

## **Alkaline Etching of Aluminum & Its Alloys— A New Caustic Soda Recovery System**

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To date, the various attempts to apply caustic soda recovery systems on long-life and/or high dissolved aluminum content solutions have yielded poor results. It appears that a high aluminum concentration is essential to achieving the good matte finish normally required in most aluminum finishing operations. It also leads to the presence of aluminum complexing agents, however, which prevents proper operation of the caustic soda recovery systems currently on the market. This paper proposes a new specialized soda recovery system that is installed on a rinse tank immediately downstream of the etching tank so that it does not affect the dissolved aluminum concentration. New types of finish-enhancing additives are also considered that do not have any significant effect on the aluminum precipitation reaction. In addition, the treatments proposed in the literature are reviewed and an accurate bibliography is provided.

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## 1 – Introduction

Alkaline etching is a standard procedure applied on aluminum which is to be anodized; by modifying the surface, this procedure can impart an aesthetic effect or finish (1,2). It is performed in caustic soda (NaOH) solutions, at times with additives. With use, the aluminum content in these solutions tends to increase (on the average from 50 to 150 g/l if expressed as  $Al_3^+$ ) depending on the dipping time and, in any case, this constitutes an ecological problem which must be reduced or resolved.

After caustic soda treatment, the aluminum is carefully rinsed in water before subsequent acid neutralization and anodizing. Because there is significant carryover (approximately 0.2 liters per  $m^2$  treated), marked amounts of aluminum (10-30 g  $Al_3^+/m^2$ ) and caustic soda (5-25 g/ $m^2$ ) are introduced into the rinse and effluent waters. The removal of aluminum from the effluent waters is, per se, relatively simple but it produces a great deal of sludge, which then must be disposed of. Moreover, reducing the alkalinity, generated by the caustic soda carried over into the effluents, also gives rise to significant amounts of sludge.

For some time technicians have been seeking recovery and recycling treatments for caustic soda solutions in order to reduce the amount of aluminum and soda (alkalinity) carried over into the effluent waters (3-11). Unfortunately, however, most of these processes are only effective

- a) in the absence of aluminum complexing additives and, therefore,
- b) with low concentrations of dissolved aluminum (on the average 30-50 g/l expressed as  $Al_3^+$ ).

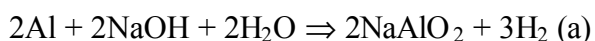
The lack of aluminum complexing additives in etch solutions effectively eliminate the achieving of excellent satin or matt finishing of aluminum, which is generally desired by most aluminum finishers. These finishes are usually only achieved when the aluminum content in the etch bath is allowed to rise to well over 120 g/l expressed as  $Al_3^+$ .

This is the condition encountered in most aluminum finishing plants where aluminum complexing additives cannot be used due to the application of the above-mentioned caustic recovery processes. These caustic recovery processes then become extremely costly, and thus, in many cases, not economically feasible (12-14).

Our present work proposes a recovery and recycling method for alkaline etching solutions which, applied in the downstream rinse tank, makes it possible to manage the caustic soda etch tank in a more standard manner, thus allowing the desired aluminum finish to be achieved.

## 2 – The Chemistry Of Aluminum In Caustic Soda Solutions

When placed in a caustic soda (NaOH) solution, aluminum dissolves according to this chemical reaction:



The aluminum is dissolved in the caustic soda, transforming it into sodium aluminate and releasing hydrogen to the surrounding atmosphere, causing the solution to bubble.

Aluminum is extremely soluble in caustic soda solutions; in fact, it can exceed 7 mol/liter, equivalent to:

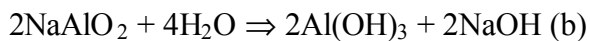
$$7 \times 27 = 189 \text{ g/l Al}^{3+} \text{ or}$$

$$7 \times 82 = 574 \text{ g/l NaAlO}_2$$

(where 27 and 82 are respectively the atomic weight of the aluminum and the molecular weight of the sodium aluminate) if

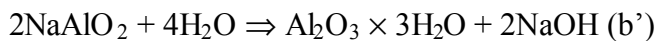
- a) an adequate concentration of free caustic soda (NaOH) is maintained,
- b) the proper temperature is maintained,
- c) adequate complexing agents are added to the solution.

When one of these conditions is not met, the result is sodium aluminate hydrolysis according to the following reaction:

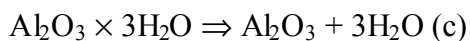


with formation of aluminum hydroxide, which precipitates to the bottom of the tank, and an increase in the free caustic soda in the solution.

As the aluminum hydroxide, formed by reaction (b) which can also be written as:



ages it dehydrates according to the reaction below:



forming a rocky precipitate at the bottom and on the walls of the tank.

In industrial processes, the etching solutions can be divided generally into three categories according to the dissolved aluminum content:

- a) low,
- b) medium,
- c) high,

as indicated in Table 1.

**Table 1 – Examples Of Etching Solutions**

Type	1	2	3
Composition And Operating