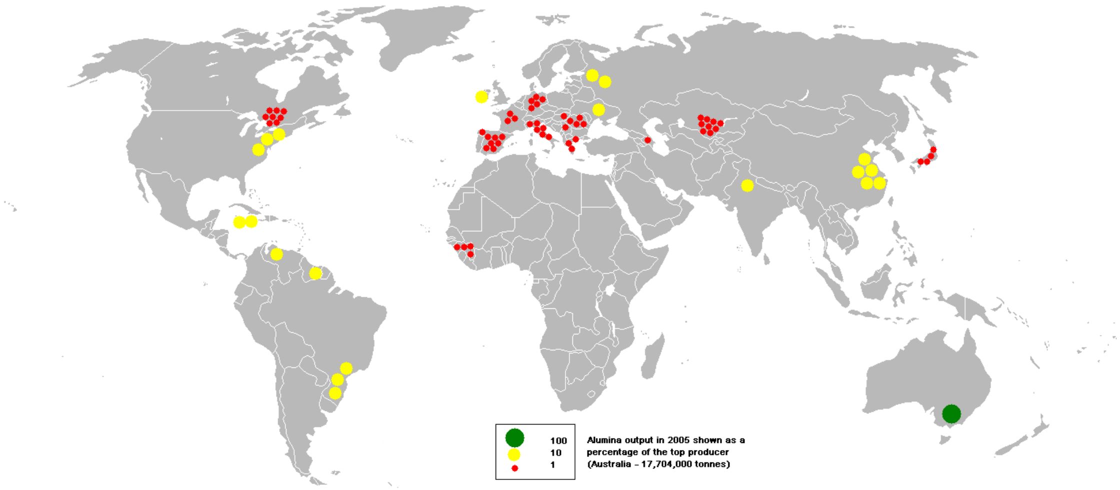


Figure 2.6 – Alumina output in 2005 shown as a percentage of the top producer (Australia – 17.704 million metric tons) [http://www.bgs.ac.uk accessed on 9th June 2007].

## 2.2 Anodizing State of the Art

### 2.2.1 General considerations

The chief surface finishing treatments for aluminum components are painting and anodizing. Anodizing industry mainly gives its services to the transport sector and the constructions one; nevertheless aluminum anodized components could be found on mp3 players, flashlights, cookware, cameras, sporting goods, in electrolytic capacitors, and on many other goods. Because of the sector's intrinsic heterogeneity, there's no statistical figure that can give back the relevance of the aluminum anodizing industry. Nonetheless, the huge size of the aluminum market shown in this work at *point 2.1* (it is well known that the surface finishing sector follows the trend of the semi-finished goods sector) and the widespread use of this finishing treatment should be sufficient for drawing an approximate scenario. Be enough to know that in 2000 only within Europe 640 thousand tons of aluminum had been anodized just for the architectural sector (see *Figure 2.7*) and that the consumption of anodized aluminum amounts to approximately one square meter per each European citizen per year [16].

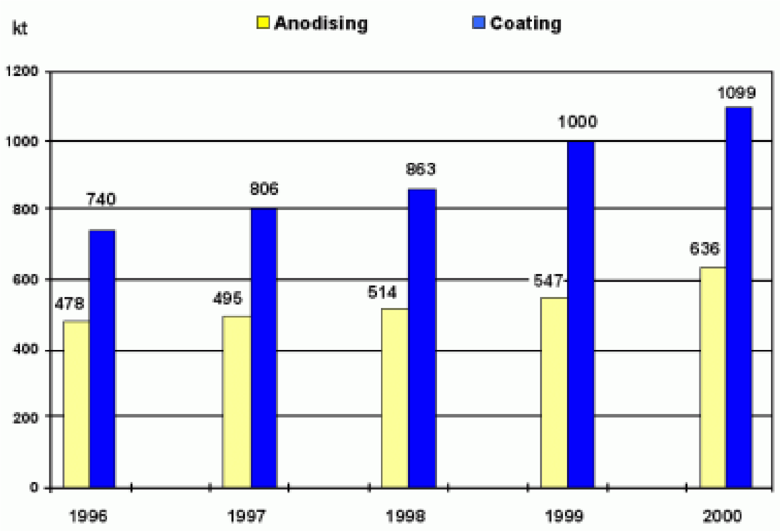


Figure 2.7 – Total production for both anodizing and other coatings for aluminum profiles in Europe [16].

Anodizing industrial scenario does not make exception to the general surface treatment one introduced in *point 1.2* of this work. This treatment is usually carried by SMEs, with a number of employers between 10 and 80. Each jobbing shop is specialized in serving a number of maximum 3-4 different customers. This comes as a result of the sector's oversaturation in which a great number of suppliers compete for a small (and lately decreasing) number of customers.

### 2.2.2 Treatment Specifics

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 (with “hard anodizing” oxide layers 150 μm thick can be obtained). The name comes from the fact that the component to be treated is made anode (positive pole) of an electrochemical cell.

The surface treatment chain usually counts on some pre-treatment steps, a core treatment, and one or more finishing steps. Anodizing shows no deviation from this common practice, and its regular layout is presented in the following. With the term "anodizing” one refers to both the whole finishing process and the core treatment from which it acquires its name.

An anodizing line generally counts on:

1. **Mechanical brushing**: treating the aluminum item via special equipments which, through disks or brushes provide the typical scratched finish.
2. **Degreasing**: the fundamental role of the degreasing action is removing the dirt, oil and lubricant (for example the cleaning pastes) from the surface of the aluminum materials. To do so, simple industrial alkali cleansers are used. A typical formulation is as follow [27]:

   Degreasing agent – 50 g/L

   Temperature – 70°C

   Dipping time – 5 to 10 min

3. **Etching/Satinizing**: these two treatments 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, mostly if a coloring step follows the anodizing one [28]. Satin finish is thus mostly pursued for architectural components, where superior decorative qualities are required.

   A typical formulation of both baths is shown hereafter [27]:

   Free soda – 50 to 120 g/L

   Dissolved aluminum – 70 to 150 g/L

Additives – 10 to 30 g/L

Temperature – 50 to 70°C

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 *(2.6)*.

$$2Al_{(s)} + 2NaOH_{(aq)} + 2H_2O_{(l)} \rightarrow 2NaAlO_{2_{(aq)}} + 3H_{2_{(g)}} \tag{2.6}$$

This is a simplified reaction but it well describes what happens. Despite the appearance it is correspondent to the Bayer process one (digestion stage), by which aluminum hydroxides and oxide hydroxides are extracted from bauxite ores (indeed it is quite probable the presence in solution of the ion $Al(OH)_4^-$ in this situation as well).

The quantity of dissolved aluminum certainly varies accordingly with the process parameter, but it can be roughly estimated in 5 mg/dm$^2$/min [29]. Another estimative tells that 2% in weight of the treated aluminum is leached in the etching step [16]. A further one states that around 5% in weight of the inlet material is leached away [30].

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 *(2.7)*:

$$NaAlO_{2_{(aq)}} + 2H_2O_{(l)} \rightarrow Al(OH)_{3_{(s)}} + NaOH_{(aq)} \tag{2.7}$$

This reaction corresponds to the Bayer one (precipitation stage).

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 (super-saturation conditions, see C*hapter 3* of this work for details). 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, continue additions of caustic soda must be guaranteed. Moreover a certain degree of treatment solution's dragging out is pursued for keeping the sodium aluminate concentration within the proper range. This kind of maintenance of the treatment solution for spreading its life can be carried until the bath is totally saturated and it has to be almost completely discarded and restored in order to assure a proper treatment. In fact, an old bath made by a viscous exhausted solution would probably lead to differentiate attack of the treated substrates, and to defects such as stains and drops [29, 31].

Beside the caustic soda, specific additives that help avoiding the aluminum trihydroxide precipitation are steadily added. These additives are complexing (chelating) agents which help stabilizing the aluminum in solution, thus decreasing its supersaturation level. Chelants, according to “ASTM-A-380”, are "*chemicals that form soluble, complex molecules with certain metal ions, inactivating the ions so that they cannot normally react with other elements or ions to produce precipitates or scale.*" The most common complexing agents are cyanides, polyphosphates, amines, citric acid, tartaric acid, gluconic acid, ammonia, NTA, EDTA, Quadrol and sodium gluconate.

In the past chelating agent EDTA was the chief chelant in the anodizing field, but because of its persistency in the environment, a new regulation on wastewater discharge imposed its substitution with highly biodegradable compounds.

Nowadays the most spread complexing agent is sodium gluconate, $NaC_6H_{11}O_7$ (*Figure 2.8*), the sodium salt of gluconic acid, which in a comparative study has shown to be the strongest chelating agent, especially in alkaline solutions, meanwhile being non corrosive, non toxic (it is also widely used in foodstuffs) and readily biodegradable (98% after 2 days) [32].

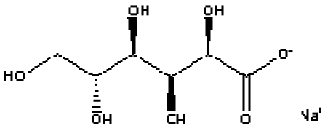


Figure 2.8 – Sodium gluconate structural formula [http://www.wuzhouchem.com/cataloged/WWP/sequestrant/sodium_gluconate.htm accessed on 10th of July 2010].

4. **Neutralization**: the aluminum material is immersed in the neutralization bath which eliminates any residual alkalinity, not to damage the following anodic oxidation bath, and eliminates any residual films on the material. In the past this bath contained a large amount of nitric acid, which nowadays is avoided because of its resistance to regular chemical-physical treatment, being almost entirely substituted by sulphuric acid. A typical formulation of the neutralization bath is as follow [27]:

    Sulphuric acid – 150 g/L

    Nitric acid – 50 g/L

    Additives – 20 to 30 g/L

    Temperature – ambient

    Dipping time – 2 to 5 min

5. **Anodizing**: aluminum is normally (90% of cases) anodized in sulphuric acid electrolyte. For special applications, aluminum may be anodized in many different types of process solution: phosphoric acid, sulphuric/oxalic acids, sulphuric/salicylic acids and chromic acid electrolytes. A wide variety of current forms and wave shapes may be used for the process, depending on the solution selected and the purpose of the anodic film. Direct current (DC), alternating current (AC), and DC with superimposed AC are all used in various processes. The workpiece or substrate to be treated is made anodic. During the anodizing process the negatively charged anion migrates to the anode where it is discharged with a loss of one or more electrons. The metal reacts with the oxygen of the anion and a layer of oxide forms on the surface [16].

   The main process parameters are [16, 27, 29]:

   Sulphuric acid concentration – 165 to 210 g/L

   Temperature – 20 ± 5 °C

   Voltage – 17 to 22 V

   Current density – 1.4 to 1.8 A/dm$^2$

   Dipping time – 1 to 60 min

   Dissolved aluminum – below 20 g/L

   Aluminum is partially dissolved during the oxide layer formation, and its concentration must be kept low (better in between 4 and 10 g/L) because a high one has a negative effect on the final surface appearance.

6. **Coloring**: the anodic oxide layer has got a porous structure, which is well suited for tinting. Normally coloring methods are identified as ‘dip dyeing’, ‘electrolytic dyeing’ or ‘two-stage color anodizing’, ‘self-coloring process’, or ‘integral color process’.

7. **Sealing**: in any case, the oxide layer’s porous structure has to be sealed. This is done for the aluminum to maintain over time its aesthetic and its corrosion resistance. The currently used sealing processes are hydration and impregnation.

8. **Rinsing**: this is not the last step in an anodizing line, but being an activity carried out after nearly all process steps it is now presented. Rinsing is a sort of cleaning step, necessary in order to prevent cross-contamination of process solutions and to ensure there will be no deterioration of the substrate surface because of residual chemicals.

*Figure 2.9* helps visualizing the sequential of phases the workpieces go through during the anodizing finishing treatment.

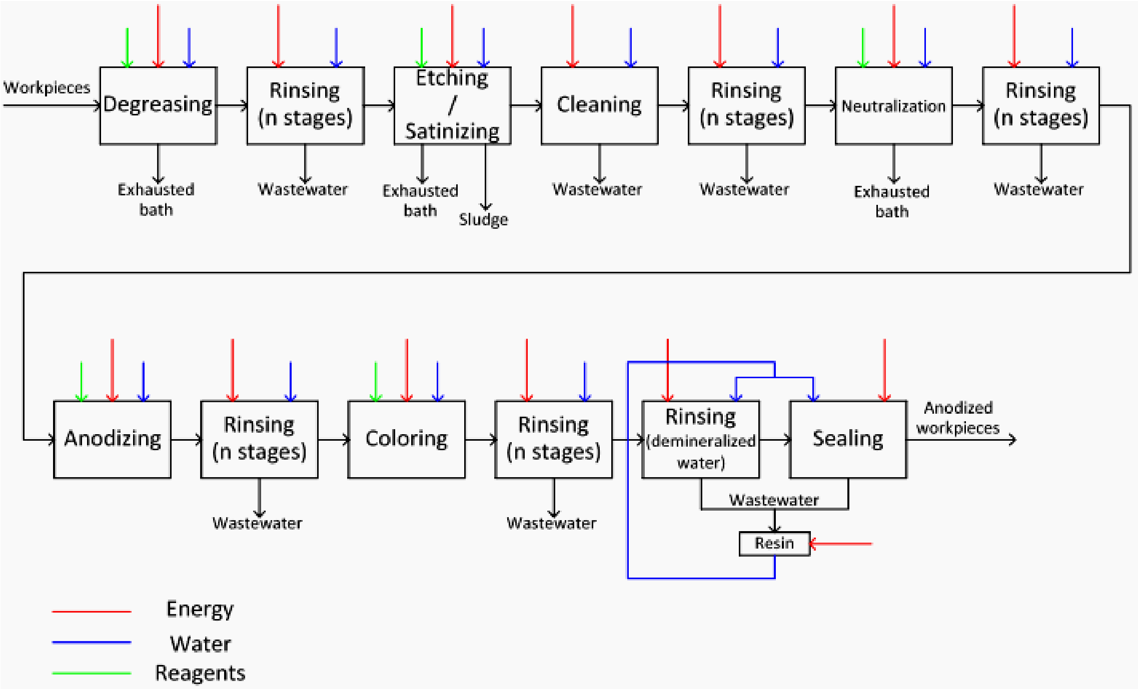


Figure 2.9 – Typical anodizing line layout.

The reason for indicating "n stages" in *Figure 2.9* is that rinsing is quite variable in its arrangement. By the way, a number of 2-3 steps for each rinsing operation represents a common choice.

### 2.2.3 End-of-Pipe Treatment in the Anodizing Industry

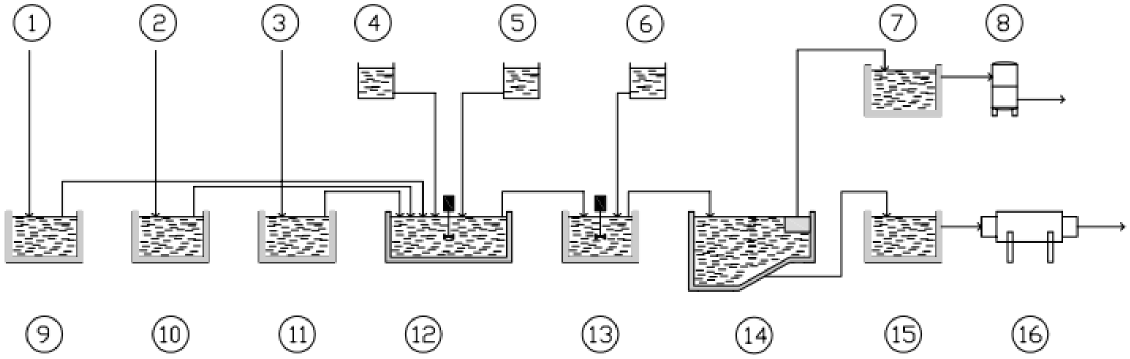
Anodizing wastewater is characterized by a number of parameters which do not respect the actual regulation on wastewater discharge, thus it has to be treated with an end-of-pipe kind of plant. These parameters are generally the pH and the content in some substances, mainly metals and organics. The treating process does not present particular difficulties, consisting in the pH adjustment followed by the precipitation and separation of polluters.

Nowadays, the main treatment systems are:

- chemical-physical treatment with settling;
- chemical treatment with ion-exchange resins.

The best performances are being achieved with the first system, which has shown to be less expensive, easier to run, reliable and with a steady yield.

A common chemical-physical treatment plant is represented with its main components in *Figure 2.10*:



1) Rinsing water
2) Acid wastewater
3) Alkaline wastewater
4) Caustic soda tank (aqueous solution with 30 % of soda)
5) Sulphuric acid tank (aqueous solution with 50 % of acid)
6) Flocculating agent tank (polyelectrolyte)
7) Basin with water after treatment and settling
8) Sand and active carbon filter
9) Rinsing water collecting basin
10) Acid wastewater collecting basin
11) Alkaline wastewater collecting basin
12) pH adjusting basin
13) Flocculation basin
14) Settling basin
15) Sludge storing basin
16) Filter-press or centrifugal filter

Figure 2.10 – Main features of a chemical-physical wastewater treatment plant [29].

Rinsing water is collected in a committed basin from which, together with the constant addition of acid and alkaline exhausted solutions, it is sent to the pH adjustment basin. By means of a measuring probe, which automatically withdraws acid and/or alkaline solution from their storing tanks, the water's

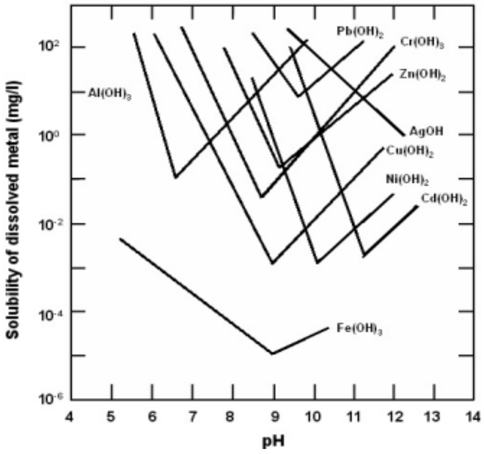


Figure 2.11 – Solubility variation of dissolved metals with pH [16].

pH is controlled to keep metals as insoluble as possible. As the transition metals are amphoteric, they show a minimum solubility at a certain pH, as shown in *Figure 2.11*. Aluminum minimum solubility happens at neutral pH, therefore in the neutralization step all the conditions for aluminum trihydroxide nucleation and precipitation are set. The neutralized water passes in a flocculation basin, in which a flocculation agent (polyelectrolyte) is added for enhancing the phenomenon. A settling tank for the deposition of solid compounds immediately follows. Treated water overflows from the top of the tank and is stored in another basin, before passing in a double layer filter (filled with sand and active carbon) and being discharged or recycled in the process. Water can be recycled up to 70% in order to avoid an excess of alkalinity within the process line. The sludge deposited in the settling tank passes through a filter-press or a centrifuge, for the solid-liquid separation. The liquid is then sent back in the treatment cycle, while the remaining sludge is stored and periodically landfilled.

The sludge initially contains a high percentage of water, around 95%, which can be reduced to 75% in the filtration step [16 - 18]. This is of course advantageous because it deeply reduces the volume and the weight of solid wastes to be transported and disposed in specific industrial landfills. The main solid components of the sludge are metal hydroxides and sulphates, among which aluminum ones stands out as the chief ones.

The quantity of sludge produced can vary within a broad range, and it greatly depends on the quantity of material that goes through the etching and/or satinizing steps. An estimative is that every 10 working hours, 3 kg of solid material (5 kg of filter-pressed sludge), are obtained per each 1,000 Ampere installed [29]. Another rough estimative can be made considering that the etching/satinizing steps are the main sludge generators within the anodizing process, being responsible for 80 to 90% of the total mud's mass [16]. As previously said, the leached Al is in the range of 2 – 5% in weight of the etched material [16, 30]. Thus considering reliable a half way, that is 3.5%, and with a calculus based on 1 ton of anodized material, it results that:

- 35 kg of Al are leached
- 101 kg of $Al(OH)_3$ are formed
- 2,020 kg of wet sludge are generated (considering a 5% solid percentage in weight)
- 404 kg of dry sludge are finally obtained after the wet sludge is filter pressed or centrifuged (considering a 25% final solid percentage in weight)

Assuming that etching and/or satinizing are responsible for the 85% total sludge, it results that around 475 kg of mud have to be landfilled for each 1 ton of anodized aluminum.

In [33] it is stated that 100,000 tons of anodizing mud are generated each year in Europe.

### 2.2.4 Environmental Concerns Risen by the Anodizing Industry

Anodizing certainly brings beneficial effects to the environment by protecting the metal made items from corrosion and thus stretching their life. On the other hand, anodizing is historically recognized as a highly polluting activity. Of course this is less true since environmental regulation required mandatory end-of-pipe treatment for the anodizing installation, but still several instances remain unsolved.

The main concerns anodizing industry brings for the environment are:

- the emission of pollutants into the water mean;
- the production of a huge amount of solid wastes, namely wastewater neutralization sludge;
- the high consume of energy;
- the high use of water;
- the inefficient use of raw materials, mainly caustic soda in the etching/satinizing step and sulphuric acid in the anodizing one;
- the emissions to air.

Among these, emissions to air are by far the less significant ones. Caustic and acid fumes are released that can be hazardous mostly to employees in the plant, because long-term exposure causes permanent health problems if precautions are not taken. Regulation requires local exhaust ventilation to be installed; that removes the fumes at the source point and a scrubber provides additional cleaning before release into the atmosphere. Scrubbing water retains the air polluters and is thus treated in the wastewater plant together with the other wastewater streams.

An anodizing plant requires high amounts of electric and thermal energy for the electrochemical processes working, the heating and cooling of treatment baths, and for the functioning of accessory equipment (they can absorb up to 30% of the total electrical energy). Electric energy is mainly used by the oxidation step and the eventual electrolytic dyeing one. According with [29] their consume settles around 5,700 Wh/m$^2$. Thermal energy consume is more difficult to estimate but certainly represents an important share. Energy consume is strictly bonded with the quantity of treated aluminum and the equipment efficiency.

Still, anodizing industry is water-based and besides using water in big quantities, it generates significant masses of polluted effluents. These effluents are polluted because:

- a non neutral pH;
- the presence of relevant quantities of metals in solution;
- a variety of organic contaminants.

The main use of water happens in the rinsing steps, but an important share is also used for preparing treatment solutions and cooling. Therefore rinsing water is a major and steady vector of pollution, even though an exhausted bath solution surely has the highest polluters concentration (water used in cooling is supposed not to get contaminated). Rinsing water is polluted because of the carryover of concentrate process baths on the workpieces, an event named drag-out.

Wastewater streams pH is far from being neutral and could damage sewage systems besides being incompatible with the receiving water body. Acidity and alkalinity result from the extensive use of sulphuric acid and caustic soda in several phases of the whole process. They are purchased chemicals that will not be incorporated in the finished goods, thus their use efficiency is quite low [19].

Organic compounds such as complexing agents and polyelectrolyte can be found in solution. These are usually added along the process for pursuing a number of goals. Troubles arise because they retain metals too strongly and for too long, and carry them all through the end-of-pipe treatment system into the sewage and aquatic ones. Furthermore, organic compounds, such as EDTA, can be difficult to be biologically decomposed, and by reaching a wild watercourse they can remobilize metals from sediment with high metals loads. The use of biodegradable chelating agents and additives is the only solution; still, they decrease the wastewater plant efficiency by making difficult the metals precipitation and separation.

Metals in wastewater results mainly from the etching/satinizing stages and in a minor way from the anodizing phase itself. The chief element by far is aluminum, but other elements can be found, such as silicon, iron, copper, manganese, magnesium, chrome, zinc and titanium (their presence and concentrations are related to the composition of anodized alloys). Metals are conservative materials, that is, they cannot be created or destroyed: they are neither created nor destroyed in the treatment processes or during wastewater treatment. Their form may be changed and/or managed so they cannot readily access environmental pathways but their disposal means that the metals still remain in part of the environment. Therefore, during the end-of-pipe wastewater treatment the metals concern is not really solved, because they are moved from the water medium to the land one, in the form of sludge.

Sludge resulting from the wastewater treatment plants is in present-days the main environmental concern that the anodizing industry places in those countries among which the end-of-pipe treatment of effluents is mandatory by law. As it had been said before, the masses produced are quite relevant and the mud is very persistent in the environment. Sludge from the anodizing process is generally classified as non-hazardous [33] (it is identified with the code “19 08 04” according with the European Waste Catalogue approved in [34]), nevertheless its transport, handling and disposal costs are very high, placing a serious problem to several SMEs’ activity. The handling and disposal cost of 1 ton of sludge sets around 180 euro [17], and it is increasing as time goes by. A cost estimative for the handling and disposal of anodizing sludge for an average installation is presented hereafter by using data from the Italian scenario [18]. In year 2002 in Italy the quantity of anodized aluminum set in 200,000 tons (60,000 for architecture and 140,000 for other industries). AITAL (Associazione Italiana Trattamenti superficiali Alluminio) estimates that around 180 anodizing enterprises are operating in

Italy. Assuming that for each 1 ton of anodized aluminum, 475 kg of sludge is generated, as calculated before, it results that on average each installation produced around 528 tons of sludge per year, with a cost of handling and disposal of 95,000 Euro. The estimative does not consider the operational cost of the end-of-pipe plant and its investment depreciation charge.

In the literature several recycling methods for the aluminum rich anodizing sludge can be found. [2] refers its use as phosphates reducing agent in municipal wastewater treatment in Swiss, while for [35] it can be used as flocculating agent in wastewater plants. The latter paper reports that the mud could be incorporated in matrix materials such as concrete, glass and ceramics, but that the resulting properties would drop. It also states that it has been suggested its use as the main compound in alumina, mullite, mullite-alumina and cordierite refractory bodies. In [33] mullite and cordierite based bodies are produced using Al-rich anodizing mud and diatomite. The resulting product could be used in low grade refractory and electrical insulating bodies.

Nevertheless, even if the anodizing mud could find alternative ways than landfilling, these are far from absorbing the whole production. The best solution would be the use in the anodizing line of systems focused on the reduction of the anodizing mud generation.

### 2.2.5 Best Available Techniques in Anodizing

BATs are defined and placed within the terms of the IPPC Directive in *point 1.1* of this work. At the same point the environmental management hierarchy introduced by IPPC is shown. Prevention, reuse and recycling within a production line are the first choices, to the detriment of end-of-pipe treatment and landfilling.

Still, it had been shown in *point 2.2.3* that the state-of-the-art in environmental managing within the anodizing industry is represented by an end-of-pipe kind of treatment.

The mismatch is pointed out by the involvement of the anodizing industry, together with the surface treatment one, in the first IPPC Directive (see *point 1.2* of the present work). Anodizing industry falls under this Law for the amount of emissions generated and for the high emission prevention potential.

Because an end-of-pipe treatment is costly for the small- and medium-sized anodizing installations, and the cost and liability of residuals disposal have increased year by year, management and production personnel may be more willing to consider production process modifications to reduce the amount of materials lost to waste. Prevention, reuse and recycling can be achieved by implementing a number of BATs that are briefly introduced in the following (a better panoramic on anodizing BATs can be found in [16]):

- Drag-out reduction: the dragging out can be reduced by a set of expedients such as placing the workpieces with the right spatial orientation in order to reduce the retention of treatment solutions, increasing the drainage time above each process tank, chancing the design of the components or provide for draining holes (in accordance with the client), decreasing of the viscosity of the treatment solutions, etc..

- Overdosage reduction: loss of chemicals because of overdosage can be decreased by implementing integrated automatic dosage systems, based on process chemicals concentrations monitoring carried by probes.
- Chemicals substitution: it is BAT to substitute polluting chemicals for less polluter ones. Examples are the substitution of EDTA in favor of gluconic acid based complexing agents, which are more biodegradable, and the substitution of nitric acid in favor of the sulphuric one, which can be more profitably treated.
- Adoption of multiple stage rinsing: it is very suitable to achieve a high rinsing rate with a small amount of rinsing water.

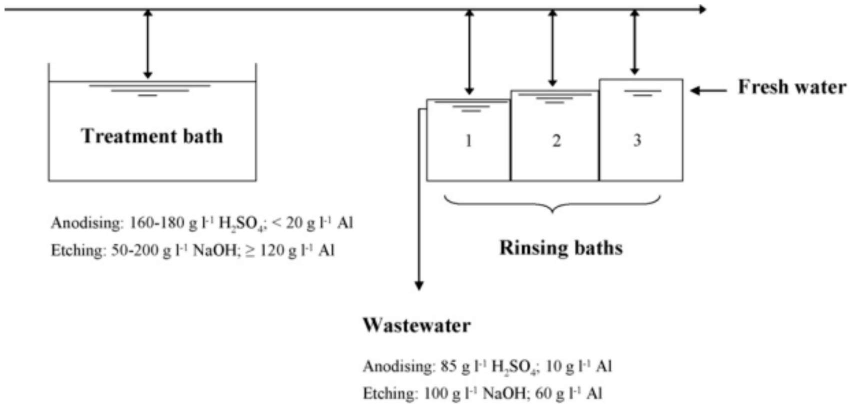


Figure 2.12 – Simplified scheme of a typical multi-stage counter-current rinsing system [35].

- Regeneration and reuse/recycling of rinsing water: it can be done by applying ion exchange and reverse osmosis technologies. It can lead to savings in water consumption and will reduce to amount of waste water to be treated in the end-of-pipe plant, reducing the waste water treatment costs for capital investment, energy usage and chemicals. However, this has to be offset by the cost of the regeneration equipment and the power and chemicals that this may incur [16].
- Process solution maintenance and closing the loop: proper control of bath operating critical parameters results in better quality of the final product as well as longer bath life. Contaminants which affect the life of the treatment baths accumulate in process solutions. Therefore instead of continue or periodical discards, batch or steady state regeneration can be implemented. Generally a regeneration technique lengthens the life of treatment baths and strongly diminishes its discards and the quantities of materials losses, thus decreasing the generation of sludge in the wastewater plant. After the regeneration step a reuse/recycling of chemicals within the process might be possible, allowing to close the loop of materials. Outputs of the regeneration could also not correspond to the treatment inputs, but they could

be recycled in other phases within the finishing process and/or in other industrial activities. A number of arrangements are possible.

General limits for the closed-loop are the operative solution concentration range to be maintained, the amount of resources and energies used to recover and reuse the input, and limits to the steady working of the technique.

A number of technologies can be implemented, accordingly with the specific instance: solutions filtration, electrodialysis, retardation (acid resin sorption), etc.

In the anodizing finishing path three technologies among the others could have a strong impact on the enterprise, from an economical and environmental perspective. These are the regeneration of the anodizing bath by electrodialysis or acid resin sorption and the “caustic etch recovery”.

Electrodialysis is an electrochemical process which allows maintaining the concentrations of chemicals in the anodizing bath within the opportune range (see *point 2.2.2* in the present work). The bath solution passes through an electrochemical cell, with a membrane to separate two solutions. $Al^{3+}$ ions pass through the membrane because of an applied voltage, and combine with $OH^-$ to form aluminum hydroxide. On the other side of the membrane sulphuric ions combine with $H^+$ to regenerate sulphuric acid. The aluminum trihydroxide sludge is filtered and separated, while the suphuric acid is recycled in the anodizing bath. Acid resin sorption has the same effect of keeping the opportune sulphuric acid concentration in the anodizing bath than electrodialysis, while producing a solution concentrated in aluminum sulphate as a byproduct [2, 36]. This technologies allow to:

- reduce the quantity of anodizing wastewater stream;
- reduce the amount of sludge produced in the wastewater treatment plant;
- reduce the purchase of sulphuric acid;
- obtain a marketable compound such as aluminum trihydroxide as a secondary output (only electrodialysis).

Being the “caustic etch recovery” the technique studied in this work (see *point 1.3*) it will be introduced in *Chapter 3*.

# CHAPTER 3

# CAUSTIC ETCH RECOVERY

## 3.1 General Considerations

It is stated along the previous chapters that the wastewater treatment sludge is the main sustainability problem that anodizing brings to society. The amount of mud produced is huge, the cost for its transport, handling and landfilling is high and increasing, and the environmental law is pressing for it to find other ways apart from final disposal.

Sludge is mainly generated in the wastewater treatment system in order to separate the metals from the aqueous solvent. The chief metal is aluminum by far, brought into solution during the etching/satinizing stage, and in a minor measure during the anodizing one.

On the one hand etching/satinizing are responsible for the 80 to 90% of the final sludge mass. On the other one, they do bring Al into the caustic solution but they do not carry it till the wastewater plant. Aluminum vector is the water of the rinsing stages that come after the etching/satinizing phase. Rinsing water after etching/satinizing is therefore the main polluted effluent generated by the anodizing industry. [10, 35].

It happens as a result of the caustic solution passage between the treatment bath and the rinsing water. This drag-out is accounted as positive by the system operators, who try to enhance it till a certain point [2, 10, 30]. It all appears as a paradox on a first sight: it is said in *point 2.2.5* of this work that the drag-out phenomenon causes losses of materials and spreading of pollutants and it is BAT to avoid it. In spite of this, anodizers pursuit this particular drag-out because it helps the etching/satinizing solution's maintenance and its life elongation, as it is seen in *point 2.2.2.* In fact, complexant agents are added to the etching/satinizing baths not only to stabilize the sodium aluminate, as previously said, but also because they thicken the caustic solution, and therefore increase the quantity of liquid that is dragged-out by sticking onto the workpieces' surface [2, 10, 30].

Together with the aluminum the drag-out depletes the etching/satinizing bath from its caustic soda content, which has to be replaced and thus represents one of the main reagents expenses in the anodizing line.

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) [2, 30, 37, 38]. The surface treatment sector's BREF refers to it as "caustic etch recovery".

It consists in the regeneration of the etching/satinizing solution by its continue recirculation between the etching/satinizing tank and a crystallizer (see *Figure 3.1* for a commercial example of crystallizer). Within this latter tank a reaction 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 [39]:

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

Figure 3.1 – Eco-Tec's caustic etch recovery system [39].

On a first sight it seems strange that this technique would reduce in such a way the generation of anodizing wastewater treatment sludge, being the rinsing water the major responsible for its production, as related above. Nevertheless, with such a technique there would be no need for the use of the drag-out as a flywheel of the chemicals concentration within the etching/satinizing bath. Therefore a drag-out control can be implemented, which would lead to its reduction and to a minor contamination of the rinsing water, that would in turn decrease the amount of sludge produced in the wastewater plant. In [2] it is stated that a 90% reduction of the annual drag-out can be achieved by the use of the technique and the consequents drag-out control measures (see *point 2.2.2* of this work for further details on drag-out control). The regeneration process would also decrease by itself the quantities dragged-out by decreasing the concentrations of aluminum and chelating agents in solution, and in turn the viscosity. A similar regeneration process applied directly to the rinsing water would face added difficulties because a lower pollutants concentrations means lower driving force for the process to take place, according to principles that are introduced in *point 3.2* of this work.

Several configurations are possible for implementing the caustic etch recovery. The reared can find some of them in [2, 10, 40, 41, 42, 43]. The basic caustic etch recovery layout is shown in *Figure 3.2*:

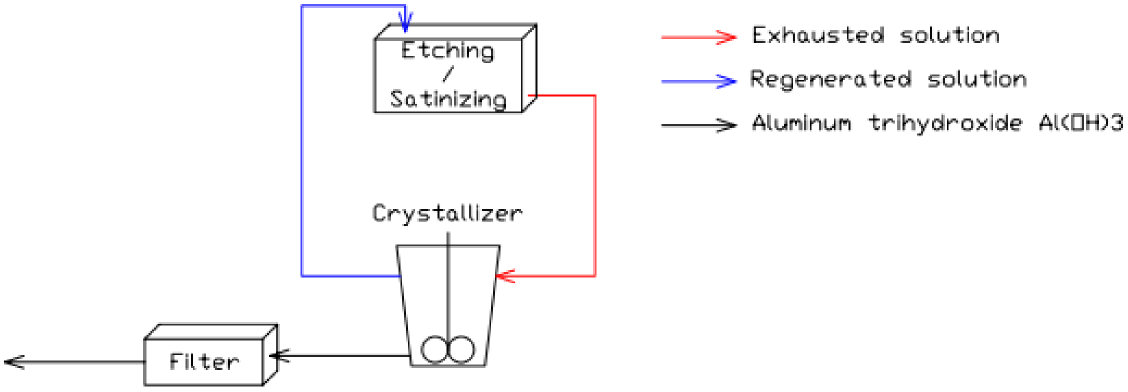


Figure 3.2 – Basic caustic etch recovery layout.

In the paper [37] H. Verheul scanned the European SMEs sector in order to find reasons for the slow diffusion of cleaner technologies. It states that SMEs are largely dependent on other organizations, namely suppliers, customers, and consultants, in their decision to adopt cleaner techs. Other reasons have been referred in *point 1.2* of this work. In particular it studied why caustic etch recovery hasn't been adopted by any installation in the Dutch anodizing sector yet, and found out that customers greatly influence anodizers moves. Caustic etch recovery is thought to alter the final product aesthetical properties by modifying chemicals concentrations in the etching/satinizing bath. In fact dissolved aluminum decreases and this is recognized as a parameter which greatly influences the matte finish. Anodizers are therefore reluctant to apply the technology, being somehow worried to lose their customers, in a sector such as the anodizing one, which is dominated by the demand. This is a peculiarly European barrier for the adoption of this technology: in the U.S. aesthetical quality requests for aluminum anodized products (mainly for the architectural market) are lower and the technology is therefore much more appreciated.

## 3.2 Principles of the Method

Caustic etch recovery technique is grounded on the same "Bayer reaction" at the base of the primary aluminum production. Having a caustic solution made of sodium aluminate and providing the required conditions for it to hydrolyze, caustic soda and aluminum trihydroxide are generated, as shown by equation *(3.1)*:

$$NaAlO_{2(aq)} + 2H_2O_{(l)} \rightarrow Al(OH)_{3(s)} + NaOH_{(aq)} \qquad (3.1)$$

Caustic soda is thus recycled in the etching/satinizing bath while aluminum trihydroxide could find its own way in the market. The technique is indeed very simple because it lets happen in a committed stage what would naturally happen in the etching/satinizing tank if the composition of the treating solution was not controlled. On the other hand the Bayer reaction is recognized as inherently slow, difficult to control and optimize, and still far from being understood in detail [44, 45]. The International

Aluminium Institute (IAI) recognized the further investigation of the Bayer reaction as a measure that could have a high potential payoff [46].

Anodizing caustic etch liquor and Bayer liquor from the alumina production process (after the digestion step) are of similar composition. They are both made by an aqueous solution of sodium aluminate and free caustic soda and they both contain organic compounds, which are usually considered impurities in the Bayer liquor and additives in the aluminum etching. This is the reason why in this work the reader can constantly find references to the Bayer process. Particularly in *point 3.2.2*, in which researches on the Bayer reaction related with the caustic etch recovery are reviewed, the author found useful to involve also results from the Bayer process field, which because of its major dimension are the great majority in the literature.

### 3.2.1 Generic on Crystallization from Solutions

The Bayer reaction is identified as a “crystallization from solution” type of process, because “only one component precipitates in a pure state from a binary, real liquid mixture” [47]. The most important process parameter according to Mersmann [47] is supersaturation, that is the difference between the actual concentration and the equilibrium concentration of the liquid, at the actual temperature. Supersaturation happens when the fluid phase contains more units of a certain chemical specie than its saturation concentration. If the solution is liquid, the saturation concentration often depends on temperature and only slightly on pressure. Crystallization processes can take place only in supersaturated phases, and the crystallization rate is often determined by the degree of supersaturation, while heat transfer is not the decisive phenomenon such as in crystallization from the melting. The degree of supersaturation is determined by the flows of materials and energies, and by crystallization kinetics, such as nucleation and growth, which are in turn mainly controlled by mass transfer.

Crystals are created when nuclei form and can grow. Supersaturation is a prerequisite for nucleation and crystal growth and can be obtained by a change in temperature (solubility usually increases with temperature), by evaporating the solvent, or by adding a reaction partner.

A nucleation that takes place in the absence of solution-own crystals is called primary nucleation (homogeneous or heterogeneous) and requires a specific degree of supersaturation, called metastable supersaturation. However, a very small degree of supersaturation is required for nucleation when solution-own crystals exist, and the nucleation is said to be secondary. Solution-own crystals can take the form of added seed crystals.

According to the classic theory on homogeneous nucleation, nuclei are formed by random addition of units: if supersaturation is sufficiently high, the probability for elementary units joining is higher and the possibility for a cluster to reach the critical nuclei diameter would be higher as well. Heterogeneous nucleation requires less work and the process is faster.

Cristal growth in a supersaturated solution is very complex and has not been well understood up to now. The main influencing steps seem to be the diffusion and the reaction ones. According to Mersmann a crystal surface grows in such a way that units are first transported by diffusion and convection and then built into the surface of the crystal by integration reaction, being supersaturation the driving force for this last phase.

### 3.2.2 Bayer Reaction State of the Art

A considerable effort has been done along the years by bauxite refining and alumina companies, academia, and research organizations to uncover the mechanisms behind the Bayer reaction, in order to control and optimize it. Despite this effort a full understanding has not yet been achieved, and contrasting results can be found in the literature [48].

Right conditions for the reaction to occur are induced by controlling the degree of actual supersaturation, which is the most important parameter in a crystallization process [45, 47]. As said in *point 3.2.1* the supersaturation degree can be changed with a temperature variation, with concentration induced by evaporation of the solvent, and with addition of a drowning-out compound or a reacting partner. Normal practice in the alumina industry is to cool the solution that comes from the bauxite digester to induce the aluminum precipitation, that is the sodium aluminate increases its solubility with temperature. Nonetheless it seems that cooling fasten the reaction till a certain point, and researchers still debate on the temperature that leads to the best results. It is stated that the temperature has a detrimental effect on the supersaturation degree [41, 45], but still highlight that it influences the solution viscosity as well, that is, a too low temperature depresses the mass transfer and lengthen the whole process. Therefore it seems that both supersaturation and diffusion control the crystallization. To increase the diffusion and contemporarily keep a high supersaturation degree the caustic liquor is usually cooled and stirred. Very few are known on the effect of the stirring intensity, mainly because this parameter is difficult to be uniquely defined, but an intense stirring is said to be positive [41]. Secondary nucleation requires far less work than primary one. Because of this gibbsite seeds are introduced into the crystallizer and act as preferential nucleation sites. The seed quantity added is a factor that influences the reaction rate and the final crystallization yield. It is usually stated that the effect of seed concentration is positive [49]. The seed quality effect, namely its size distribution and morphology, has also been evaluated. In a study of Zeng et al. [48] the gibbsite seed is treated in boiling distilled water for a certain time in order to activate it, and the results in terms of precipitation rate and final recovery yield are encouraging. Moreover mechanical activation can be implemented: through grinding the seed specific surface increases and more defects that can work as nucleation preferred sites appear on the particles surface. Zhang at al. [45] also stated that the stirrer can act as a grinder on seed particles, thus a more intense stirring is considered to have a positive effect. The addition of reacting partners to intensify precipitation has widely been studied. Barakat et al. [50] use hydrated lime, dry lime and hydrogen peroxide as precipitating agents to hydrolyze the sodium aluminate contained in a rinsing effluent. Aluminum recovery yield after a very short time are claimed to be very high. The addition of $NaHCO_3$ and the use of a high temperature lead to the precipitation of dawsonite, $NaAl(OH)_2CO_3$, an appreciated marketable material used as fire retardant, antacids, and also in the preparation of ceramic materials [38]. The paper also refers to other works in which zeolites are sintered by adding silicon to the sodium aluminate solution. Drowning-out compounds have also been added to the solution for decreasing the stability of the system. Zang et al. [45] showed that methanol has a relevant effect in reducing the precipitation induction time and increasing the recovery yield. By looking at the Bayer reaction another important parameter that influences the system is the quantity of water. By diluting the solution the equilibrium should shift toward the right that is toward the products. On the other hand the minor concentration of solution components decreases the driving force for the reaction to take place and makes mass transfer phenomenon more difficult. The water addition influence was studied by Ribeiro et al. [51] and the authors find it to be a significant factor, with positive effect on aluminum recovery yield. Precipitation intensification methods such as magnetic field, laser [52] and ultrasonic sound irradiation [53] have been implemented and have shown positive results. Some efforts have also been spent to investigate the crystallization of boehmite, AlO(OH), instead of gibbsite, by using boehmite seeds and altering the other process parameters (mainly temperature), but the process is still far from being optimized [54, 55].

### 3.2.3 Organics' Effect on the Bayer Reaction

The evolution of the Bayer reaction in caustic sodium aluminate solution has been found to be affected by the presence of organic compounds. In the Bayer process many organics build up as a result of the recirculation of solution through the digestion and precipitation stages. They are the alkaline-degradation product of the Bauxite ore's organic fraction. In both the Bayer process and the etching/satinizing stage (anodizing line) organic chelating agents are also added to avoid the aluminum trihydroxide precipitation within the inappropriate tank [56].

The common feature of these compounds is the presence in their structure of adjacent hydroxyl groups [57]. Among the organics which are known to affect the Bayer reaction there are polyols, in particular alditols, and hydroxycarboxylates.

Their action consist in the inhibition of the gibbsite precipitation by decreasing its crystallization rate and the final process yield, and by lengthening the crystallization induction period. They are also found to affect the quality of the final product, namely its particle size distribution, impurity levels (soda content), and color. They are thought to act in the whole three processes that are involved in gibbsite precipitation from sodium aluminate solutions, that is secondary nucleation, agglomeration and ordered growth (it consist in the slow deposition of new gibbsite on well formed particles). Particularly, researchers believe they strongly inhibit the secondary nucleation phase, that is the growth on seeds' surface of dendrites which then brake out and form new nuclei, that is considered to be the core of seeded gibbsite nucleation [56, 58].

Their action mechanism seems to involve the very fast formation of bonds between the organics' hydroxyl groups and actively growing sites on seed's surface, which are therefore inhibited for further growth. The chain length, the number of hydroxyl groups and their stereochemistry are believed to be important for the poisoning effect. It has been also found that a very low concentration of organics is enough for poisoning the liquor, even with a strong seeding action [59]. Despite it, their effect increases with the concentration.

The presence of these organic compounds in solution represents a problem for both the alumina production industry and the "caustic etch recovery" effectiveness, because of the previously related effects on gibbsite precipitation [58, 60].

As referred in *point 2.2.2* of this work, sodium gluconate is the main organic chelating agent used in the etching/satinizing of aluminum nowadays. It has been found to be the strongest inhibitor of gibbsite crystallization in caustic sodium aluminate solutions, and all that has been previously said about organics' effect on the Bayer reaction is valid for this particular chemical.

## 3.3 Aluminum Hydroxides and Aluminas

The caustic etch recovery byproduct is aluminum trihydroxide, an inorganic compound that has its own applications and represents the starting point of numerous alumina chemical products.

The broad term alumina includes a large number of compounds having a wide variety of properties and applications. The main use of alumina is as raw material for the production of aluminum, though an increasing 10% of world production is finding applications in the chemicals fields. Uses includes ceramics, fillers, catalysts, adsorbents, refractories, and abrasives.

Industrial alumina chemicals can be divided into three classes: aluminum hydroxides, activated aluminas, and calcined aluminas.

### 3.3.1 Aluminum Hydroxides

A general classification of the various modifications of aluminum hydroxides is shown in *Figure 3.3*. Three trihydroxides, gibbsite, bayerite, and nordstrandite, together with two oxide-hydroxide, boehmite and diaspore, have been clearly defined. Besides, several other forms have been claimed, such as the gelatinous forms, but are still incompletely studied and described. They are almost totally produced by Bayer process, but sintering techniques are industrially applied for products that require them special properties.

Aluminum hydroxides are technically the most widely used and important members of the alumina chemicals family. A wide range of product is available for a large number of industrial applications. Besides being the raw material for metallurgical grade alumina production, for the production of activated and calcined aluminas, and of aluminum chemicals, important uses are as fillers in polymers, rubbers, and toothpastes, and as additive in the paper industry.

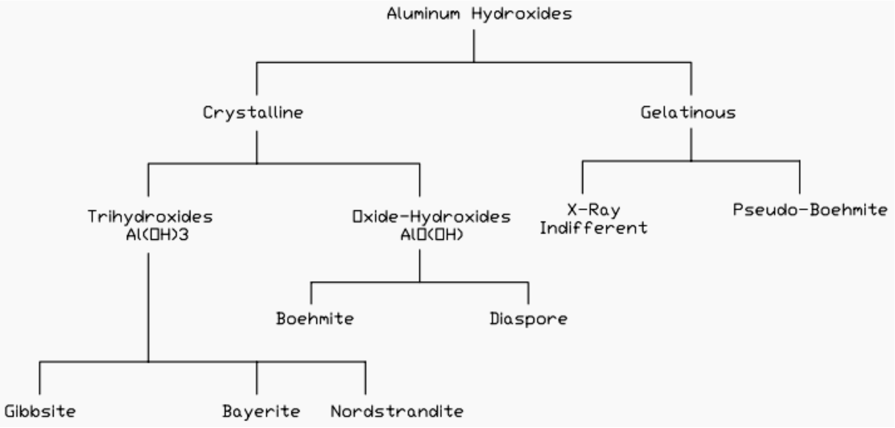


Figure 3.3 – Classification of aluminum hydroxides [61]

Their use as a filler is strongly related to their fire-retardant and smoke-suppressant properties. Aluminum hydroxide decomposes at 200°C to give alumina and release vapor by the reaction *(3.2)*:

$$2Al(OH)_3 \rightarrow Al_2O_3 + 3H_2O \tag{3.2}$$

This reaction is strongly endothermic. Thus, when a polymer containing aluminum hydroxide is heated, the aluminum hydroxide decomposes, acts as a heat sink, and slows the rates of temperature rise and of decomposition of the polymer.

Fine precipitated aluminum hydroxide having a uniform particle size of 1 micron is used in the paper industry both as a filler pigment and for coating applications. Aluminum hydroxide gives a coat of high brightness, opacity, and gloss, and at the same time grants high ink receptivity.

Aluminum hydroxides dissolves readily in strong acids and alkalis. For these reasons they are the preferred base raw material for the production of a large number of aluminum compounds of both commercial and laboratory significance. The following is a summary of some of the aluminum chemicals produced from aluminum hydroxide: aluminum sulfate and alums, aluminum fluoride, synthetic zeolites, sodium aluminate, alumina adsorbents and catalysts. Aluminum hydroxides are also used in the glass, ceramics and refractories, cosmetic and pharmaceutical industries.

### 3.3.2 Activated Aluminas

Activated aluminas are obtained by thermal dehydration of different aluminum hydroxides in the 250 - 800°C range. The dehydrated product is a porous material with a high surface area. The nature of the starting hydroxide and the thermal hystory of dehydration affect the final product properties. A wide range of aluminas is obtained by controlling the hydroxide preparation and its dehydration. Their properties are important factors for deciding their final application.

The dehydration sequence of the various aluminum aluminum hydroxides is shown in *Figure 3.4*:

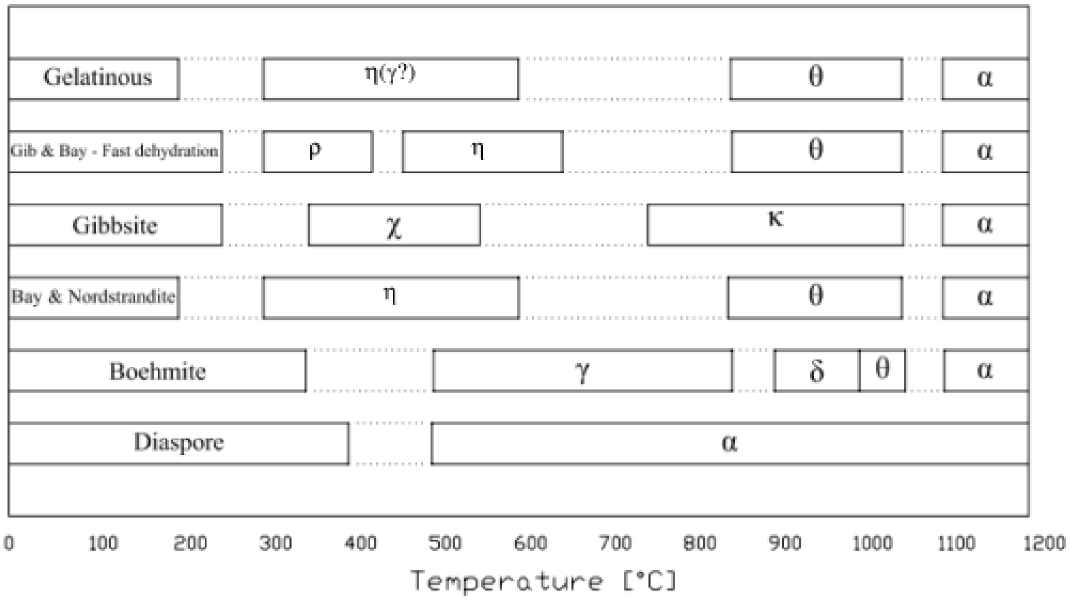


Figure 3.4– Dehydration sequence of aluminum hydroxides [61]

Activated aluminas principal uses are as drying agents, adsorbents, catalysts, and catalysts carriers. In the field of adsorption the high surface area and the chemical inertness are factors favouring its application. Important uses include gas and liquid drying, water purification, selective adsorption in the petroleum industry, and chromatographic separation processes. Alumina is used in many industrial catalytic processes both as a catalyst by itself and, to a greater extent, as a support for catalytically active components. In many instances catalytic uses of alumina take advantage of its heat resistance and inertness. Such applications include low surface area catalyst supports and as an inert bed for supporting the catalyst charge in catalytic reactor. Examples of commercial catalytic processes using alumina catalysts are alcohol dehydration and claus catalyst. Surface area is an important property of the support because catalytic rates depend to a large extent on the amount of available active surface. Another important property in catalytic processes is catalytic porosity and pore size distribution. Pore size is important to catalyst performance because it determines the accessibility of reactants to the active catalyst sites as well as catalyst stability, resistance to fouling and heat transfer. Examples of catalytic processes using alumina-supported catalysts are: chromia-alumina dehydrogenation catalyst, molybdenum-alumina hydrorefining catalyst and automotive exhaust catalyst [61].

### 3.3.3 Calcined Aluminas

Calcined aluminas, produced by calcinations of aluminum hydroxides at higher temperature than those for activated aluminas (about 1100℃). They are usually identified with corundum, $\alpha$-$Al_2O_3$ phase, that is the final product of thermal and hydrothermal decomposition of all aluminum hydroxides and the only stable aluminum oxide. Calcined aluminas are used in large quantities by the ceramic, refractory, and abrasive industries.

# CHAPTER 4

## 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.

Despite it, in the literature it is present only faint and not well founded information. It usually comes from cleaner technologies suppliers and guides, and registered patents. A source of indirect information is represented by the huge amount of material on the "Bayer process", that shares its basic principles with the caustic etch recovery. Few are the contributions from independent and academic organizations.

This work is meant to partially fill the hole and contribute to the spreading of knowledge on the caustic etch recovery.

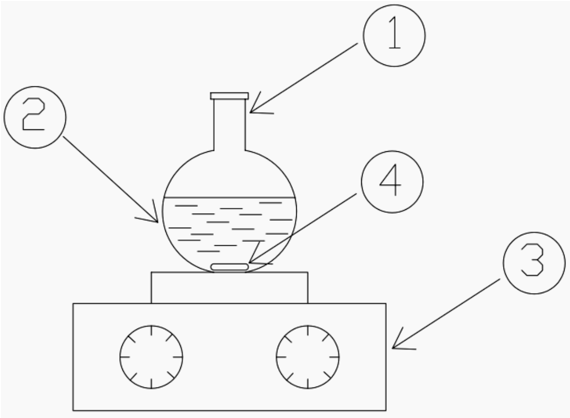
### 4.1 Materials and Methods

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 4.1*). System parameters which were thought to affect the process were set on different levels, according with the author experience and the literature review (see *Chapter 3* of this work for further details). Several series of trails were carried and each was planned according with the feedback of the previous ones.



1) Flat-bottom flask

2) Caustic etch solution

3) Magnetic stirrer

4) Stir bar (flea)

Figure 4.1 – Basic layout used in the caustic etch recovery laboratory tests

Every series of tests was made by a number of this basic system configurations, 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. On a second phase their influence was also investigated by structurally and morphologically characterizing the solid byproduct of the process.

Particles size distribution was measured by means of a laser diffraction instrument, the CILAS 920.

Dissolved aluminum and caustic soda concentrations were measured at certain time intervals by titration. All the tests of a series were sampled at the same time, and each sample was firstly filtered on a Whatman “42 ashless” filter paper for fine crystalline retention. The liquid fraction was then titrated, the method being explained in the following.

An arbitrary volume $V_A$ of filtered solution is sampled and placed in a erlenmeyer. A little demineralized water is added to make operations easier. 3-4 drops of phenolphthalein indicator (0,1% p/v in 70% v ethanol solution) are also mixed. A solution of HCl (for ex. 1 M or 2 M) is used to titrate. Titration is complete when the pink color of the sample disappears. The volume of HCl used, named $V_1$, titrate both the caustic soda and the dissolved aluminum, being that until neutral pH reactions *(4.1)* and *(4.2)* take place:

$$NaAlO_{2_{(aq)}} + HCl_{(aq)} + H_2O \rightarrow NaCl_{(aq)} + Al(OH)_{3_{(s)}} \tag{4.1}$$

$$NaOH_{(aq)} + HCl_{(aq)} \rightarrow NaCl_{(aq)} + H_2O \tag{4.2}$$

Each reaction is responsible respectively for the titrating volume $V_{1a}$ and $V_{1b}$, fractions of $V_1$ according with equation *(4.3)*:

$$V_1 = V_{1a} + V_{1b} \tag{4.3}$$

At neutral pH it is assumed that the reactions are complete, that is all the caustic soda and sodium aluminate have reacted.

Then the solution color turns back to pink as a variable quantity of sodium fluoride is placed in the erlenmeyer. HCl is dropped until the solution becomes transparent. Sodium fluoride is added again: if the color does not turn the titration is complete, otherwise one has to continue until the color does not change anymore. During this second part of the method aluminum fluoride is formed and OH$^-$ groups are liberated and titrated according with equations *(4.4)* and *(4.5)*:

$$Al(OH)_{3_{(s)}} + 3F^-_{(aq)} \rightarrow AlF_{3_{(s)}} + 3OH^-_{(aq)} \quad (4.4)$$

$$3HCl_{(aq)} + 3OH^-_{(aq)} \rightarrow 3Cl^-_{(aq)} + 3H_2O \quad (4.5)$$

It has to be observed that 3 moles of HCl titrate 1 mole of aluminum. Measured volume $V_2$ thus gives back the concentration of dissolved aluminum.

*Figure 4.2* represents the sequential steps of this titrating process:

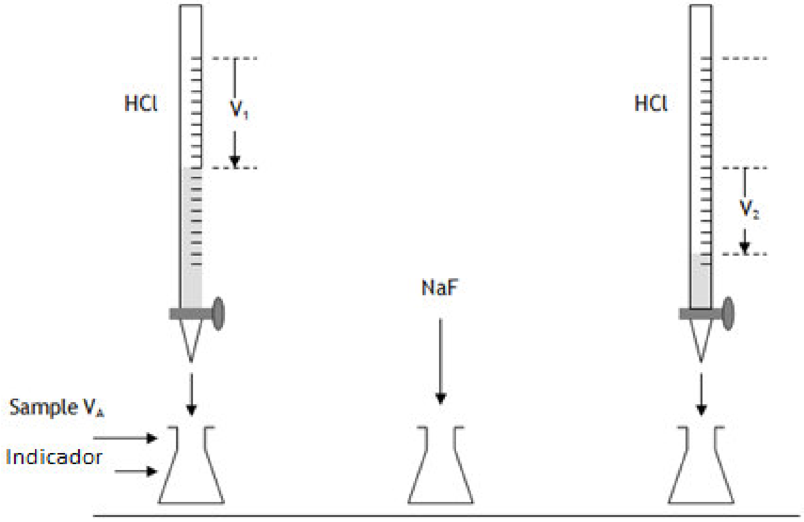


Figure 4.2 – Titrating stages

Considering the previous reactions it results that dissolved aluminum and caustic soda concentrations (in g/L) are calculated by equations *(4.6)*, *(4.7)*:

$$C_{Al} = 9 \cdot V_2 \frac{[HCl]}{V_A} \quad (4.6) \qquad C_{NaOH} = 40 \cdot (V_1 - \frac{V_2}{3}) \cdot \frac{[HCl]}{V_A} \quad (4.7)$$

and recovery yields (in percentage) are in turn computed by equations *(4.8)*, *(4.9)*:

$$\eta_{Al} = \frac{\left(C_{Al_{initial}} - C_{Al_{final}}\right)}{C_{Al_{initial}}} \cdot 100 \quad (4.8) \qquad \eta_{NaOH} = \frac{\left(C_{NaOH_{final}} - C_{NaOH_{initial}}\right)}{\frac{C_{Al_{initial}}}{M_{Al}} \cdot M_{NaOH}} \cdot 100 \quad (4.9)$$

Caustic soda yield calculation is based on the fact that the maximum number of moles of NaOH that can be recovered is equal to the number of moles of sodium aluminate that are initially in solution, according with the Bayer reaction.

## 4.2 Results and Discussion

Hereafter the various series of tests that had been performed are related and their results discussed.

### 4.2.1 Exploratory Tests Series

This first series of tests was meant to explore the process and extend the author’s knowledge on the field, which at the time was entirely made by literature readings.

Seeded crystallization was performed, a sort of mandatory choice according with the author’s background (see *Chapter 3* of this work). The (seed quantity)/(caustic solution) ratio was kept constant among the various tests, together with the stirring intensity. The varying parameter was the percentage of added water, that was thought to be the main factor to affect the process.

Tests conditions are reported in *Table 4.1*:

Table 4.1 – Experimental conditions of the exploratory tests series

| Test ID | Solution volume | Added water | | Total volume | Seed concentration | | Stirring intensity | T |
|---|---|---|---|---|---|---|---|---|
| | [mL] | [mL] | [%] | [mL] | [g/L of solution] | [g/L] | | [℃] |
| S1 | 250 | 150 | 60 | 400 | 20 | 12.05 | Very low | 25 |
| S2 | 250 | 200 | 80 | 450 | 20 | 11.01 | Very low | 25 |
| S3 | 250 | 250 | 100 | 500 | 20 | 10.00 | Very low | 25 |
| S4 | 250 | 300 | 120 | 550 | 20 | 9.01 | Very low | 25 |

Water was added in high percentages because it was thought to have a positive effect on the process course, according with the Bayer reaction and with [51].

The reader should notice that the stirring intensity does not refer to an absolute measuring system, being quantified by means of an arbitrary scale according with the author’s sensibility. This choice was induced by the use of magnetic stirrers of different brands, each with its own control system. The choice is maintained throughout the whole work.

The process did not develop in all the tests of this series. Indeed, 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 unexpected 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 fasten. This upper limit should set in the 60 - 80% range.

Chemicals concentrations and recovery yield temporal progressions for S1 are shown in *Figures 4.3* and *4.4* (data originating the graphs are reported in *Table I.1, Annex I*):

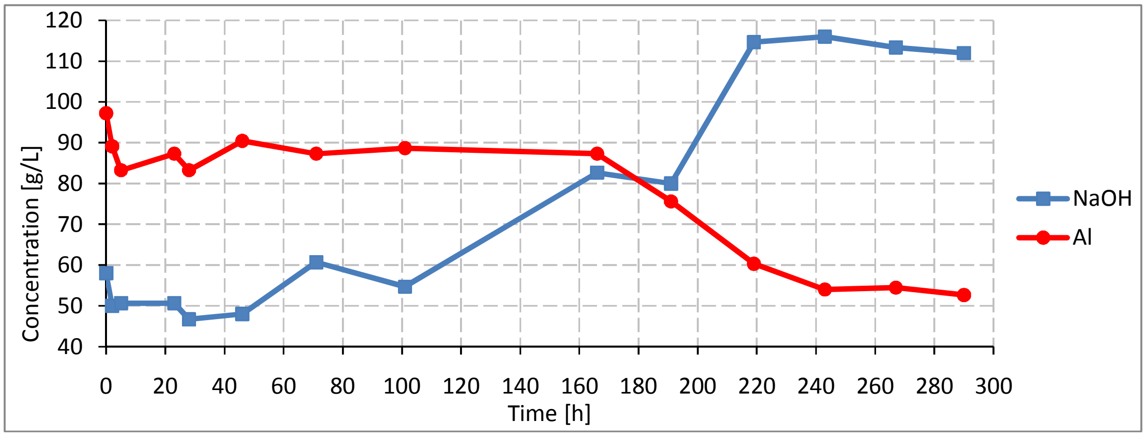


Figure 4.3 – Temporal evolution of chemicals concentrations in test S1

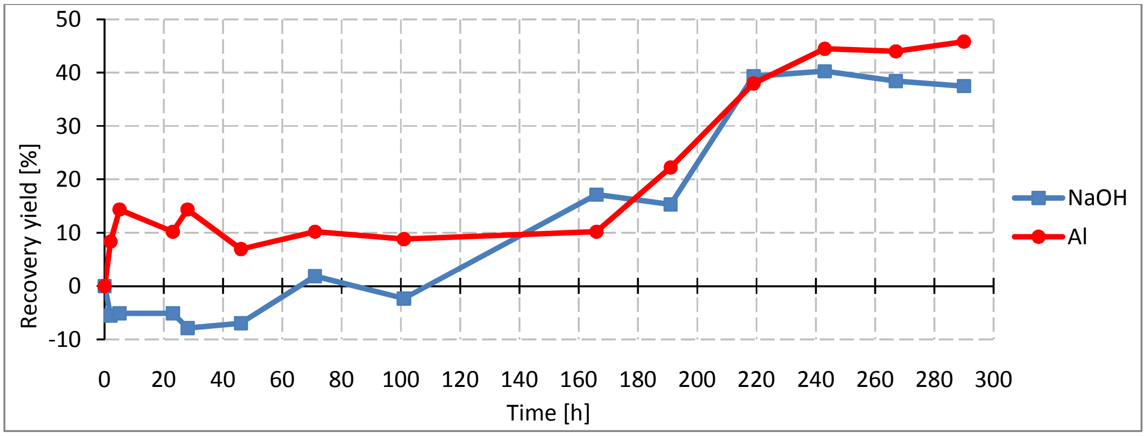


Figure 4.4 – Temporal evolution of chemicals recovery yields in test S1

Titrating volumes are reported in *Table I.1* with the aim of qualitatively showing the intrinsic error of the method: a little variation in titrating volumes is magnified in concentrations and recovery yields. Nevertheless the method is considered reliable in revealing tendencies and it is well suited for the laboratory scale of this work.

Therefore it can be said that ≈ 44% of aluminum is precipitated and ≈ 38% of caustic soda is recovered after ≈ 240 h.

It is also 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” (in this work three levels were used: “very low”, “low” and “high”).

A second hypothesis arises: stirring intensity is a factor that affect the process and it has a lower limit underneath which the normal course of the reaction is not fasten.

The changeover is confirmed by the particles size distribution sharp variation, as it is shown in the column "$d_{50}$" in *Table I.1* (*Annex I*) ($d_{50}$ is the diameter that divides in two the particles size distribution). Seed's particle size distribution was also measured, and it is shown as a reference in *Figure 4.5*:

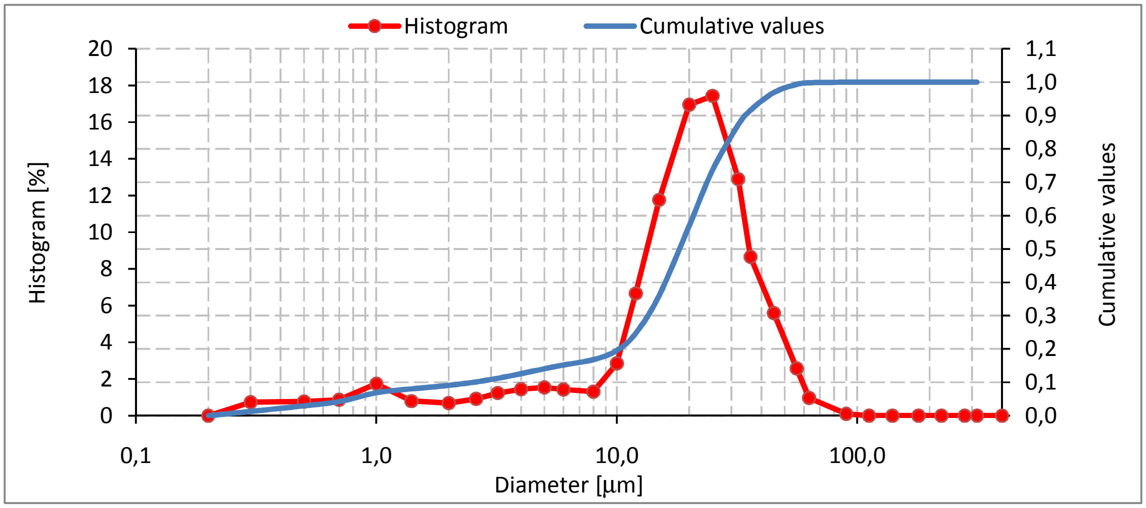


Figure 4.5 – Seed size distribution and cumulative curve

The seed particles size distribution is very close to a normal distribution, with a $d_{50}$ of 18.19 µm.

The evolution of the particles size distribution with time for the test S1 is shown in *Figure 4.6*:

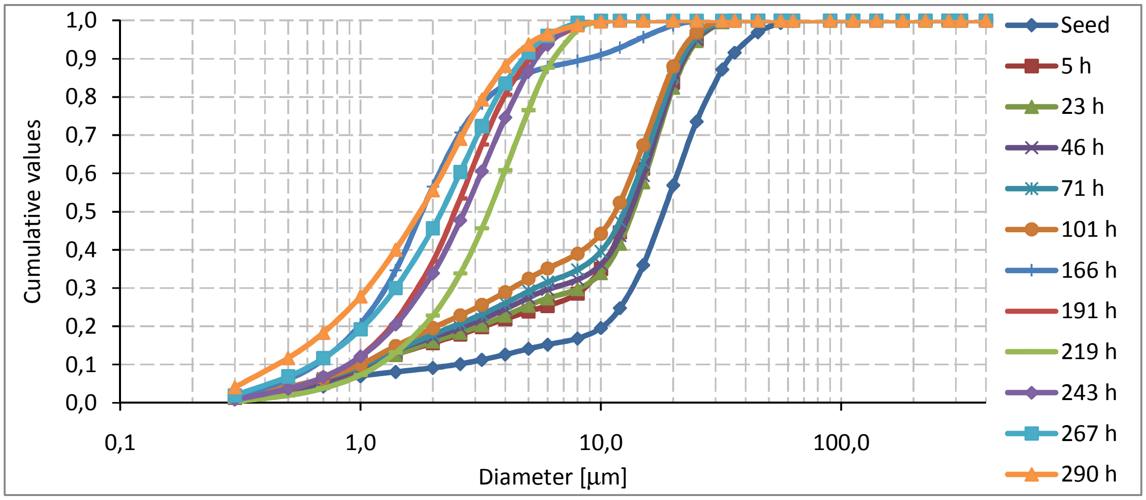


Figure 4.6 – Temporal evolution of the particles size distribution in test S1

It can be seen that between 101h and 166h the cumulative curve 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 166h no substantial further evolution can be revealed. This is more easily understood by looking at the particles size distribution histograms created by CILAS 920 (*Figure 4.7*).

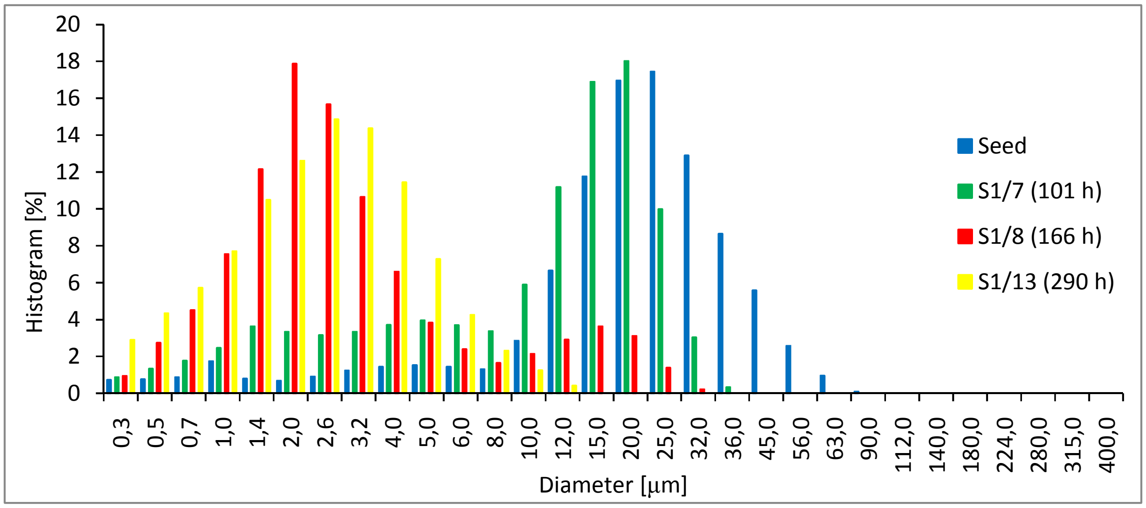


Figure 4.7 – Particles size distribution histograms for test S1

The fact that it exists a lower limit for the stirring intensity is an indication that diffusion phenomenon are critical for the process. Moreover it could confirm that an enough intense stirring is important because it grinds the seed, increasing the seed's surface area, its number of defects, and causes the fracture of the dendritic structures that grow on seed's surface by secondary nucleation, turning them into new nuclei (see *point 3.2* of this work for further details).

### 4.2.2 Influence of Water Addition and Seed Concentration

In this second series, tests were configured to investigate the water and seed addition effects on the process. 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. Tests conditions are reported in *Table 4.2*:

Table 4.2 – Experimental conditions of the second series of tests

| Test ID | Solution volume | Added water | | Total volume | Seed concentration | | Stirring intensity | T |
|---|---|---|---|---|---|---|---|---|
| | [mL] | [mL] | [%] | [mL] | [g/L of solution] | [g/L] | | [°C] |
| S5 | 130 | 0 | 0 | 130 | 60 | 60.0 | Low | 25 |
| S6 | 130 | 39 | 30 | 169 | 60 | 46.2 | Low | 25 |
| S7 | 130 | 78 | 60 | 208 | 60 | 37.5 | Low | 25 |
| S8 | 130 | 39 | 30 | 169 | 20 | 15.4 | Low | 25 |
| S9 | 130 | 39 | 30 | 169 | 100 | 76.9 | Low | 25 |

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 hypothesis about water addition and stirring intensity derived in the previous point of this work.

Results are reported in *Figures 4.8* and *4.9* (for solution concentrations) and in *Figures 4.10* and *4.11* (for recovery yields) (original data is found from *Table II.1* to *Table II.5*, *Annex II*).

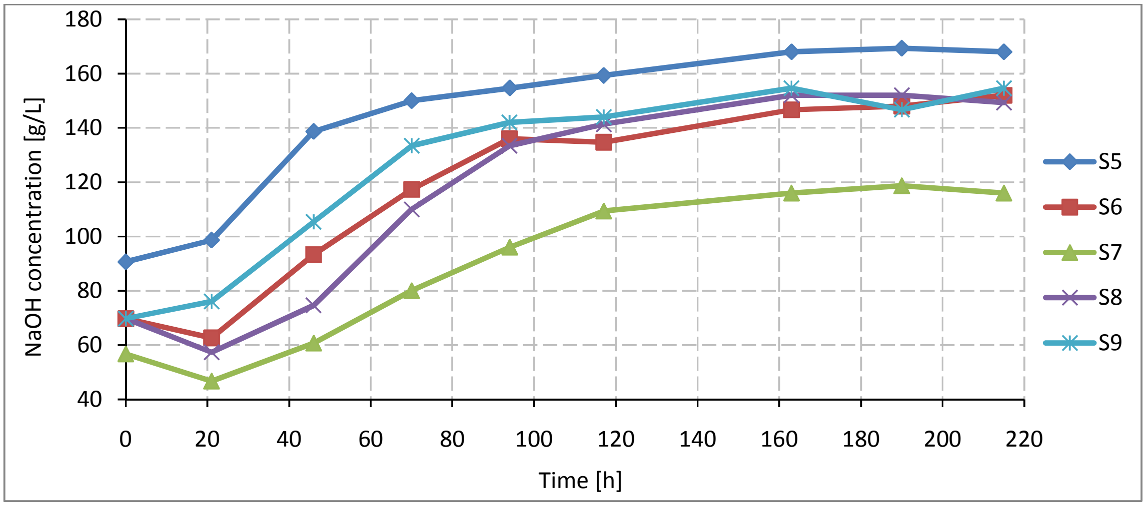


Figure 4.8 – Temporal evolution of caustic soda concentration in the second series of tests

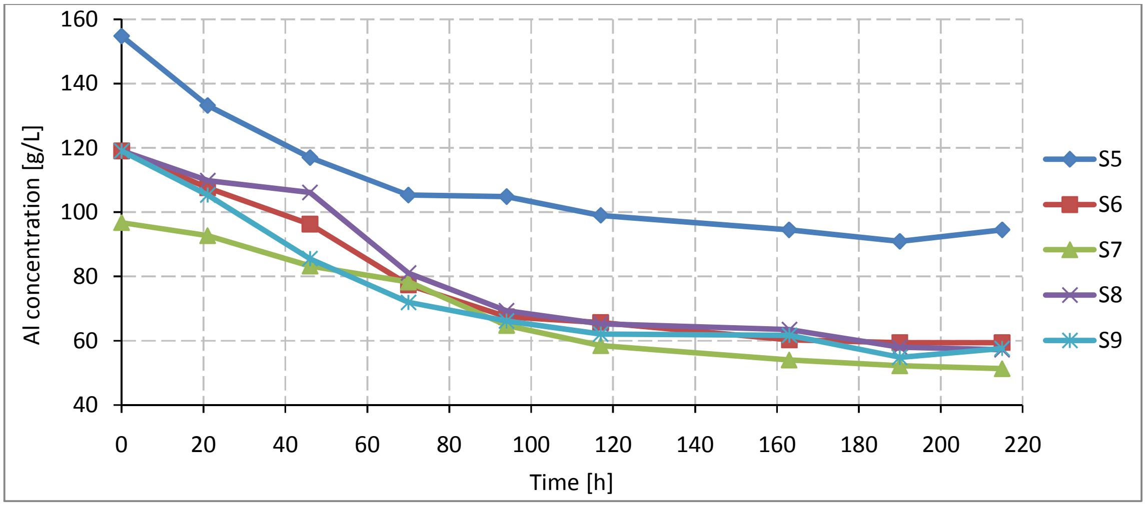


Figure 4.9 – Temporal evolution of dissolved aluminum concentration in the second series of tests

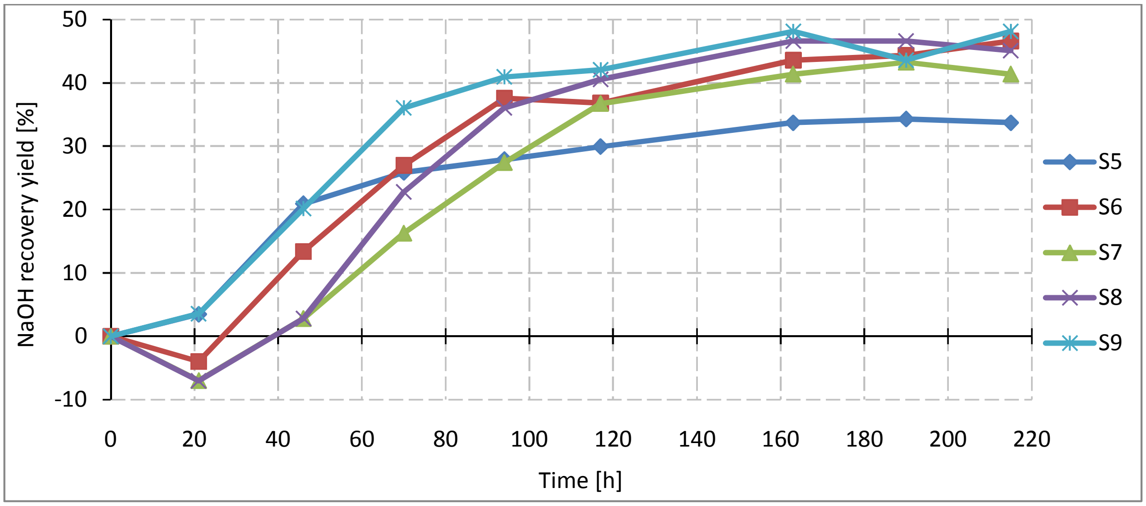


Figure 4.10 – Temporal evolution of caustic soda recovery yield in the second series of tests

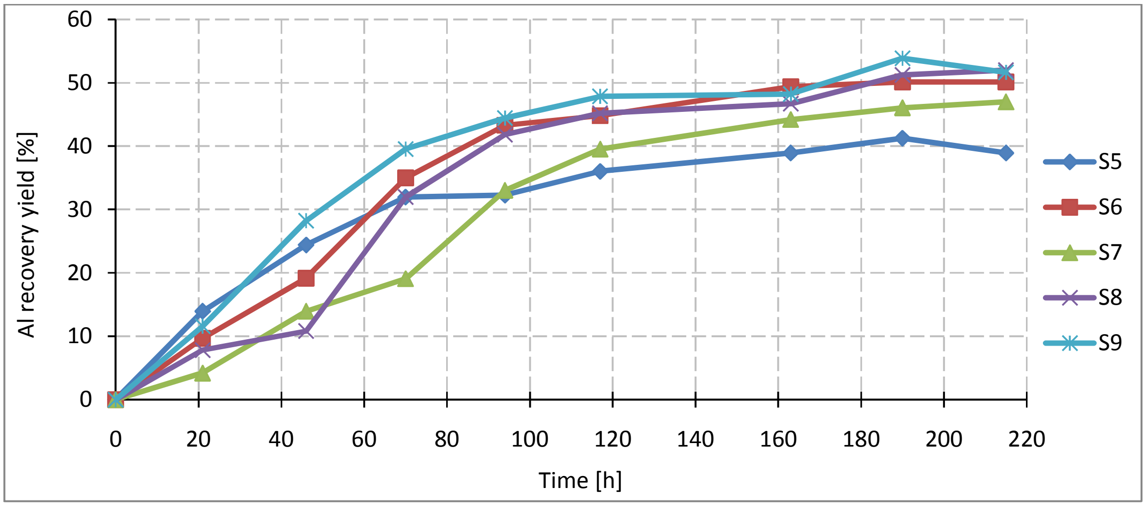


Figure 4.11 – Temporal evolution of aluminum recovery yield in the second series of tests

An additional confirmation of the hypothesis that water addition effect is detrimental for the process progression comes from the analysis of the results. 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 clearly the slower system to develop up to 80 – 100h, 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 46h. This could be explained assuming that in the mother solution it is already present enough water for the sodium aluminate hydrolyzing process to start, and a supplementary dilution only leads to a decreasing of the supersaturation degree and the diffusion phenomenon, and in turn to the decreasing of the reaction rate. The water addition effect is also revealed by comparing the temporal evolution of the particles size distribution of S5 and S7 (see *Figures 4.12* and *4.13*). They are indeed very similar, but after 21h 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. On the other hand after 215h recovery yields are higher for those systems with added water, though the difference is not dramatic. Following the previous reasoning, it is possible that as the process goes by water is consumed and runs out in S5. This lack of readily available water for the hydrolyzing to take place diminishes the reaction rate. Systems with added water are now favored and their development can achieve higher degrees.

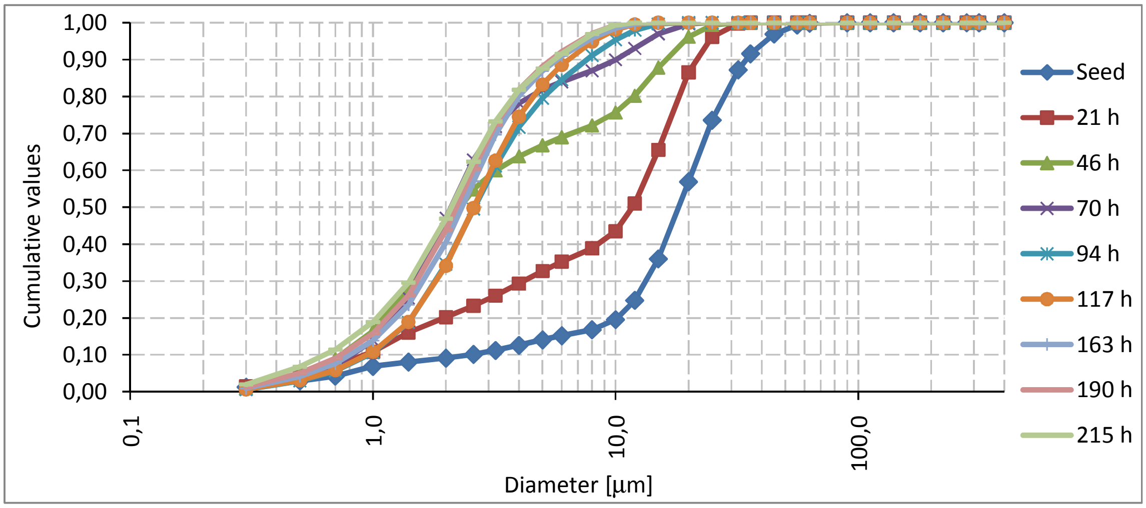


Figure 4.32 – Temporal evolution of the particles size distribution in test S7

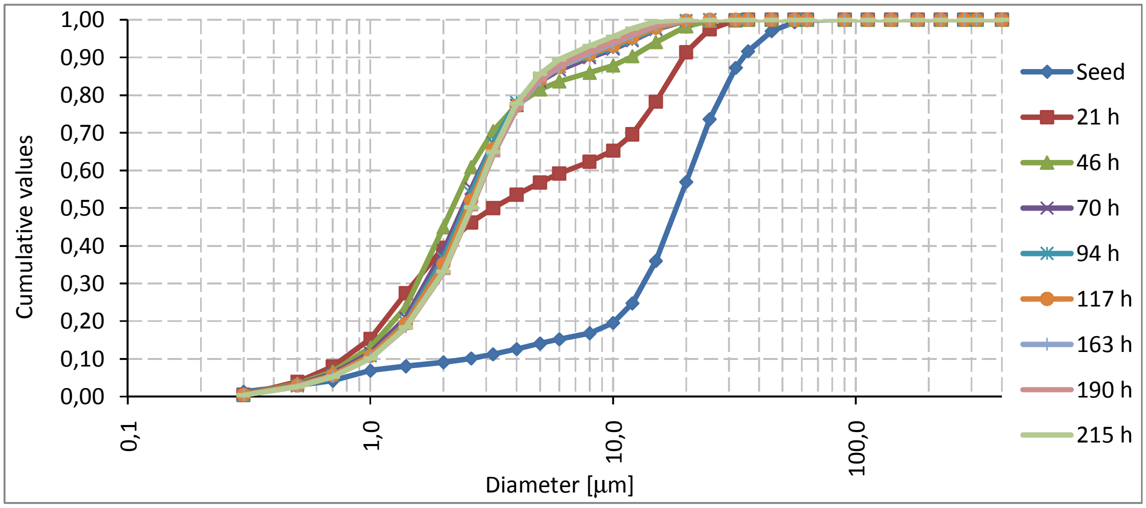


Figure 4.13 – Temporal evolution of the particles size distribution in test S5

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.

### 4.2.3 Systematic Tests Series Using Factorial Experimental Design

This 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. Results from the factorial design allowed to represent the system response with a linear regression model of independent variables (first order function).

#### 4.2.3.1 Factorial Experimental Design

Factorial design is an efficient methodology in which the several factors affecting a variable (called response) are combined in all possible ways. Tests are conducted in accordance with a previously established plan, where all factors are changed simultaneously rather than one at a time. In this way, it becomes possible to evaluate the effect of each factor and of any possible factors interaction on the system response. Due to their orthogonal property, factorial program tests tend to discriminate the effects resulting by the factors in analysis and allows to differentiate them from natural, environmental or technical variations occurring in experimentation which constitute sources of errors. Experimental errors can be estimated by means of various techniques, such as the central point method. Factorial design is preferable to the classical Cartesian experimental method, being the latter one unable to correctly explain complex processes influenced by interacting variables.

A factorial experimental design consists in a number of tests made by all the possible combinations of the independent variables $x_i$ (named factors) to measure the system response Y (dependent variable). The mathematical function that represents the system is:

$$Y = f(x_1, x_2, \dots, x_i, \dots, x_k) + \varepsilon \qquad (4.10)$$

where ε is the error and k is the number of factors. Values assumed by factors are called levels. Values assumed by function Y for different levels are called responses, $Y_m$, and m indicates each set of experimental conditions. When two levels are associated to each factor, an upper one and a lower one within the range under study, the factorial design is a $2^k$ type. The number of tests needed is then calculated by $p=2^k$ and corresponds to the number of possible combinations of k factors for the considered two levels. In order to simplify calculations it is convenient to work with codified factors, that is the two levels are represented by the unitary values +1 and -1, respectively for the upper level and for the lower one.

Factors and their interactions' influence on the dependent variable, the so called effect, is calculated from the experimental measured values of the responses. For each factor $x_i$, it is defined the individual effect $E(x_i)$ as the difference between the average of the responses obtained for the upper level of $x_i$ and the average of the responses obtained for the lower level of $x_i$:

$$E(x_i) = \frac{2}{p}\sum_m Y_{m,x_i=+1} - \frac{2}{p}\sum_m Y_{m,x_i=-1} \qquad (4.11)$$

A positive effect means that the average responses achieved in the highest level is higher than the average responses obtained in the lower level. The interaction between two factor is calculated in a similar way, with the generic expression:

$$E(x_i x_j) = \frac{2}{p}\sum_m Y_{m,x_i=x_j} - \frac{2}{p}\sum_m Y_{m,x_i\neq x_j} \qquad (4.12)$$

The interaction is positive when a factor effect (positive or negative) on the response is enhanced by the upper level of the other factor, otherwise it is negative [62 - 65].

In this work the factorial program used is a $2^3$, therefore 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 (S) (referred to the caustic solution volume), and stirring intensity (I). The factorial program is presented in *Table 4.3*, 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.

Table 4.3 – Factorial program

| Factorial program code | 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] | | | | | | | | |
| 1 | S10 | 0 | 10 | Low | -1 | -1 | -1 | +1 | +1 | +1 | -1 |
| 2 | S11 | 60 | 10 | Low | +1 | -1 | -1 | -1 | -1 | +1 | +1 |
| 3 | S5 | 0 | 60 | Low | -1 | +1 | -1 | -1 | +1 | -1 | +1 |
| 4 | S7 | 60 | 60 | Low | +1 | +1 | -1 | +1 | -1 | -1 | -1 |
| 5 | S12 | 0 | 10 | High | -1 | -1 | +1 | +1 | -1 | -1 | +1 |
| 6 | S13 | 60 | 10 | High | +1 | -1 | +1 | -1 | +1 | -1 | -1 |
| 7 | S14 | 0 | 60 | High | -1 | +1 | +1 | -1 | -1 | +1 | -1 |
| 8 | S15 | 60 | 60 | High | +1 | +1 | +1 | +1 | +1 | +1 | +1 |
| 9 | SI | 30 | 35 | Medium | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| 10 | SII | 30 | 35 | Medium | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| 11 | SIII | 30 | 35 | Medium | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| 12 | SIV | 30 | 35 | Medium | 0 | 0 | 0 | 0 | 0 | 0 | 0 |

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 and the effect of stirring intensity.

The reader should notice that the factorial program codes 3 and 4 correspond to the samples ID S5 and S7, in other words the results of two previously carried tests were used in this factorial. Therefore the number of new tests to be carried to complete the program was reduced to ten.

The experimental application of the above factorial program is presented in *Table 4.4*:

Table 4.4 – Experimental conditions for the implementation of the factorial program

| Factorial program code | Test ID | Solution volume | Water addition | | Total volume | Seed concentration | | Stirring intensity | T |
|---|---|---|---|---|---|---|---|---|---|
| | | [mL] | [mL] | [%] | [mL] | [g/L of solution] | [g/L] | | [°C] |
| 1 | S10 | 130 | 0 | 0 | 130 | 10 | 10.0 | Low | 25 |
| 2 | S11 | 130 | 78 | 60 | 208 | 10 | 6.3 | Low | 25 |
| 3 | S5 | 130 | 0 | 0 | 130 | 60 | 60.0 | Low | 25 |
| 4 | S7 | 130 | 78 | 60 | 208 | 60 | 37.5 | Low | 25 |
| 5 | S12 | 130 | 0 | 0 | 130 | 10 | 10.0 | High | 25 |
| 6 | S13 | 130 | 78 | 60 | 208 | 10 | 6.3 | High | 25 |
| 7 | S14 | 130 | 0 | 0 | 130 | 60 | 60.0 | High | 25 |
| 8 | S14 | 130 | 78 | 60 | 208 | 60 | 37.5 | High | 25 |
| 9 | SI | 70 | 21 | 30 | 91 | 35 | 26.9 | Medium | 25 |
| 10 | SII | 70 | 21 | 30 | 91 | 35 | 26.9 | Medium | 25 |
| 11 | SIII | 70 | 21 | 30 | 91 | 35 | 26.9 | Medium | 25 |
| 12 | SIV | 70 | 21 | 30 | 91 | 35 | 26.9 | Medium | 25 |

#### 4.2.3.2 Factorial Program's Results

The results of the factorial experimental tests are presented from *Figure 4.14* to *Figure 4.17* (original data are found from *Table III.1* to *Table III.6* in *Annex III*). Central point tests' outcomes are all placed in *Annex III* for their minor interest.

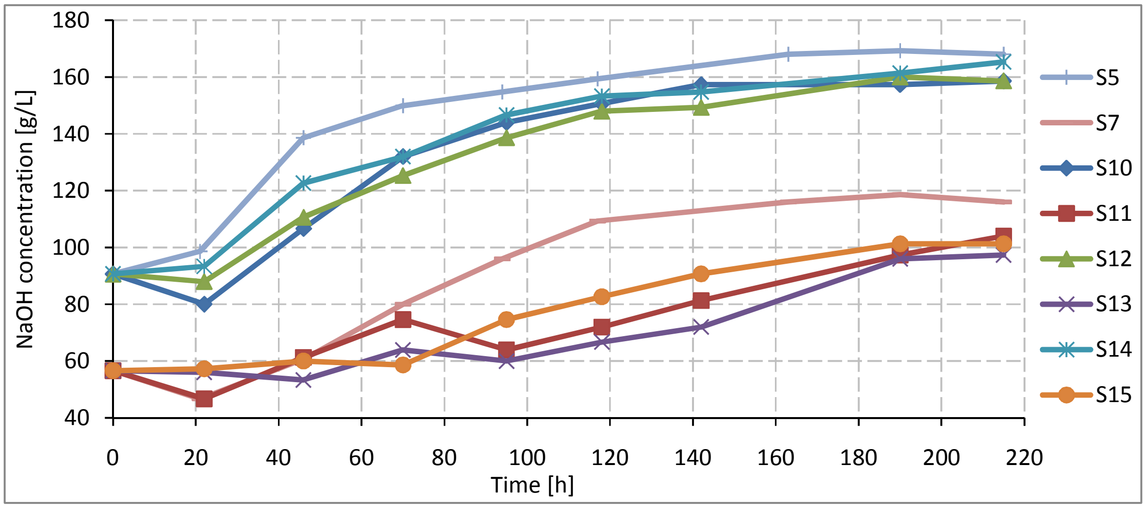


Figura 4.14 – Temporal evolution of caustic soda concentration in the factorial program's tests

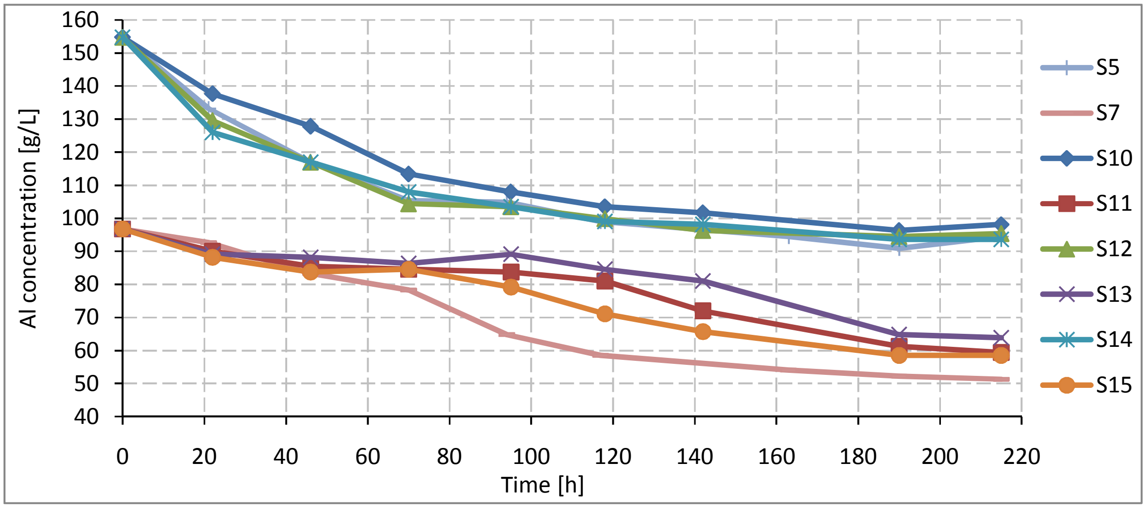


Figura 4.15 – Temporal evolution of dissolved aluminum concentration in the factorial program's tests

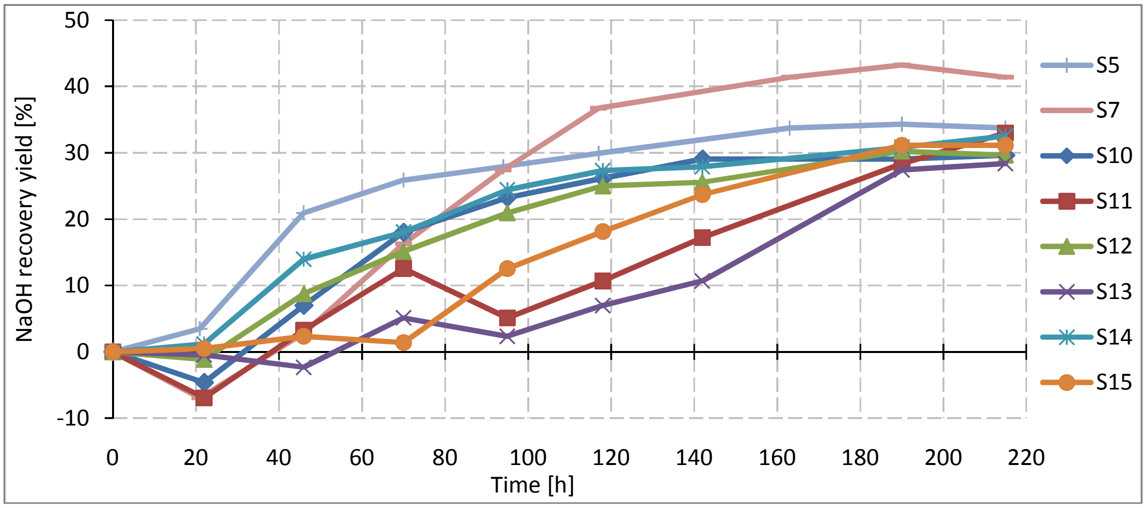


Figura 4.16 – Temporal evolution of caustic soda recovery yield in the factorial program's tests

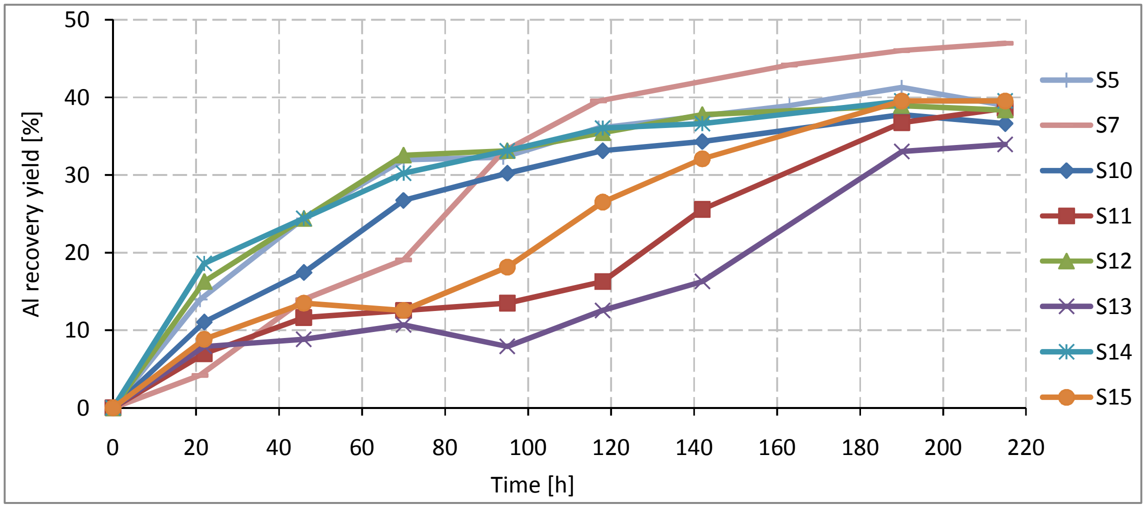


Figura 4.17 – Temporal evolution of aluminum recovery yield in the factorial program's tests

For simplicity of reading the calculation of the effects of factors and their interaction is related in the following point together with the evaluation of their significance.

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.

It is also qualitatively confirmed that water addition has an important detrimental effect for the fastening of the process. In fact in *Figure 4.14* and *4.15* it is clearly seen that the initial (first 80 -100h of reaction) slope of the chemicals concentration curves is higher for those tests in which no water was added.

Granulometric analysis were performed regularly in this series of tests because of instrumental troubles. Particles diameters evolutions are not reported, but they are comparable with those obtained in the former series. Only the final (215h) particles parameters are presented for each test of the factorial program in *Table 4.5*, together with the parameters average, in order to dimensionally characterize the solid final product of the process.

Table 4.5 – 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 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 (averages after 215h, see *Table 4.5*). This byproduct is structurally and morphologically studied in *Chapter 5*.

#### 4.2.3.3 Analysis of Variance of Factors

The factorial experimental design requires a statistical analysis of the factors' effect, in order to reveal whether or not they are significant. This significance evaluation can be carried by means of the analysis of variance ANOVA method. ANOVA allows to quantify the effects' relevance degree and reveal if they are only the result of experimental errors oscillations.

For a $2^3$ design the variance represents the dispersion among the average responses in each level of the factor $x_i$ and the average value of all the eight responses. The sum of squares is calculated by:

$$SS(x_i) = \frac{1}{8}\left(\sum_m Y_{m,x_i=+1} - \sum_m Y_{m,x_i=-1}\right)^2 = \frac{1}{8}[4E(x_i)]^2 = 2E(x_i)^2 \qquad (4.13)$$

The previous equation is valid for all factors (main and interactions) and reflects the relation between the factors relative influence over the dependent variable and the sum of squares. The variance or mean square MS($x_i$) is computed as the quotient between the SS($x_i$) value and the associated value of degree of freedom N, which for a two levels factorial program is unitary (N=1). Therefore:

$$MS(x_i) = SS(x_i) \qquad (4.14)$$

Finally it is important to estimate the error associated with the observations: when the central point method is used (the central point of a factor represents the average between the upper level and the lower level, in natural values), n responses of function Y are obtained, called $Y_{0,j}$ (j = 1 to n), that lead to the estimative of the experimental error's sum of square and variance, respectively $SS_E$ and $MS_E$:

$$SS_E = \sum_{j=1}^{n}(Y_{0,j} - \bar{Y}_0)^2 \qquad (4.15) \qquad\qquad \bar{Y}_0 = \sum_{j=1}^{n}\frac{Y_{0,j}}{N} \qquad (4.16)$$

$$MS_E = \frac{SS_E}{N-1} \qquad (4.17)$$

N corresponds to the degree of freedom associated to *$MS_E$.*

ANOVA reveals whether two independent estimative of variance (the factor's variance and the error one) belong to the same population or not. If they are significantly different, the factor has got statistical relevance. In order to establish this statistic evaluation, it can be used the Fisher-Snedecor distribution, which establishes a relation between factor mean square and deviation mean square due to errors, by using the expression:

$$F_{exp}(x_i) = \frac{MS(x_i)}{MS_E} \qquad (4.18)$$

which is as higher as the statistical significance of the factor in analysis. It is necessary to calculate the significance level *α* as well as the confidence degree *1-α* to validate the factors significance [62 - 65].

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 analysis of variance results, that is all the information about factors' (and their interaction) effects, their significance as well as the confidence degree associated to their significance, is shown from *Table 4.6* to *Table 4.11*, and in *Annex IV* from *Figure IV.1* to *Figure IV.12*.

Table 4.6 – Effects of factors and their interactions on aluminum recovery yield after 46h. ANOVA.

| Source of variation | Effects | Sum of squares SS | Degrees of freedom N | Mean squares MS | $F_{exp}$ | Significance level α | Confidence degree (1-α)·100 |
|---|---|---|---|---|---|---|---|
| *Principal factors* | | | | | | | |
| W | -10.25 | 210.1 | 1 | 210.1 | 14.0 | 0.03328 | 96.67 $^{(*)}$ |
| S | 3.25 | 21.1 | 1 | 21.1 | 1.4 | 0.32075 | 67.93 $^{(o)}$ |
| I | 0.75 | 1.1 | 1 | 1.1 | 0.1 | 0.80196 | 19.80 $^{(o)}$ |
| *Interactions* | | | | | | | |
| W·S | -0.25 | 0.1 | 1 | 0.1 | 0.0 | 0.93302 | 6.70 $^{(o)}$ |
| W·I | -2.75 | 15.1 | 1 | 15.1 | 1.0 | 0.38929 | 61.07 $^{(o)}$ |
| S·I | -1.25 | 3.1 | 1 | 3.1 | 0.2 | 0.67909 | 32.09 $^{(o)}$ |
| W·S·I | 2.25 | 10.1 | 1 | 10.1 | 0.7 | 0.47152 | 52.85 $^{(o)}$ |
| *Experimental deviation* | - | 45.0 | 3 | 15.0 | - | - | - |
| *Total* | - | 305.9 | 10 | - | - | - | - |

(***) = Highly significant (**) = Very significant (*) = Significant (o) = Not significant

Table 4.7 – Effects of factors and their interactions on soda recovery yield after 46h. ANOVA.

| Source of variation | Effects | Sum of squares SS | Degrees of freedom N | Mean squares MS | $F_{exp}$ | Significance level α | Confidence degree (1-α)·100 |
|---|---|---|---|---|---|---|---|
| *Principal factors* | | | | | | | |
| W | -11.25 | 253.1 | 1 | 253.1 | 42.2 | 0.00741 | 99.26 $^{(**)}$ |
| S | 5.75 | 66.1 | 1 | 66.1 | 11.0 | 0.04506 | 95.49 $^{(*)}$ |
| I | -2.75 | 15.1 | 1 | 15.1 | 2.5 | 0.21055 | 78.94 $^{(o)}$ |
| *Interactions* | | | | | | | |
| W·S | -3.75 | 28.1 | 1 | 28.1 | 4.7 | 0.11901 | 88.10 $^{(o)}$ |
| W·I | -0.25 | 0.1 | 1 | 0.1 | 0.0 | 0.89438 | 10.56 $^{(o)}$ |
| S·I | -1.25 | 3.1 | 1 | 3.1 | 0.5 | 0.52265 | 47.74 $^{(o)}$ |
| W·S·I | 3.25 | 21.1 | 1 | 21.1 | 3.5 | 0.15726 | 84.27 $^{(o)}$ |
| *Experimental deviation* | - | 18.0 | 3 | 6.0 | - | - | - |
| *Total* | - | 404.9 | 10 | - | - | - | - |

(***) = Highly significant (**) = Very significant (*) = Significant (o) = Not significant

Table 4.8 – Effects of factors and their interactions on aluminum recovery yield after 95h. ANOVA.

| Source of variation | Effects | Sum of squares SS | Degrees of freedom N | Mean squares MS | $F_{exp}$ | Significance level α | Confidence degree (1-α)·100 |
|---|---|---|---|---|---|---|---|
| *Principal factors* | | | | | | | |
| W | -14.03 | 393.4 | 1 | 393.4 | 62.9 | 0.00418 | 99.58 $^{(**)}$ |
| S | 8.03 | 128.8 | 1 | 128.8 | 20.6 | 0.02001 | 98.00 $^{(*)}$ |
| I | -4.03 | 32.4 | 1 | 32.4 | 5.2 | 0.10724 | 89.28 $^{(o)}$ |
| *Interactions* | | | | | | | |
| W·S | 7.03 | 98.7 | 1 | 98.7 | 15.8 | 0.02849 | 97.15 $^{(*)}$ |
| W·I | -6.03 | 72.6 | 1 | 72.6 | 11.6 | 0.04220 | 95.78 $^{(*)}$ |
| S·I | -2.98 | 17.7 | 1 | 17.7 | 2.8 | 0.19098 | 80.90 $^{(o)}$ |
| W·S·I | -1.98 | 7.8 | 1 | 7.8 | 1.2 | 0.34531 | 65.47 $^{(o)}$ |
| *Experimental deviation* | - | 18.8 | 3 | 6.3 | - | - | - |
| *Total* | - | 770.2 | 10 | - | - | - | - |

(***) = Highly significant (**) = Very significant (*) = Significant (o) = Not significant

Table 4.9 – Effects of factors and their interactions on soda recovery yield after 95h. ANOVA.

| Source of variation | Effects | Sum of squares SS | Degrees of freedom N | Mean squares MS | $F_{exp}$ | Significance level α | Confidence degree (1-α)·100 |
|---|---|---|---|---|---|---|---|
| *Principal factors* | | | | | | | |
| W | -12.18 | 296.5 | 1 | 296.5 | 19.3 | 0.02180 | 97.82 $^{(*)}$ |
| S | 10.18 | 207.1 | 1 | 207.1 | 13.5 | 0.03488 | 96.51 $^{(*)}$ |
| I | -5.68 | 64.4 | 1 | 64.4 | 4.2 | 0.13282 | 86.72 $^{(o)}$ |
| *Interactions* | | | | | | | |
| W·S | 6.18 | 76.3 | 1 | 76.3 | 5.0 | 0.11198 | 88.80 $^{(o)}$ |
| W·I | -2.68 | 14.3 | 1 | 14.3 | 0.9 | 0.40526 | 59.47 $^{(o)}$ |
| S·I | -3.33 | 22.1 | 1 | 22.1 | 1.4 | 0.31598 | 68.40 $^{(o)}$ |
| W·S·I | -2.33 | 10.8 | 1 | 10.8 | 0.7 | 0.46273 | 53.73 $^{(o)}$ |
| *Experimental deviation* | - | 46.0 | 3 | 15.3 | - | - | - |
| *Total* | - | 737.4 | 10 | - | - | - | - |

(***) = Highly significant (**) = Very significant (*) = Significant (o) = Not significant

Table 4.10 – Effects of factors and their interactions on aluminum recovery yield after 215h. ANOVA.

| Source of variation | Effects | Sum of squares SS | Degrees of freedom N | Mean squares MS | $F_{exp}$ | Significance level α | Confidence degree (1-α)·100 |
|---|---|---|---|---|---|---|---|
| *Principal factors* | | | | | | | |
| W | 1.50 | 4.5 | 1 | 4.5 | 1.5 | 0.30245 | 69.76 $^{(o)}$ |
| S | 4.50 | 40.5 | 1 | 40.5 | 13.9 | 0.03366 | 96.63 $^{(*)}$ |
| I | -2.50 | 12.5 | 1 | 12.5 | 4.3 | 0.13022 | 86.98 $^{(o)}$ |
| *Interactions* | | | | | | | |
| W·S | 2.50 | 12.5 | 1 | 12.5 | 4.3 | 0.13022 | 86.98 $^{(o)}$ |
| W·I | -3.50 | 24.5 | 1 | 24.5 | 8.4 | 0.06259 | 93.74 $^{(o)}$ |
| S·I | -0.50 | 0.5 | 1 | 0.5 | 0.2 | 0.70667 | 29.33 $^{(o)}$ |
| W·S·I | -0.50 | 0.5 | 1 | 0.5 | 0.2 | 0.70667 | 29.33 $^{(o)}$ |
| *Experimental deviation* | - | 8.8 | 3 | 2.9 | - | - | - |
| *Total* | - | 104.3 | 10 | - | - | - | - |

(***) = Highly significant (**) = Very significant (*) = Significant (o) = Not significant

Table 4.11 – Effects of factors and their interactions on soda recovery yield after 215h. ANOVA.

| Source of variation | Effects | Sum of squares SS | Degrees of freedom N | Mean squares MS | $F_{exp}$ | Significance level α | Confidence degree (1-α)·100 |
|---|---|---|---|---|---|---|---|
| *Principal factors* | | | | | | | |
| W | 1.50 | 4.5 | 1 | 4.5 | 0.6 | 0.48131 | 51.87 $^{(o)}$ |
| S | 4.50 | 40.5 | 1 | 40.5 | 5.8 | 0.09541 | 90.46 $^{(o)}$ |
| I | -4.00 | 32.0 | 1 | 32.0 | 4.6 | 0.12207 | 87.79 $^{(o)}$ |
| *Interactions* | | | | | | | |
| W·S | 1.00 | 2.0 | 1 | 2.0 | 0.3 | 0.63006 | 36.99 $^{(o)}$ |
| W·I | -3.50 | 24.5 | 1 | 24.5 | 3.5 | 0.15812 | 84.19 $^{(o)}$ |
| S·I | -1.50 | 4.5 | 1 | 4.5 | 0.6 | 0.48131 | 51.87 $^{(o)}$ |
| W·S·I | -1.00 | 2.0 | 1 | 2.0 | 0.3 | 0.63006 | 36.99 $^{(o)}$ |
| *Experimental deviation* | - | 21.0 | 3 | 7.0 | - | - | - |
| *Total* | - | 131.0 | 10 | - | - | - | - |

(***) = Highly significant (**) = Very significant (*) = Significant (o) = Not significant

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).

#### 4.2.3.4 Determination of the Polynomial Regression Model and Analysis of Variance of Regression

Results from the factorial experimental design allow to adjust a polynomial regression model. Factorial program $2^k$ does not generate enough data to implement a $2^{nd}$ order model, therefore the model is linear:

$$Y_e = b_0 + b_1x_1 + b_2x_2 + b_3x_3 + b_{12}x_1x_2 + b_{23}x_2x_3 + b_{123}x_1x_2x_3 \tag{4.19}$$

The polynomial independent term $b_0$ can be calculated by dividing the system responses $Y_m$ for the total observations, including the ones done in the central point. Other parameters are estimated by means of the minimum squares method:

$$b_{ijl} = \frac{E(x_ix_jx_l)}{2}\ ,\ \ i < j < l \tag{4.20}$$

Models for simulating the system response (Al and NaOH recovery yields) after 95h are reported hereafter, together with the analysis of variance of regression.

The equation modeling the Al recovery yield is:

$$\mathrm{Y_{Al,95\ h}} = 26.7 - 7 \cdot \mathrm{x_1} + 4 \cdot \mathrm{x_2} - 2 \cdot \mathrm{x_3} + 3.5 \cdot \mathrm{x_1} \cdot \mathrm{x_2} - 3 \cdot \mathrm{x_1} \cdot \mathrm{x_3} - 1.5 \cdot \mathrm{x_2} \cdot \mathrm{x_3} - \mathrm{x_1} \cdot \mathrm{x_2} \cdot \mathrm{x_3} \tag{4.21}$$

The model's fitting to the experimental results is shown in *Figure 4.18* and further analyzed in *Table 4.12*.

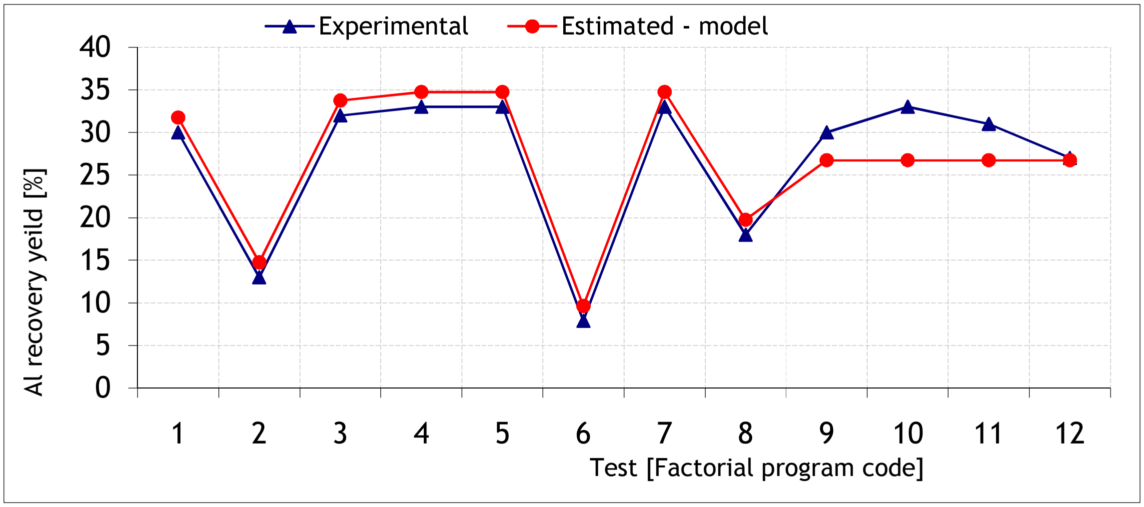


Figure 4.18 – Experimental and estimated aluminum recovery yields after 95 h.

Table 4.12 – Analysis of variance of regression. Model for estimating the aluminum recovery yield after 95h.

| Source of variation | Sum of squares SS | Degrees of freedom N | Mean squares MS | Significance | | | |
|---|---|---|---|---|---|---|---|
| | | | | Experimental deviation | | Total residuals | |
| | | | | Fexp | (1-α)100 | Fexp | (1-α)100 |
| *Regression* | | | | | | | |
| 1st order terms | 554.6 | 3 | 184.9 | 29.6 | 99.01 | - | - |
| Interactions | 196.8 | 4 | 49.2 | 7.9 | 93.92 | - | - |
| Total | 751.4 | 7 | 107.3 | 17.2 | 98.01 | 3.9 | 89.50 |
| *Residuals* | | | | | | | |
| Quadratic terms | 92.6 | 1 | 92.6 | 14.8 | 96.90 | - | - |
| Experimental deviation | 18.8 | 3 | 6.3 | - | - | - | - |
| Total | 111.4 | 4 | 27.8 | - | - | - | - |
| *Total* | 862.8 | 11 | - | - | - | - | - |
| *Correlation coefficient R* | 0.89 | - | - | - | - | - | - |

The equation modeling the NaOH recovery yield is:

$$Y_{\mathrm{Al,95\,h}} = 20.3 - 6.1 \cdot x_1 + 5.1 \cdot x_2 - 2.8 \cdot x_3 + 3.1 \cdot x_1 \cdot x_2 - 1.3 \cdot x_1 \cdot x_3 - 1.7 \cdot x_2 \cdot x_3 - 1.2 \cdot x_1 \cdot x_2 \cdot x_3 \quad (4.22)$$

The model's fitting to the experimental results is shown in *Figure 4.19* and further analyzed in *Table 4.13*.

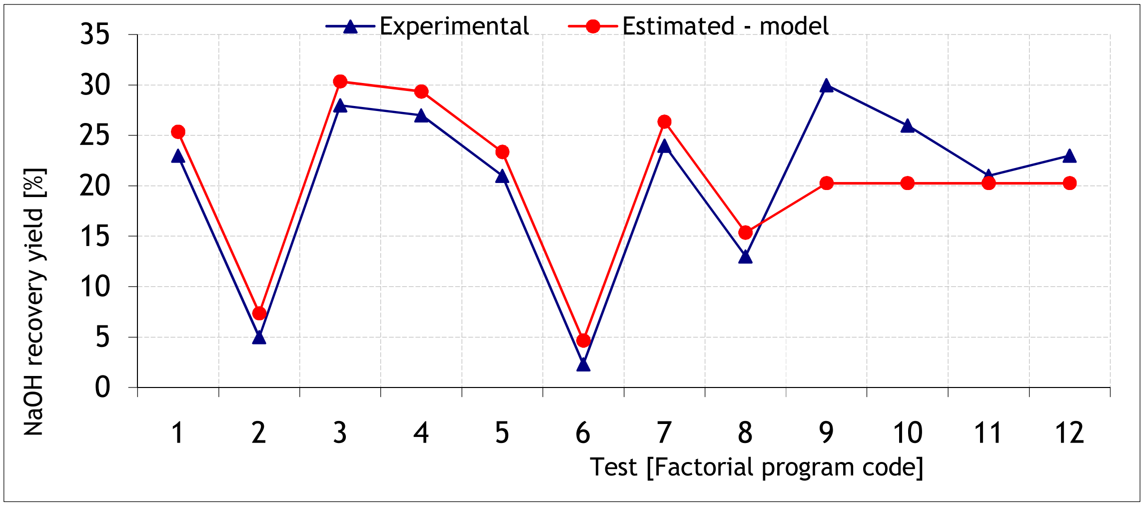


Figure 4.19 – Experimental and estimated caustic soda recovery yields after 95h.

Table 4.13 – Analysis of variance of regression. Model for estimating the caustic soda recovery yield after 95h.

| Source of variation | Sum of squares SS | Degrees of freedom N | Mean squares MS | Significance | | | |
|---|---|---|---|---|---|---|---|
| | | | | Experimental deviation | | Total residuals | |
| | | | | Fexp | (1-α)100 | Fexp | (1-α)100 |
| *Regression* | | | | | | | |
| 1st order terms | 567.9 | 3 | 189.3 | 12.3 | 96.60 | - | - |
| Interactions | 123.5 | 4 | 30.9 | 2.0 | 70.41 | - | - |
| Total | 691.4 | 7 | 98.8 | 6.4 | 92.30 | 2.2 | 76.67 |
| *Residuals* | | | | | | | |
| Quadratic terms | 134.0 | 1 | 134.0 | 8.7 | 94.02 | - | - |
| Experimental deviation | 46.0 | 3 | 15.3 | - | - | - | - |
| Total | 180.0 | 4 | 45.0 | - | - | - | - |
| *Total* | 871.4 | 11 | - | - | - | - | - |
| *Correlation coefficient R* | 0.79 | - | - | - | - | - | - |

By looking at *Figures 4.18* and *4.19* it is seen that the model fitting is good but some deviations are found concerning the fitting of values of the central point (factorial program codes from 9 to 12). This lack of fit observed in the central point can be an indication of possible curvature of the model, not seen in its linear form. Therefore, it means that the process would be probably better simulated with a second grade polynomial model. The global significance of the proposed model is presented in *Tables 4.12* and *4.13*, which also shows the experimental deviation and the sum of squares associated to quadratic terms (deviations that are not explained by the model). The low values of global model adjustment (89.50% and 76.67%) and the low correlation coefficients (0.89 and 0.79) confirm the first graphical impression that the model is inadequate and further investigation is needed to optimize it [66].

### 4.3 Conclusions

Qualitative and statistical analysis of the experimental results allows to state 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.

# CHAPTER 5

# STRUCTURAL AND MORPHOLOGICAL CHARACHTERIZATION 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 (from 9 to 3 years according to data collected for a specific case-study [2]), 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 4*, and their results are presented in this chapter.

## 5.1 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℃ 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 (*Figure 5.1*).

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).

Figure 5.1 – Caustic etch recovery byproduct after filtration and drying

## 5.2 Results and Discussion

The structural and morphological analysis involved the byproducts produced in the factorial program's tests presented in *point 4.2.3* of this work.

XRD patterns are reported in *Figure V.1* in *Annex V*. By observing the figure 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 X-Ray diffraction patterns in *Annex V* are generated by the diffraction grating of gibbsite, $\gamma$-$Al(OH)_3$, and not by other polymorphs. Data about the gibbsite which was found to have the best fitting with the experimental ones are reported in *Table 5.1*:

Table 5.1 – Gibbsite identification (best fitting), and respective structure and cell parameters [68]

| | |
|---|---|
| Powder Diffraction File (PDF) | 00-033-0018 |
| Mineral name | Gibbsite, syn |
| Empirical formula | $AlH_3O_3$ |
| Chemical formula | $Al(OH)_3$ |
| Crystal system | Monoclinic |
| Space group | P21/n |
| Space group number | 14 |

| | |
|---|---|
| a [Å] | 86.552 |
| b [Å] | 50.722 |
| c [Å] | 97.161 |
| Alpha [°] | 900.000 |
| Beta [°] | 946.070 |
| Gamma [°] | 900.000 |
| Calculated density [$g/cm^3$] | 2.44 |

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.

SEM analysis's results are presented in *Figures V.2* and *V.3*, *Annex V*. A low-magnification and a high-magnification images are reported for each sample. 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. This is the typical morphology that results from sodium aluminate solutions. In fact alkali ions largely affects the crystals morphology: prismatic crystals are usually grown from potassium and cesium hydroxide solutions [67]. Crystals do form clusters of various sizes and shapes, usually rounded and similar to the sandy conformation called "desert rose" (see *Figure V.3*), but at this point a distinction has to be made: while for tests S5, S10, S12, and S14 these clusters are well identifiable, for the remaining tests an undifferentiated mass of cemented crystals is seen. By chance the two group of tests can be distinguished on another basis than crystals' agglomeration: the water addition (see *Table 4.3* for further details). For those tests with no added water clusters of crystals can be clearly identified, while for those tests with 60% of water addition this is not possible. It seems that crystallization conditions do have a certain effect on the final gibbsite morphology. Sweegers et al. [67] stated that agglomeration is increased for higher driving forces, and this theory seems to be confirmed by the obtained results. In fact no added water means higher chemicals concentrations and in turns higher driving force for the crystallization to take place.

Strangely the granulometric analysis could not distinguish a difference in particles' size between the two group.

By cross-linking the granulometric and SEM results, a crystallization macro-mechanism based on the fracture of the dendrites that nucleate on the seeds' surface (see *point 3.2.3*) seems to be probable. It is seen in *Figure V.2* and *V.3* that the size of the great majority of clusters ranges from 2 to 6 μm and a minority is made of bigger clusters in the 10 - 30 μm size class. The two clusters' size respectively correspond to the final gibbsite population and to the initial seed population, according with the granulometric analysis results (see *Figure 4.7*). It appears clearly that the dissolved aluminum is mainly recovered because of the formation and growth of new nuclei rather than for seed's growth. Therefore how do seeding fasten the gibbsite crystallization? An idea arises by comparing the SEM image of a virgin seed with one of a big cluster from test S14 (*Figures 5.2* and *5.3*). Seed morphology in *Figure 5.2* is something completely different from what is found in the SEM images reported in *Annex V*. A seed looks like big a cluster (10 to 30 μm) of block-like crystals. Nevertheless the seed dimension is comparable with the one of the big cluster in *Figure 5.3*, but still the two particles look different. According with the previously mentioned theory, these results can be explained by considering that seeds could have act as preferential sites for the secondary nucleation of gibbsite made dendrites. At this point, favored by their thin plate morphology (and by an enough intense stirring), these structures could have broken out and formed new growing nuclei, which in turn become the new hot spots of the crystallization process. Seeds are still in the final solid, but they do look different and can be recognized only because of their size, which is comparable with the initial one and it is substantially bigger than the one of the new formed clusters.

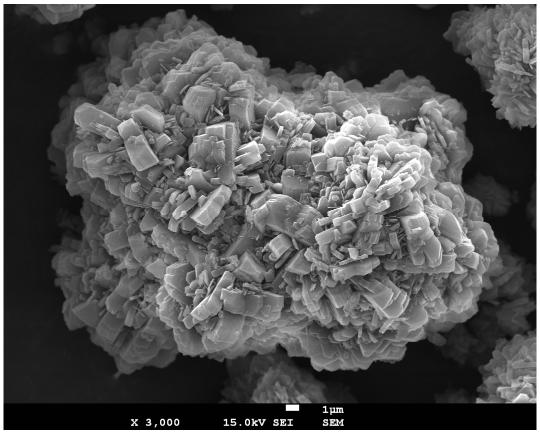


Figure 5.2 – Gibbsite seed (x3000).

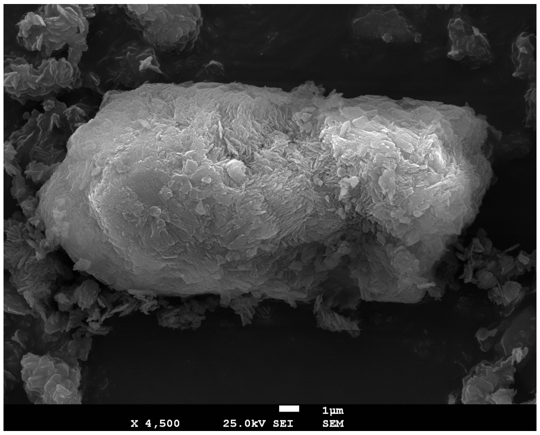
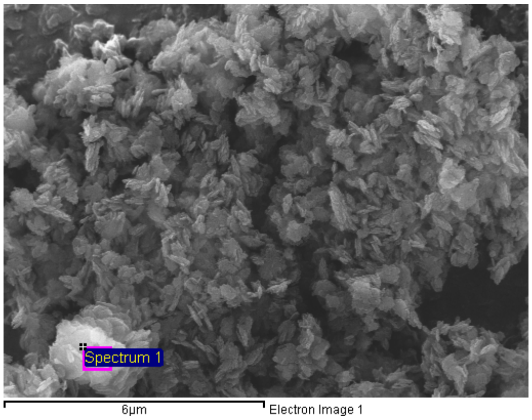


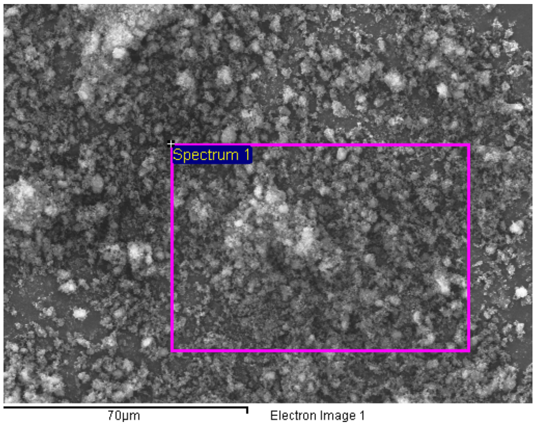
Figure 5.3 – Big gibbsite cluster in S14 (x4500).

Atomic composition analysis of the samples were also performed taking advantage of the EDS feature of the SEM (a demonstrative complete EDS analysis's report is shown in *Figure V.4*, *ANNEX V*). Analysis were performed in specific spots of interest and in larger areas, as shown in *Figure 5.4* and *5.5* (figures come with the correspondent atomic composition). As expected samples are entirely made of aluminum and oxygen (hydrogen cannot be detected because of its too low weight). Sodium was still found in each sample despite the performed washing, but its atomic percentage was always below the 0.5%, and usually between 0.2% and 0.3%, a quite low content being 0.1% in weight the limit for classifying the particular alumina as “low-soda”. The reader should not consider the elements C and Au which are results of the samples preparation for the SEM analysis.



| Element | App Conc. | Intensity Corrn. | Weight % | Weight % Sigma | Atomic % |
|---|---|---|---|---|---|
| C K | 127.89 | 0.5183 | 25.57 | 0.75 | 34.49 |
| O K | 377.30 | 0.6865 | 56.96 | 0.67 | 57.68 |
| Na K | 1.31 | 0.5968 | 0.23 | 0.09 | 0.16 |
| Al K | 84.62 | 0.7275 | 12.05 | 0.20 | 7.24 |
| Au M | 39.77 | 0.7944 | 5.19 | 0.24 | 0.43 |
| Totals | | | 100.00 | | |

Figure 5.4 – SEM image of a specific spot analyzed by EDS in sample S13, with correspondent atomic composition.



| Element | App Conc. | Intensity Corrn. | Weight % | Weight % Sigma | Atomic % |
|---|---|---|---|---|---|
| C K | 88.07 | 0.5583 | 29.76 | 0.99 | 38.94 |
| O K | 186.85 | 0.6365 | 55.41 | 0.91 | 54.42 |
| Na K | 0.73 | 0.5964 | 0.23 | 0.13 | 0.16 |
| Al K | 40.81 | 0.7277 | 10.58 | 0.25 | 6.16 |
| Au M | 17.14 | 0.8057 | 4.01 | 0.31 | 0.32 |
| Totals | | | 100.00 | | |

Figure 5.5 – SEM image of a large area analyzed by EDS in sample S13, with correspondent atomic composition.

## 5.3 Conclusions

Gibbsite ($\gamma$-$Al(OH)_3$) was crystallized from caustic sodium aluminate solutions from the aluminum satinizing by treating and seeding it with gibbsite seed. After 215h of reaction time 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, see *Table 4.5*). Powder has a flour-like consistency and its color is a bright white (see *Figure 5.1*). The powder is generally made of crystals clusters, each cluster being 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 (see *point 3.3.1* for further details on aluminum hydroxides applications).

# CHAPTER 6

## GIBBSITE DEHYDRATION AND CALCINATION: 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 (see *point 3.3.2* for details). 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.

### 6.1 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 (details regarding these techniques are already referred in *points 4.1* and *5.1*).

### 6.2 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 reported in *Table 6.1*, while the heating profiles are presented in *Figure 6.1*. The temperature rising step was accomplished within 70 – 80 min and afterwards the temperature was maintained constant for the required time (varying from 0.5 to 7 hours according with *Table 6.1*).

Table 6.1 – S7 samples calcination conditions and respective samples' ID.

| | | *Time [h]* | | |
|---|---|---|---|---|
| | | 0.5 | 3 | 7 |
| *Temp [℃]* | 450 | S7 450 0.5 | S7 450 3 | S7 450 7 |
| | 600 | - | S7 600 3 | - |
| | 1000 | S7 1000 0.5 | S7 1000 3 | S7 1000 7 |
| | 1200 | - | - | S7 1200 7 |

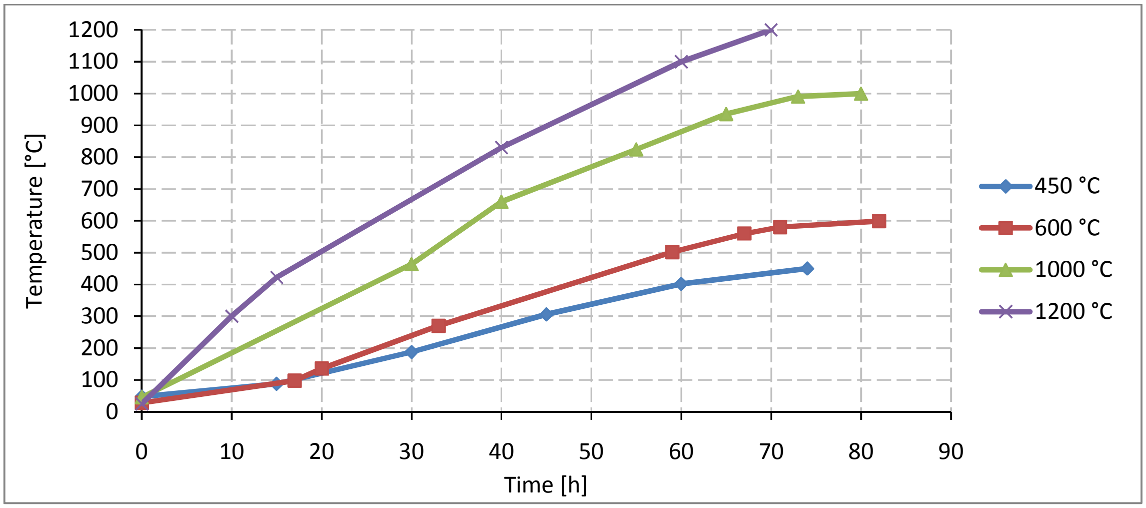


Figure 6.1 – Temperature profiles in S7 samples calcinations. Temperature rising stage.

The calcined samples were characterized by X-Ray diffraction in order to identify the phases formed. The obtained diffraction patterns are shown in *Figure VI.1*, *Annex VI*. The various phases of alumina were identified by means of an iterative comparison process, such as the one for the identification of gibbsite referred in *point 5.2*, and by the use of [69]. It is seen that by heating the gibbsite at 450℃ and for 30 minutes, the main produced phase is a hexagonal χ-$Al_2O_3$ (Powder Diffraction File: [70]). Still, the dehydration process is not complete and a residual orthorhombic phase with chemical formula AlO(OH) can be distinguished (PDF: [71]). 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-$Al_2O_3$ (PDF: [72]) becomes the main phase, no matter which the heating time is. This result is quite unexpected according with *Figure 3.4* (see *point 3.3.2* of this work). At 1200℃ a radical change is clearly seen as the material converts its structure in the rhombohedric α-$Al_2O_3$ (PDF: [73]), 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, produced by dehydration of gibbsite. They are variably X-Ray indifferent and have a range of different properties according with the preparation conditions. χ-$Al_2O_3$ is the one with the highest specific surface area, and is suited for those applications that requires it, such as adsorbents and catalysts. γ-$Al_2O_3$ has a high surface area as well and it is used as catalysts support. α-$Al_2O_3$ is classified as calcined alumina and is far more X-Ray sensitive than the previous ones. Its thermodynamic stability, inertness, and hardness, make it the most suited phase to be used by the ceramic, refractory, and abrasives industries. Other applications are found in electronics as an insulator (for its wide band gap) and optics (for its transparency and thermal stability) [74]. For further information on aluminas' uses the reader should refer to *point 3.3*.

The calcined S7 samples were also studied by means of SEM and the results are presented in *Figures VI.2* and *VI.3*, *Annex VI*. No morphology evolution can be detected between the starting material (*Figures V.2* and *V.3*, *Annex V*) and the various calcined samples, except for the case of the one heated at 1200℃ for 7h. With these conditions new crystals with a globular shape appear among the original plate-like ones.

Results of the granulometric analysis are shown in *Figure 6.2*:

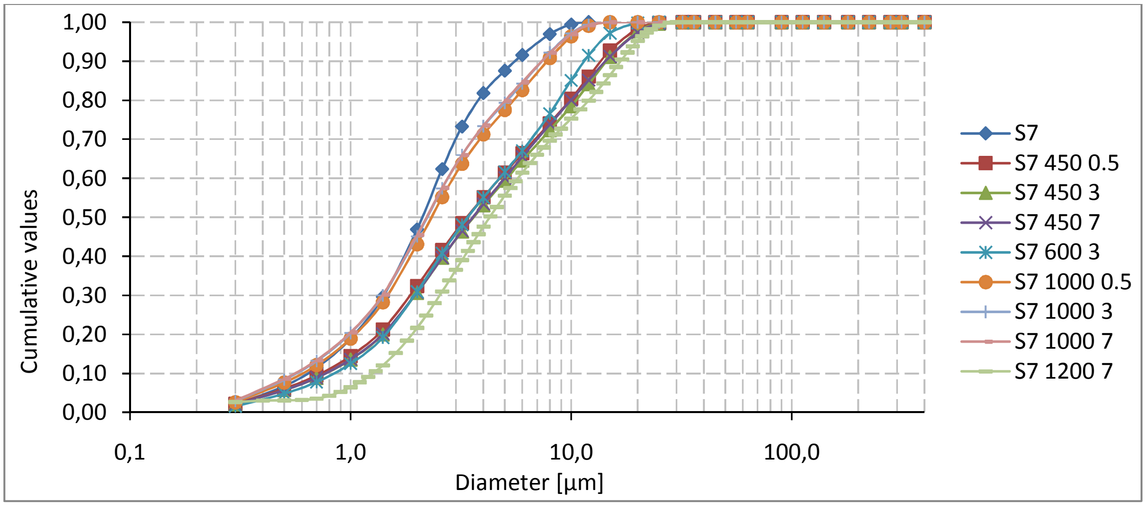


Figure 6.2 – Evolution of S7 particles size distribution with calcination. Effect of temperature and time.

Though no tendency in particles' size variation is detected by observing *Figure 6.2*, a curious phenomenon can be pointed out. All the samples heated at 450 and 600℃ increased their original $d_{50}$ of about 1 – 2 µm, while all those heated at 1000℃ maintained the original $d_{50}$ size. Density always increases in aluminum hydroxides heating, while specific surface area reaches a maximum at around 400℃ [61]. The above particles' size variation could be explained assuming that up to 600℃ the increment in internal surface are due to pores and cracks formation is predominant on the densification, while the two phenomenon have inverse behavior at 1000℃ and balance each other. This theory is challenged by the granulometric analysis of sample "S7 1200 7", which gave back a cumulative curve very similar with those of samples heated at 450℃. Therefore there is no evidence of a clear relation between the heating temperature and the particles' size variation.

## 6.3 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 presented in *point 4.2.3.1*. Conditions of temperature and time were selected randomly, and are 1000℃ and 7 h. The final material was studied by XRD and SEM.

X-Ray patterns are reported in *Figure VI.4*, *Annex VI*. It is clearly seen that the different crystallization conditions have no significant effect on the final alumina structure. A cubic γ-$Al_2O_3$ (PDF: [72]) 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 (SEM images are not reported because of their similarity with those in *Figure V.2* and *V.3*, *Annex V*).

## 6.4 Conclusions

A number of marketable activated and calcined aluminas were produced by dehydration and calcination of the gibbsite obtained as a byproduct of the caustic etch recovery process. They range from the porous and high-surface χ and γ phases, suited for adsorbents and catalysts, to the hard and inert α phase, used by 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. Therefore no best thermal treatment is identified: this can be optimized according with each particular situation's requirements.

# CHAPTER 7

## CONCLUSIONS

“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 to state 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, as it is referred in *point 3.1*). 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 ($\gamma$-$Al(OH)_3$) 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 being 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 these 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.

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# ANNEX I

## EXPLORATORY TESTS SERIES - RESULTS

Table I.1 – Test S1 results

| **Sample ID** | **Time** | **Titrating volume** | | **Concentration** | | **Recovery yield** | | **Particle size** |
|---|---|---|---|---|---|---|---|---|
| | | **V1** | **V2** | **Al** | **NaOH** | **Al** | **NaOH** | **$d_{50}$** |
| | **[h]** | **[mL]** | **[mL]** | **[g/L]** | **[g/L]** | **[%]** | **[%]** | **[μm]** |
| S1/0 | 0 | 5.05 | 10.80 | 97.2 | 58.0 | 0.0 | 0.0 | 18.19 |
| S1/1 | 2 | 4.55 | 9.90 | 89.1 | 50.0 | 8.3 | -5.6 | - |
| S1/2 | 5 | 4.35 | 9.25 | 83.3 | 50.7 | 14.4 | -5.1 | 12.90 |
| S1/3 | 23 | 4.50 | 9.70 | 87.3 | 50.7 | 10.2 | -5.1 | 13.47 |
| S1/4 | 28 | 4.25 | 9.25 | 83.3 | 46.7 | 14.4 | -7.9 | - |
| S1/5 | 46 | 4.55 | 10.05 | 90.5 | 48.0 | 6.9 | -6.9 | 13.11 |
| S1/6 | 71 | 4.75 | 9.70 | 87.3 | 60.7 | 10.2 | 1.9 | 12.44 |
| S1/7 | 101 | 4.65 | 9.85 | 88.7 | 54.7 | 8.8 | -2.3 | 11.38 |
| S1/8 | 166 | 5.30 | 9.70 | 87.3 | 82.7 | 10.2 | 17.1 | 1.80 |
| S1/9 | 191 | 4.80 | 8.40 | 75.6 | 80.0 | 22.2 | 15.3 | 2.46 |
| S1/10 | 219 | 5.10 | 6.70 | 60.3 | 114.7 | 38.0 | 39.3 | 3.41 |
| S1/11 | 243 | 4.90 | 6.00 | 54.0 | 116.0 | 44.4 | 40.3 | 2.70 |
| S1/12 | 267 | 4.85 | 6.05 | 54.5 | 113.3 | 44.0 | 38.4 | 2.16 |
| S1/13 | 290 | 4.75 | 5.85 | 52.7 | 112.0 | 45.8 | 37.5 | 1.76 |

# ANNEX II

## INFLUENCE OF WATER ADDITION AND SEED CONCENTRATION - RESULTS

Table II.1 - Test S5 results

| Sample ID | Time | Concentration | | Recovery yield | |
|---|---|---|---|---|---|
| | | Al | NaOH | Al | NaOH |
| | [h] | [g/L] | [g/L] | [%] | [%] |
| S5/0 | 0 | 154.8 | 90.7 | 0.0 | 0.0 |
| S5/1 | 21 | 133.2 | 98.7 | 14.0 | 3.5 |
| S5/2 | 46 | 117.0 | 138.7 | 24.4 | 20.9 |
| S5/3 | 70 | 105.3 | 150.0 | 32.0 | 25.9 |
| S5/4 | 94 | 104.9 | 154.7 | 32.3 | 27.9 |
| S5/5 | 117 | 99.0 | 159.3 | 36.0 | 29.9 |
| S5/6 | 163 | 94.5 | 168.0 | 39.0 | 33.7 |
| S5/7 | 190 | 90.9 | 169.3 | 41.3 | 34.3 |
| S5/8 | 215 | 94.5 | 168.0 | 39.0 | 33.7 |

Table II.2 - Test S6 results

| Sample ID | Time | Concentration | | Recovery yield | |
|---|---|---|---|---|---|
| | | Al | NaOH | Al | NaOH |
| | [h] | [g/L] | [g/L] | [%] | [%] |
| S6/0 | 0 | 119.1 | 69.7 | 0.0 | 0.0 |
| S6/1 | 21 | 107.6 | 62.7 | 9.7 | -4.0 |
| S6/2 | 46 | 96.3 | 93.3 | 19.1 | 13.4 |
| S6/3 | 70 | 77.4 | 117.3 | 35.0 | 27.0 |
| S6/4 | 94 | 67.5 | 136.0 | 43.3 | 37.5 |
| S6/5 | 117 | 65.7 | 134.7 | 44.8 | 36.8 |
| S6/6 | 163 | 60.3 | 146.7 | 49.4 | 43.6 |
| S6/7 | 190 | 59.4 | 148.0 | 50.1 | 44.3 |
| S6/8 | 215 | 59.4 | 152.0 | 50.1 | 46.6 |

Table II.3 - Test S7 results

| Sample ID | Time | Concentration | | Recovery yield | |
|---|---|---|---|---|---|
| | | Al | NaOH | Al | NaOH |
| | [h] | [g/L] | [g/L] | [%] | [%] |
| S7/0 | 0 | 96.8 | 56.7 | 0.0 | 0.0 |
| S7/1 | 21 | 92.7 | 46.7 | 4.2 | -7.0 |
| S7/2 | 46 | 83.3 | 60.7 | 14.0 | 2.8 |
| S7/3 | 70 | 78.3 | 80.0 | 19.1 | 16.3 |
| S7/4 | 94 | 64.8 | 96.0 | 33.0 | 27.4 |
| S7/5 | 117 | 58.5 | 109.3 | 39.5 | 36.7 |
| S7/6 | 163 | 54.0 | 116.0 | 44.2 | 41.4 |
| S7/7 | 190 | 52.2 | 118.7 | 46.0 | 43.2 |
| S7/8 | 215 | 51.3 | 116.0 | 47.0 | 41.4 |

Table II.4 - Test S8 results

| Sample ID | Time | Concentration | | Recovery yield | |
|---|---|---|---|---|---|
| | | Al | NaOH | Al | NaOH |
| | [h] | [g/L] | [g/L] | [%] | [%] |
| S8/0 | 0 | 119.1 | 69.7 | 0.0 | 0.0 |
| S8/1 | 21 | 109.8 | 57.3 | 7.8 | -7.0 |
| S8/2 | 46 | 106.2 | 74.7 | 10.8 | 2.8 |
| S8/3 | 70 | 81.0 | 110.0 | 32.0 | 22.8 |
| S8/4 | 94 | 69.3 | 133.3 | 41.8 | 36.0 |
| S8/5 | 117 | 65.3 | 141.3 | 45.2 | 40.6 |
| S8/6 | 163 | 63.5 | 152.0 | 46.7 | 46.6 |
| S8/7 | 190 | 58.1 | 152.0 | 51.3 | 46.6 |
| S8/8 | 215 | 57.2 | 149.3 | 52.0 | 45.1 |

Table II.5 - Test S9 results

| Sample ID | Time | Concentration | | Recovery yield | |
|---|---|---|---|---|---|
| | | Al | NaOH | Al | NaOH |
| | [h] | [g/L] | [g/L] | [%] | [%] |
| S9/0 | 0 | 119.1 | 69.7 | 0.0 | 0.0 |
| S9/1 | 21 | 105.3 | 76.0 | 11.6 | 3.5 |
| S9/2 | 46 | 85.5 | 105.3 | 28.2 | 20.2 |
| S9/3 | 70 | 72.0 | 133.3 | 39.5 | 36.0 |
| S9/4 | 94 | 66.2 | 142.0 | 44.4 | 40.9 |
| S9/5 | 117 | 62.1 | 144.0 | 47.8 | 42.1 |
| S9/6 | 163 | 61.7 | 154.7 | 48.2 | 48.1 |
| S9/7 | 190 | 54.9 | 146.7 | 53.9 | 43.6 |
| S9/8 | 215 | 57.6 | 154.7 | 51.6 | 48.1 |

# ANNEX III

## FACTORIAL PROGRAM - RESULTS

Table III.1 – Test S10 results

| Sample ID | Time | Concentration | | Recovery yield | |
|---|---|---|---|---|---|
| | | Al | NaOH | Al | NaOH |
| | [h] | [g/L] | [g/L] | [%] | [%] |
| S10/0 | 0 | 154.8 | 90.7 | 0.0 | 0.0 |
| S10/1 | 22 | 137.7 | 80.0 | 11.0 | -4.6 |
| S10/2 | 46 | 127.8 | 106.7 | 17.4 | 7.0 |
| S10/3 | 70 | 113.4 | 132.0 | 26.7 | 18.0 |
| S10/4 | 95 | 108.0 | 144.0 | 30.2 | 23.2 |
| S10/5 | 118 | 103.5 | 150.7 | 33.1 | 26.2 |
| S10/6 | 142 | 101.7 | 157.3 | 34.3 | 29.1 |
| S10/7 | 190 | 96.3 | 157.3 | 37.8 | 29.1 |
| S10/8 | 215 | 98.1 | 158.7 | 36.6 | 29.6 |

Table III.2 – Test S11 results

| Sample ID | Time | Concentration | | Recovery yield | |
|---|---|---|---|---|---|
| | | Al | NaOH | Al | NaOH |
| | [h] | [g/L] | [g/L] | [%] | [%] |
| S11/0 | 0 | 96.8 | 56.7 | 0.0 | 0.0 |
| S11/1 | 22 | 90.0 | 46.7 | 7.0 | -7.0 |
| S11/2 | 46 | 85.5 | 61.3 | 11.6 | 3.3 |
| S11/3 | 70 | 84.6 | 74.7 | 12.6 | 12.6 |
| S11/4 | 95 | 83.7 | 64.0 | 13.5 | 5.1 |
| S11/5 | 118 | 81.0 | 72.0 | 16.3 | 10.7 |
| S11/6 | 142 | 72.0 | 81.3 | 25.6 | 17.2 |
| S11/7 | 190 | 61.2 | 97.3 | 36.7 | 28.4 |
| S11/8 | 215 | 59.4 | 104.0 | 38.6 | 33.0 |

Table III.3 – Test S12 results

| Sample ID | Time | Concentration | | Recovery yield | |
|---|---|---|---|---|---|
| | | Al | NaOH | Al | NaOH |
| | [h] | [g/L] | [g/L] | [%] | [%] |
| S12/0 | 0 | 154.8 | 90.7 | 0.0 | 0.0 |
| S12/1 | 22 | 129.6 | 88.0 | 16.3 | -1.2 |
| S12/2 | 46 | 117.0 | 110.7 | 24.4 | 8.7 |
| S12/3 | 70 | 104.4 | 125.3 | 32.6 | 15.1 |
| S12/4 | 95 | 103.5 | 138.7 | 33.1 | 20.9 |
| S12/5 | 118 | 99.9 | 148.0 | 35.5 | 25.0 |
| S12/6 | 142 | 96.3 | 149.3 | 37.8 | 25.6 |
| S12/7 | 190 | 94.5 | 160.0 | 39.0 | 30.2 |
| S12/8 | 215 | 95.4 | 158.7 | 38.4 | 29.6 |

Table III.4 – Test S13 results

| Sample ID | Time | Concentration | | Recovery yield | |
|---|---|---|---|---|---|
| | | Al | NaOH | Al | NaOH |
| | [h] | [g/L] | [g/L] | [%] | [%] |
| S13/0 | 0 | 96.8 | 56.7 | 0.0 | 0.0 |
| S13/1 | 22 | 89.1 | 56.0 | 7.9 | -0.5 |
| S13/2 | 46 | 88.2 | 53.3 | 8.8 | -2.3 |
| S13/3 | 70 | 86.4 | 64.0 | 10.7 | 5.1 |
| S13/4 | 95 | 89.1 | 60.0 | 7.9 | 2.3 |
| S13/5 | 118 | 84.6 | 66.7 | 12.6 | 7.0 |
| S13/6 | 142 | 81.0 | 72.0 | 16.3 | 10.7 |
| S13/7 | 190 | 64.8 | 96.0 | 33.0 | 27.4 |
| S13/8 | 215 | 63.9 | 97.3 | 34.0 | 28.4 |

Table III.5 – Test S14 results

| Sample ID | Time | Concentration | | Recovery yield | |
|---|---|---|---|---|---|
| | | Al | NaOH | Al | NaOH |
| | [h] | [g/L] | [g/L] | [%] | [%] |
| S14/0 | 0 | 154.8 | 90.7 | 0.0 | 0.0 |
| S14/1 | 22 | 126.0 | 93.3 | 18.6 | 1.2 |
| S14/2 | 46 | 117.0 | 122.7 | 24.4 | 13.9 |
| S14/3 | 70 | 108.0 | 132.0 | 30.2 | 18.0 |
| S14/4 | 95 | 103.5 | 146.7 | 33.1 | 24.4 |
| S14/5 | 118 | 99.0 | 153.3 | 36.0 | 27.3 |
| S14/6 | 142 | 98.1 | 154.7 | 36.6 | 27.9 |
| S14/7 | 190 | 93.6 | 161.3 | 39.5 | 30.8 |
| S14/8 | 215 | 93.6 | 165.3 | 39.5 | 32.5 |

Table III.6 – Test S15 results

| Sample ID | Time | Concentration | | Recovery yield | |
|---|---|---|---|---|---|
| | | Al | NaOH | Al | NaOH |
| | [h] | [g/L] | [g/L] | [%] | [%] |
| S15/0 | 0 | 96.8 | 56.7 | 0.0 | 0.0 |
| S15/1 | 22 | 88.2 | 57.3 | 8.8 | 0.5 |
| S15/2 | 46 | 83.7 | 60.0 | 13.5 | 2.3 |
| S15/3 | 70 | 84.6 | 58.7 | 12.6 | 1.4 |
| S15/4 | 95 | 79.2 | 74.7 | 18.1 | 12.6 |
| S15/5 | 118 | 71.1 | 82.7 | 26.5 | 18.1 |
| S15/6 | 142 | 65.7 | 90.7 | 32.1 | 23.7 |
| S15/7 | 190 | 58.5 | 101.3 | 39.5 | 31.1 |
| S15/8 | 215 | 58.5 | 101.3 | 39.5 | 31.1 |

Table III.7 – Tests SI, SII, SIII, SIV results

| Time | SI | | SII | | SIII | | SIV | |
|---|---|---|---|---|---|---|---|---|
| | Recovery yield | | Recovery yield | | Recovery yield | | Recovery yield | |
| | Al | NaOH | Al | NaOH | Al | NaOH | Al | NaOH |
| [h] | [%] | [%] | [%] | [%] | [%] | [%] | [%] | [%] |
| 0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 |
| 24 | 9.5 | 1.7 | 13.8 | 2.3 | 15.5 | 0.1 | 11.2 | 6.6 |
| 48 | 13.8 | 4.8 | 17.2 | 5.3 | 23.1 | 1.9 | 16.4 | 8.5 |
| 72 | 20.7 | 17.0 | 26.7 | 10.8 | 29.3 | 7.6 | 24.1 | 14.0 |
| 96 | 30.2 | 30.0 | 33.2 | 26.1 | 31.0 | 20.9 | 27.1 | 23.0 |
| 144 | 33.6 | 31.0 | 35.3 | 27.6 | 34.5 | 22.3 | 30.9 | 29.7 |
| 192 | 37.1 | 32.5 | 40.7 | 29.2 | 37.1 | 25.6 | 36.7 | 32.8 |
| 216 | 37.9 | 34.0 | 42.1 | 30.8 | 40.9 | 27.9 | 40.1 | 33.1 |

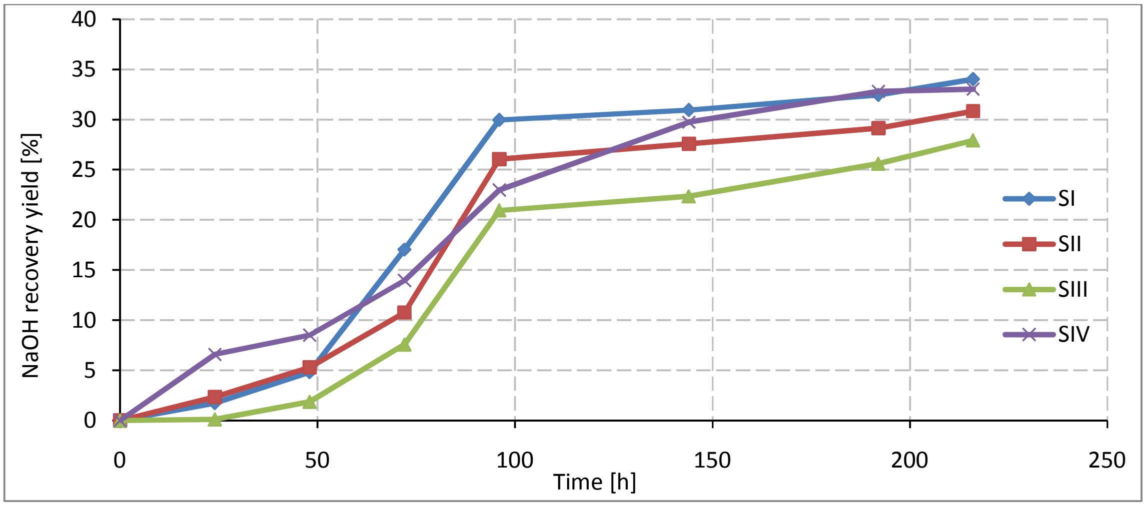


Figure III.1 – Temporal evolution of caustic soda recovery yield in tests SI, SII, SIII, SIV

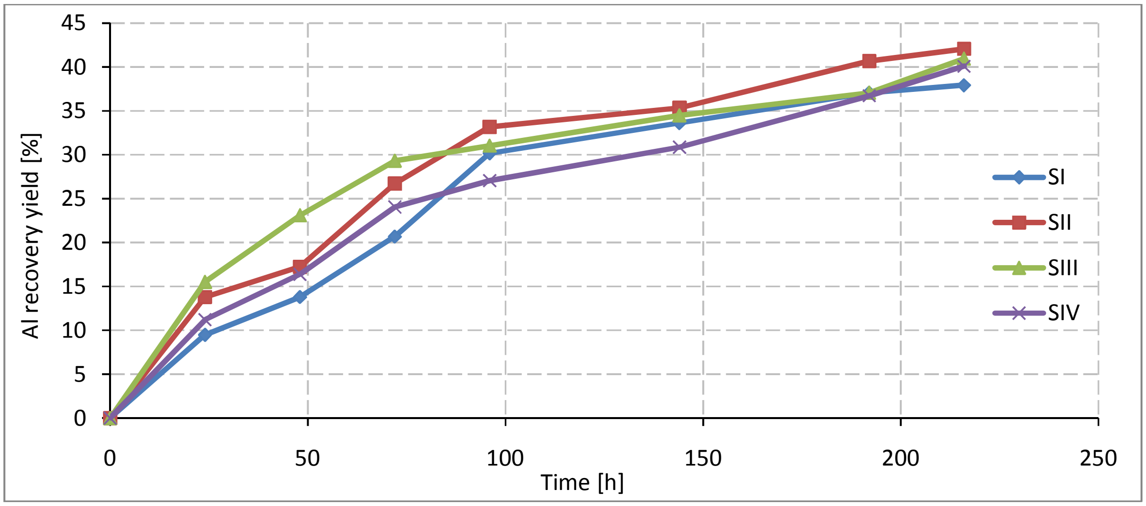


Figure III.2 – Temporal evolution of aluminum recovery yield in tests SI, SII, SIII, SIV

# ANNEX IV

## ANALYSIS OF VARIANCE OF FACTORS - RESULTS

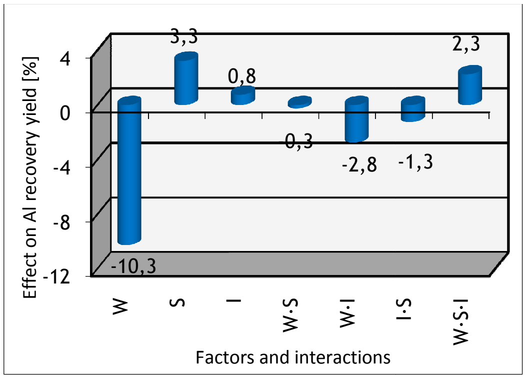


Figure IV.1 – Factors and interactions effects on Al recovery yield. 46 h.

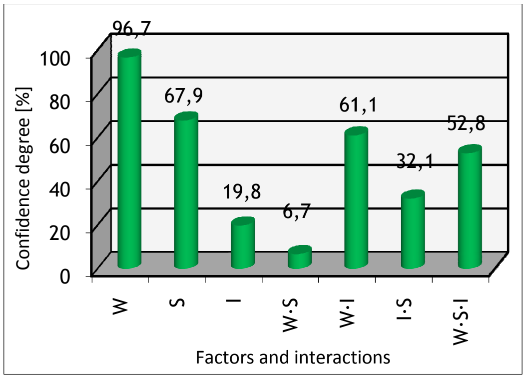


Figure IV.2 – Confidence degrees on effects on Al recovery yield. 46 h.

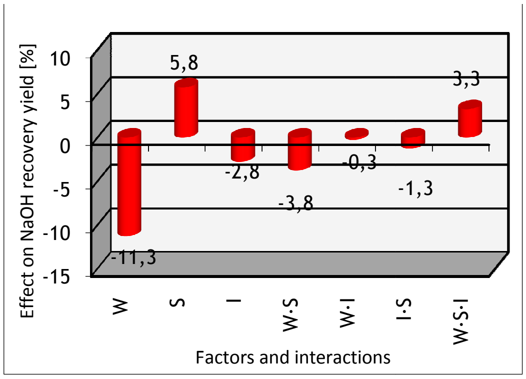


Figure IV.3 – Factors and interactions effects on NaOH recovery yield. 46 h.

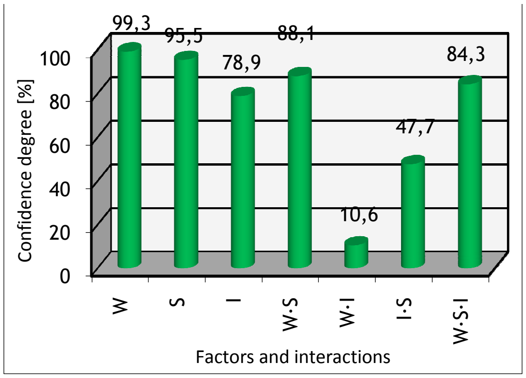


Figure IV.4 – Confidence degrees on effects on NaOH recovery yield. 46 h.

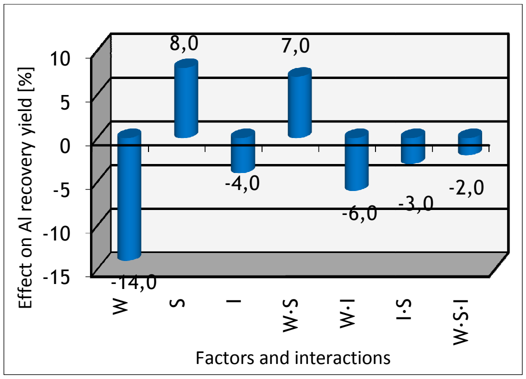


Figure IV.5 – Factors and interactions effects on Al recovery yield. 95 h.

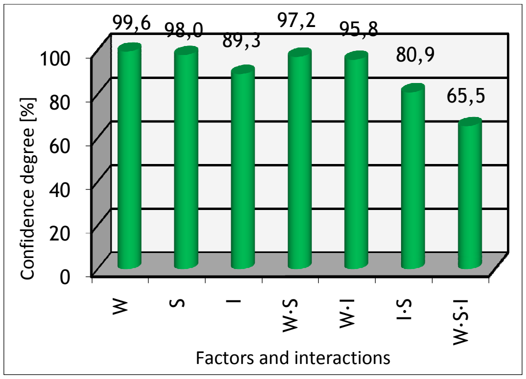


Figure IV.6 – Confidence degrees on effects on Al recovery yield. 95 h.

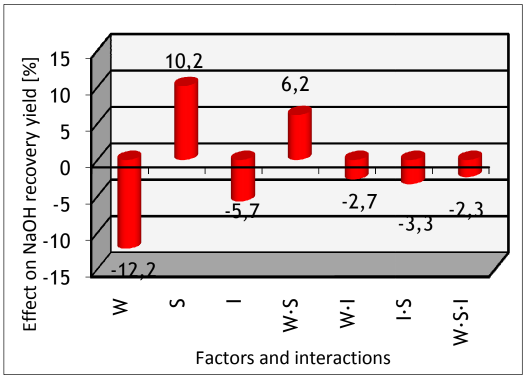


Figure IV.7 – Factors and interactions effects on NaOH recovery yield. 95 h.

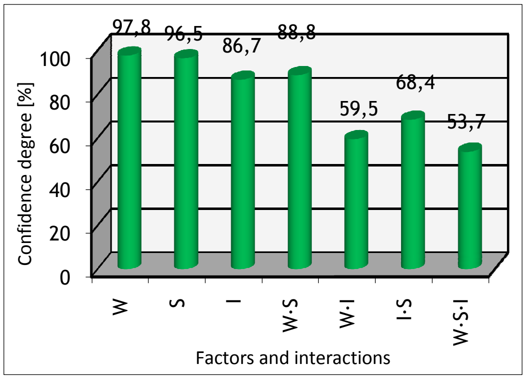


Figure IV.8 – Confidence degrees on effects on NaOH recovery yield. 95 h.

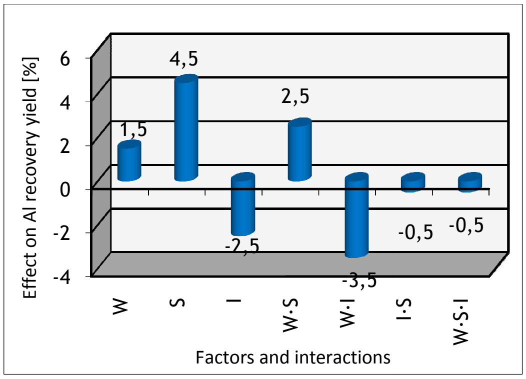


Figure IV.9 – Factors and interactions effects on Al recovery yield. 215 h.

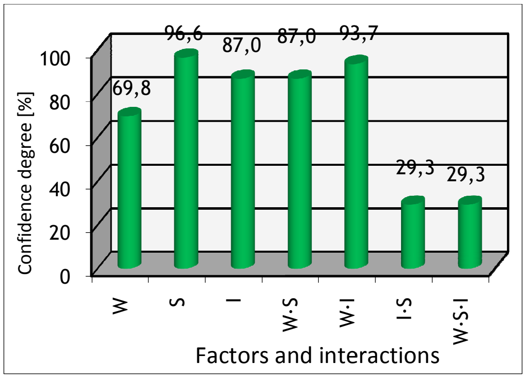


Figure IV.10 – Confidence degrees on effects on Al recovery yield. 215 h.

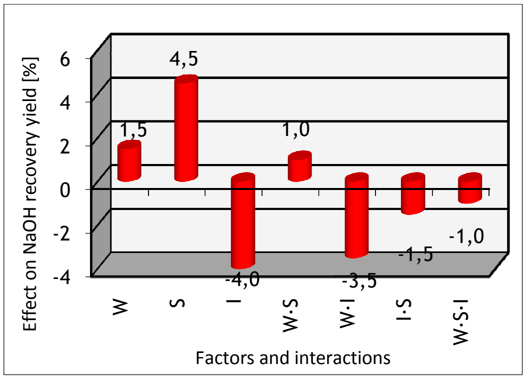


Figure IV.11 – Factors and interactions effects on NaOH recovery yield. 215 h.

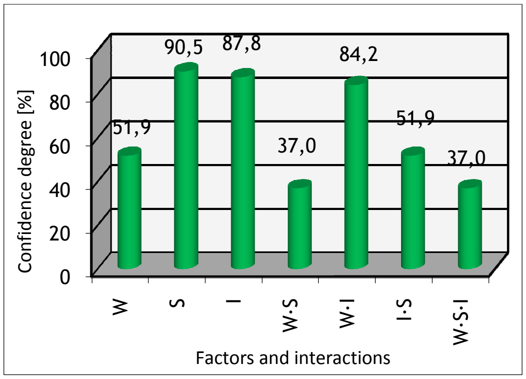


Figure IV.12 – Confidence degrees on effects on NaOH recovery yield. 215 h.

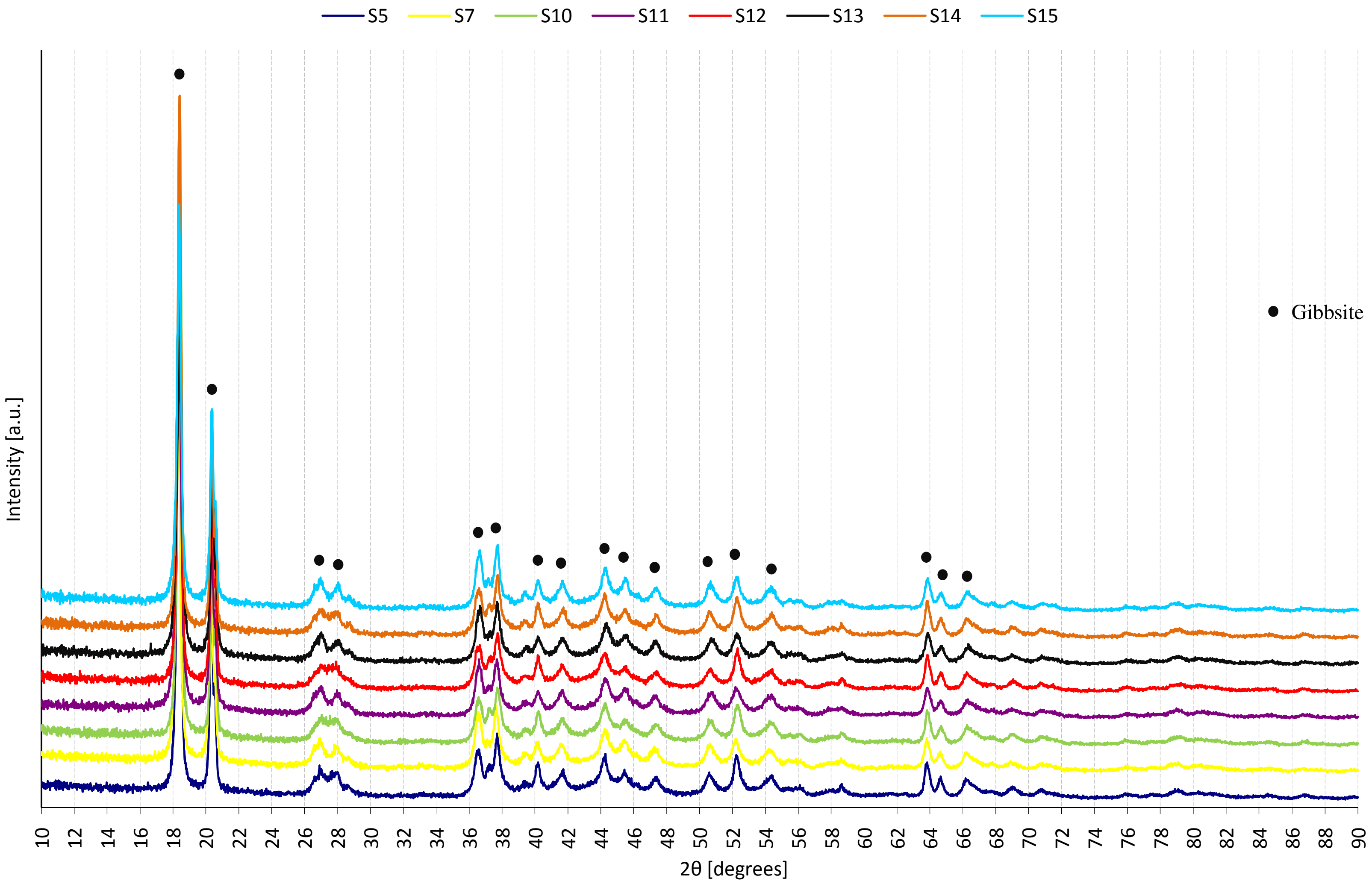


Figure V.1 – X-Ray diffraction patterns of the byproduct produced in the factorial program tests.

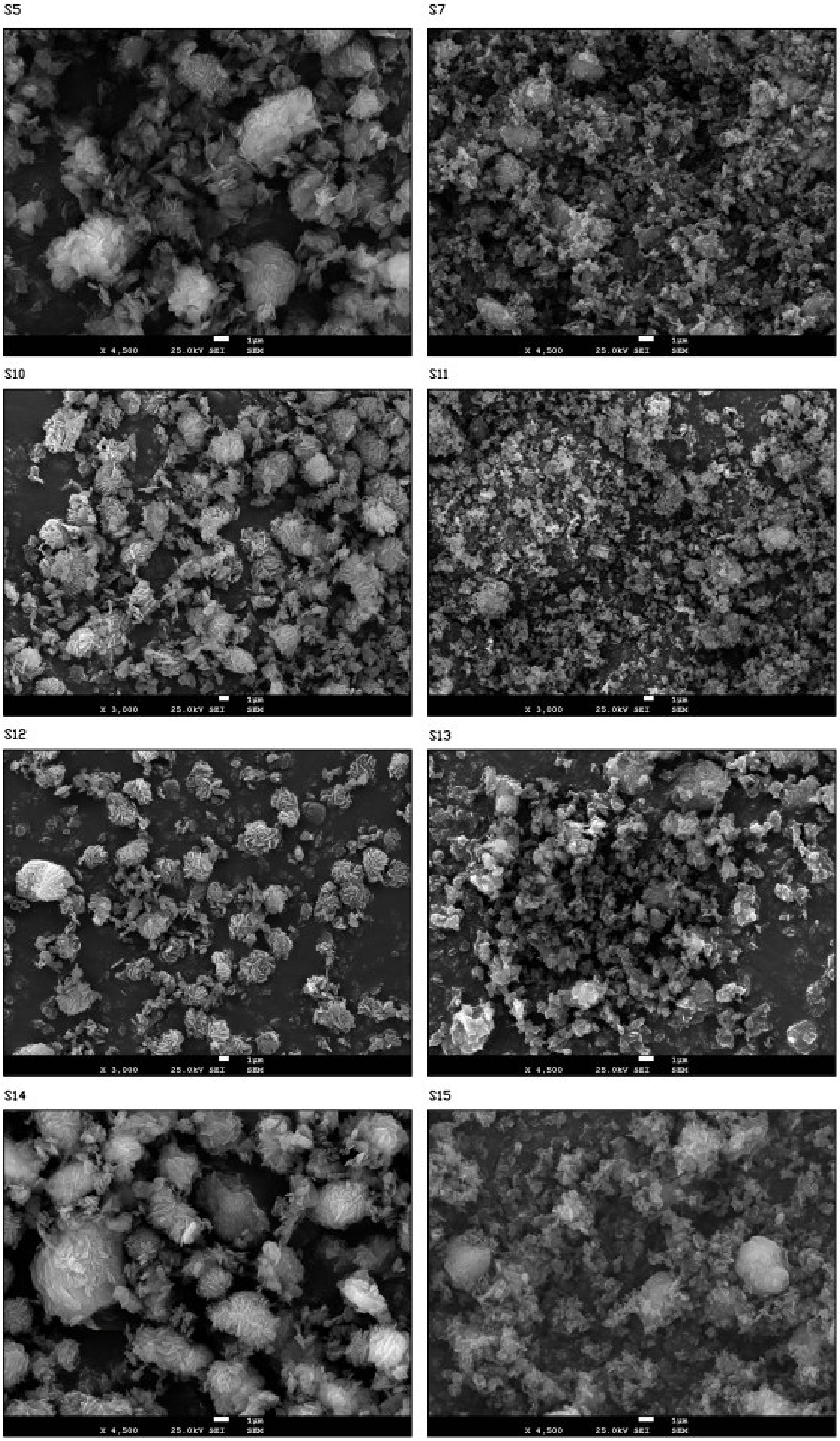


Figure V.2 – Low-magnification SEM images (x3000 and x4500) of the gibbsite produced in the factorial program tests.

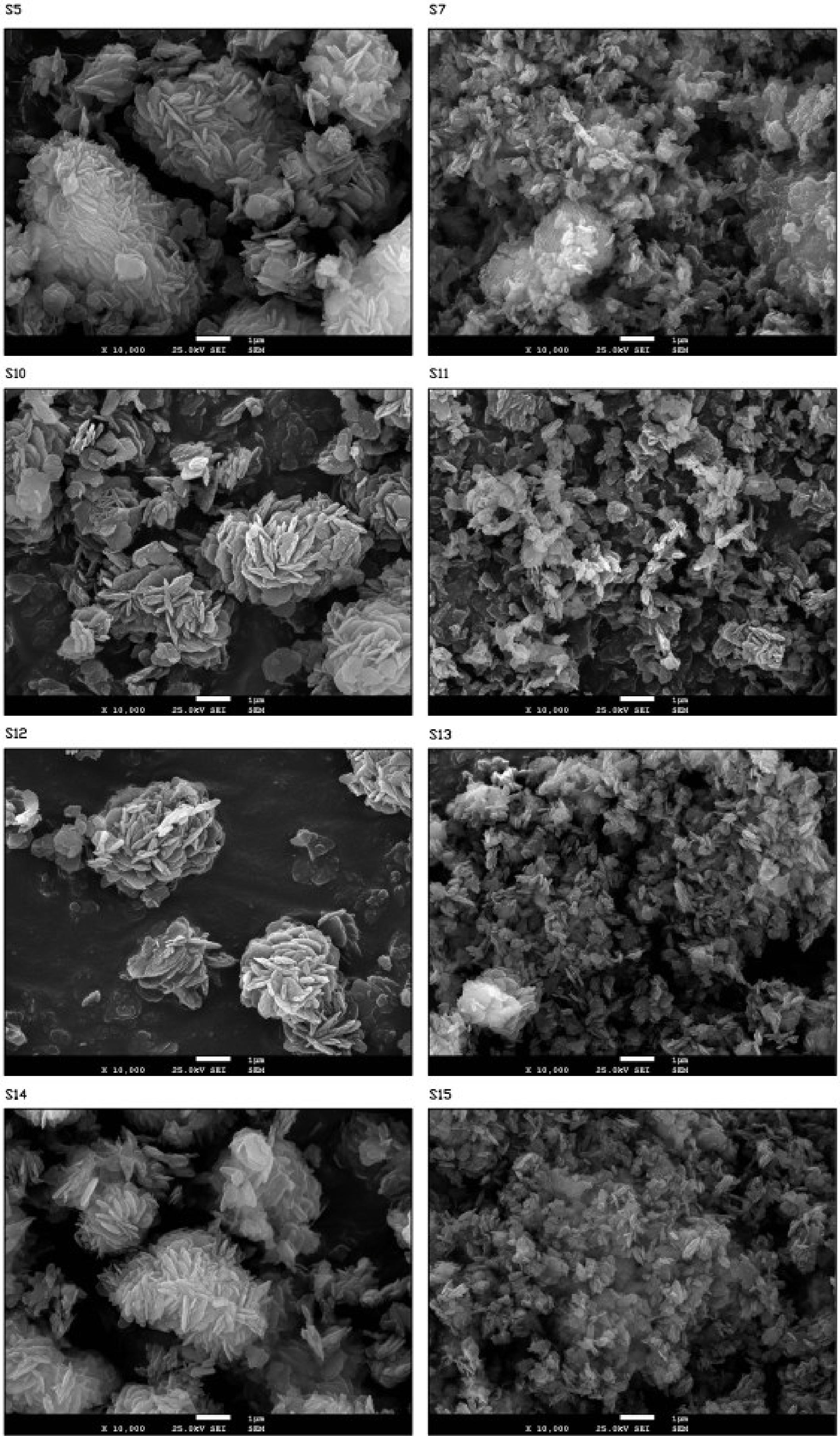
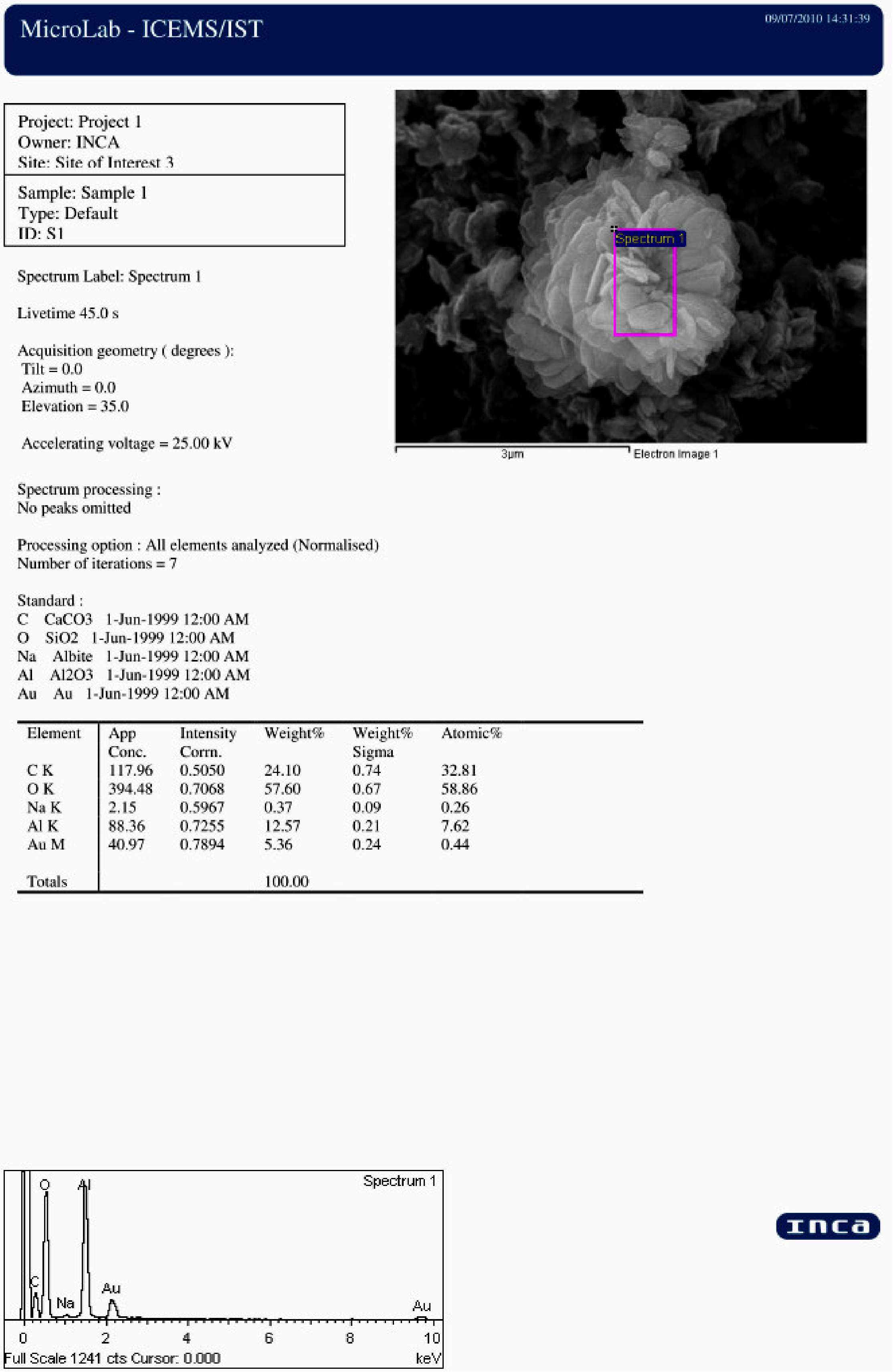

S5 S7 S10 S11 S12 S13 S14 S15

Figure V.3 – High-magnification SEM images (x10000) of the gibbsite produced in the factorial program tests.



MicroLab - ICEMS/IST

09/07/2010 14:31:39

Project: Project 1
Owner: INCA
Site: Site of Interest 3

Sample: Sample 1
Type: Default
ID: S1

Spectrum Label: Spectrum 1

Livetime 45.0 s

Acquisition geometry ( degrees ):
Tilt = 0.0
Azimuth = 0.0
Elevation = 35.0

Accelerating voltage = 25.00 kV

Spectrum processing :
No peaks omitted

Processing option : All elements analyzed (Normalised)
Number of iterations = 7

Standard :
C CaCO3 1-Jun-1999 12:00 AM
O SiO2 1-Jun-1999 12:00 AM
Na Albite 1-Jun-1999 12:00 AM
Al Al2O3 1-Jun-1999 12:00 AM
Au Au 1-Jun-1999 12:00 AM

| Element | App Conc. | Intensity Corrn. | Weight% | Weight% Sigma | Atomic% |
|---|---|---|---|---|---|
| C K | 117.96 | 0.5050 | 24.10 | 0.74 | 32.81 |
| O K | 394.48 | 0.7068 | 57.60 | 0.67 | 58.86 |
| Na K | 2.15 | 0.5967 | 0.37 | 0.09 | 0.26 |
| Al K | 88.36 | 0.7255 | 12.57 | 0.21 | 7.62 |
| Au M | 40.97 | 0.7894 | 5.36 | 0.24 | 0.44 |
| Totals | | | 100.00 | | |

Figure V.4 – Demonstrative EDS analysis on test S1.

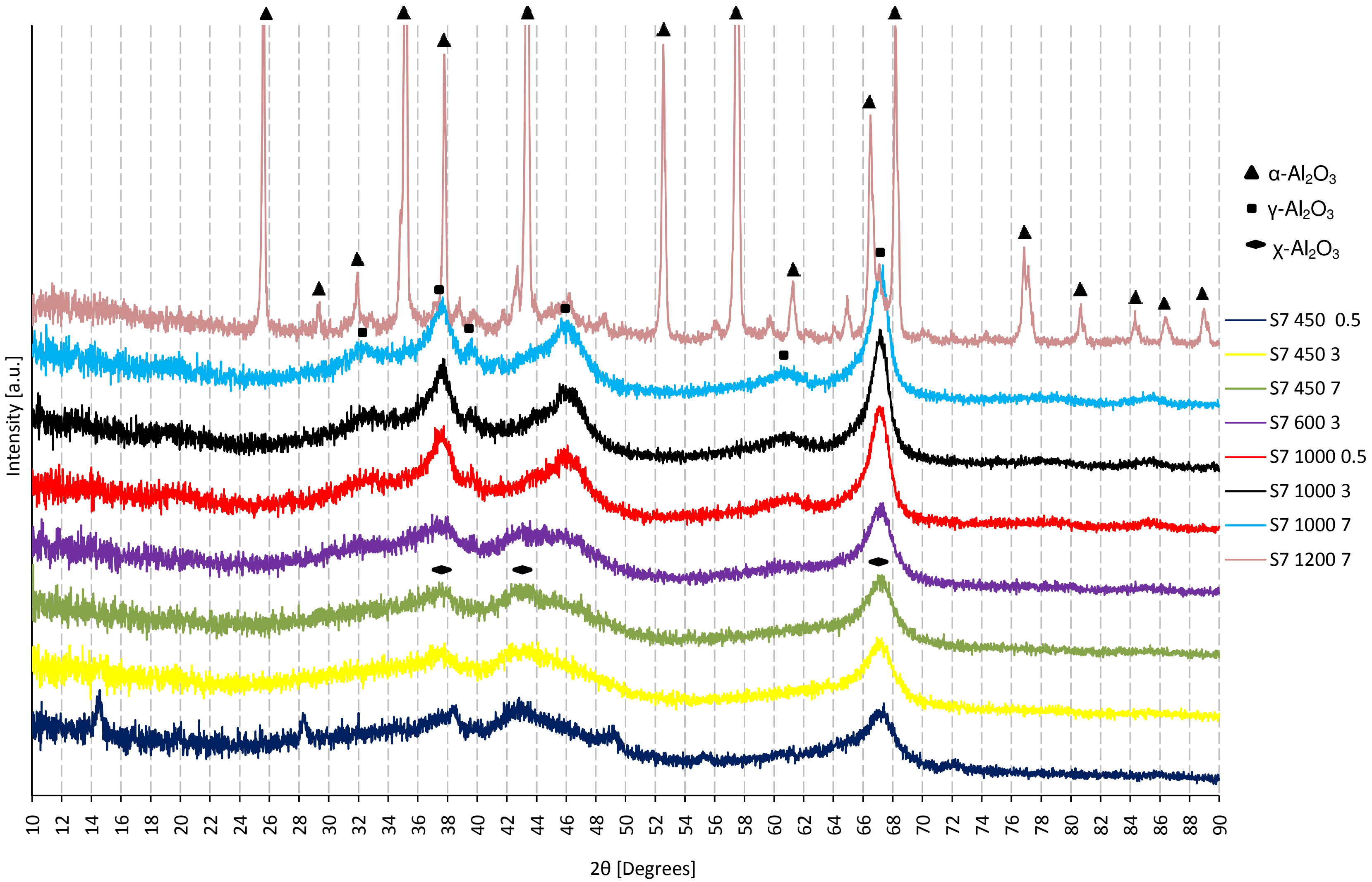
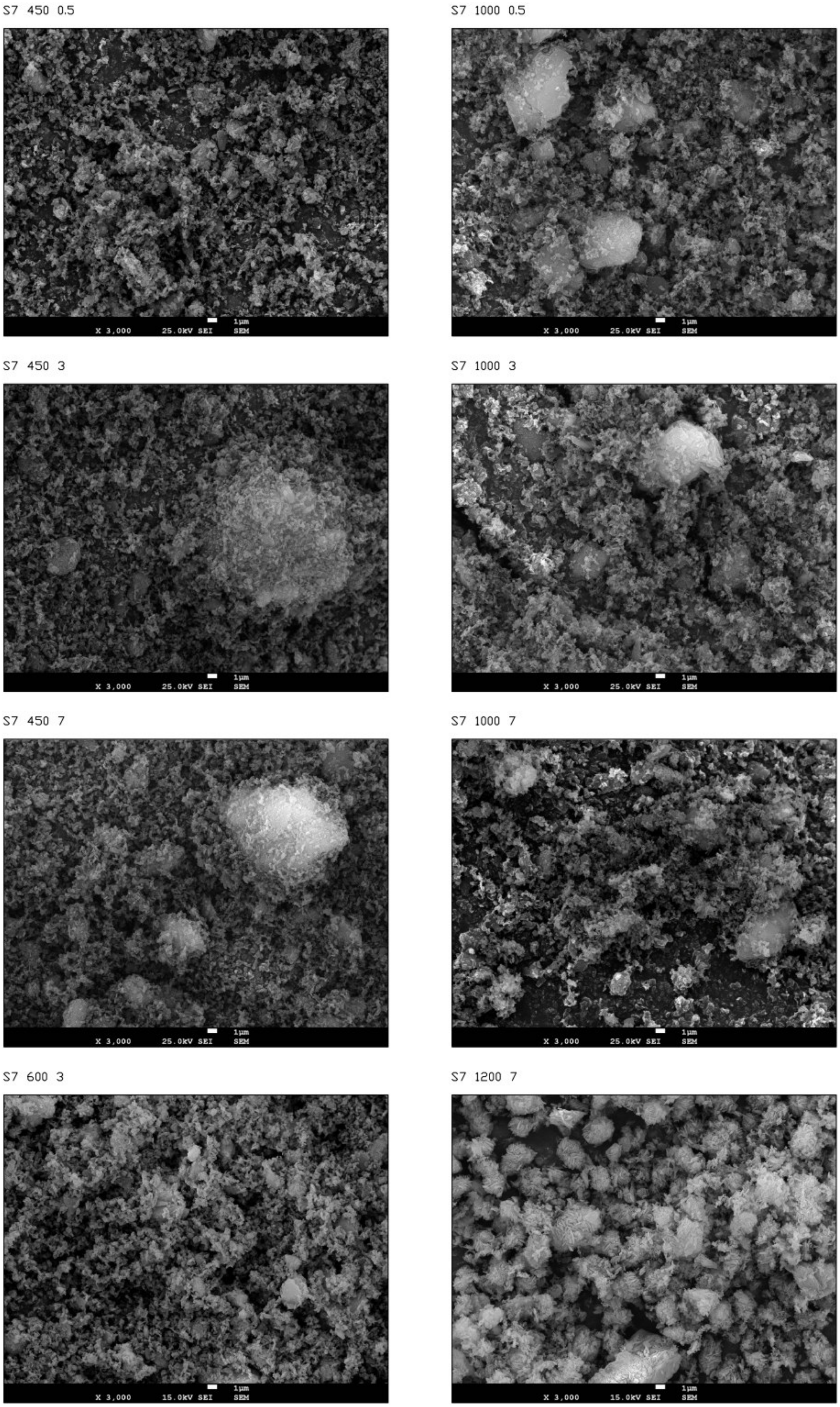


Figure VI.1 – X-Ray diffraction patterns of S7 calcined samples. Effect of heating temperature and time on aluminas' structure.



S7 450 0.5

S7 1000 0.5

S7 450 3

S7 1000 3

S7 450 7

S7 1000 7

S7 600 3

S7 1200 7

Figure VI.2 – Low-magnification SEM images (x3000) of the S7 calcined samples. Influence of temperature and time on aluminas' morphologies.

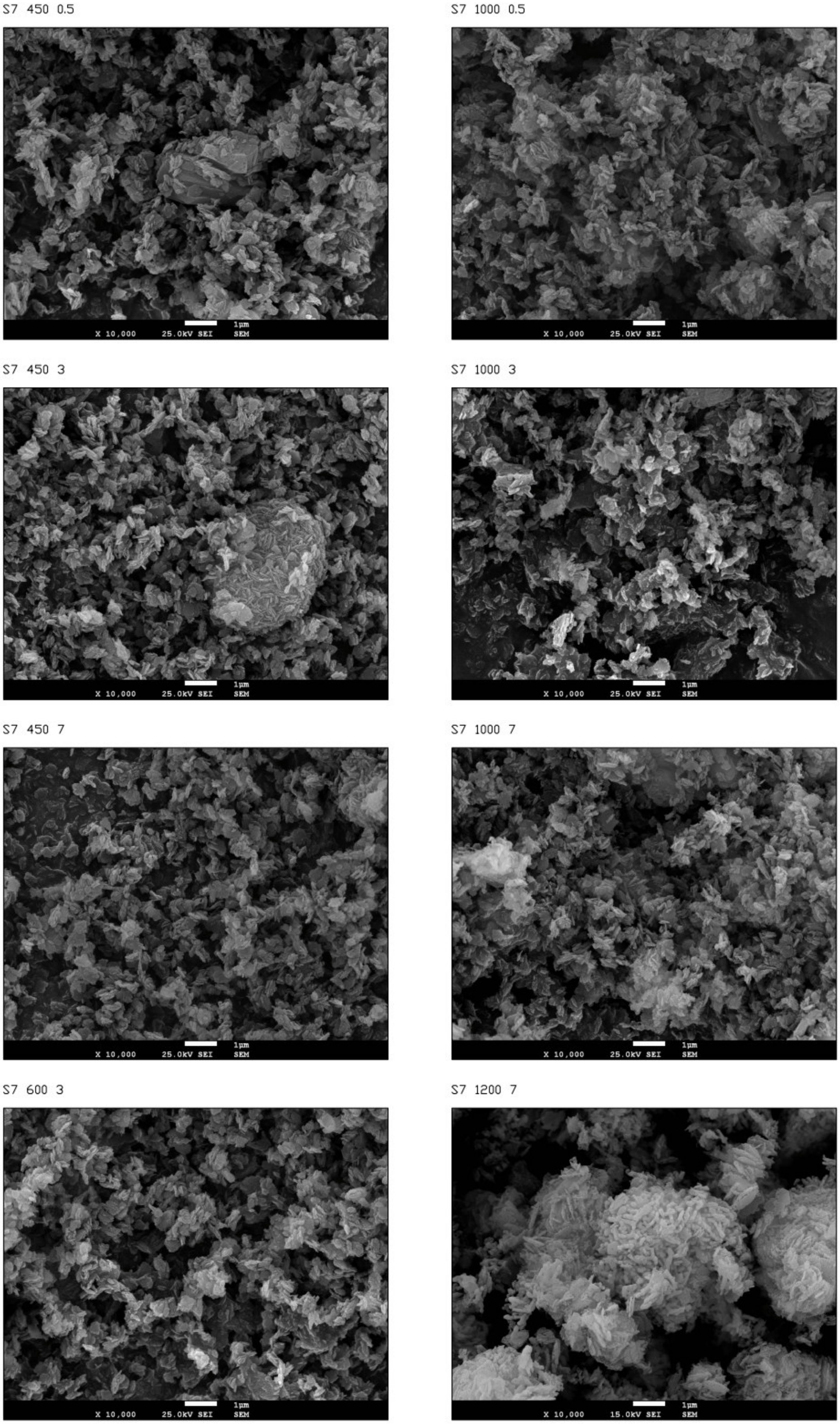


Figure VI.3 – High-magnification SEM images (x10000) of the S7 calcined samples. Influence of temperature and time on aluminas' morphologies.

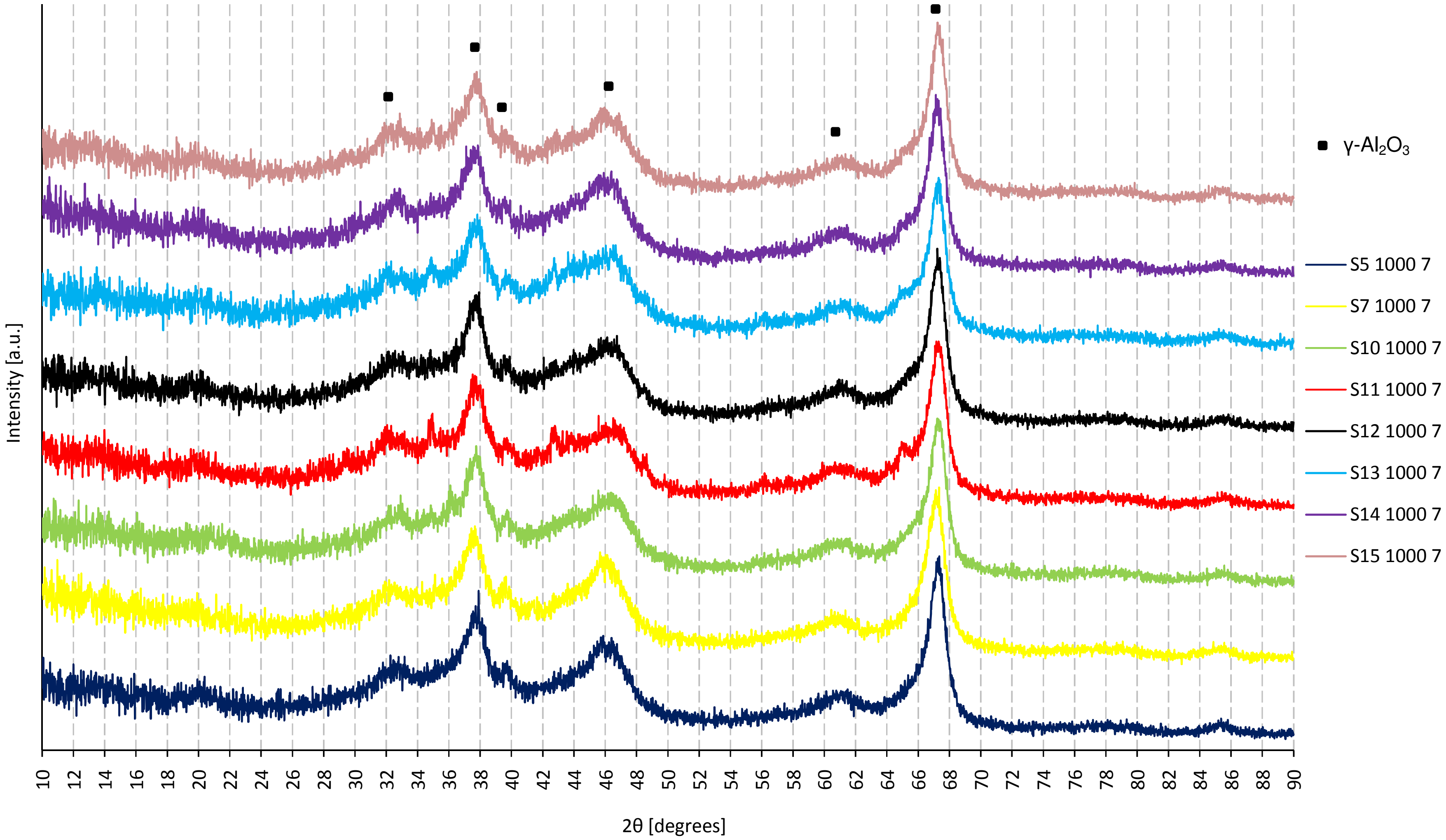


Figure VI.4 – X-Ray diffraction patterns of the factorial program tests calcined samples (1000 °C for 7 h). Effect of starting material on aluminas’ structure.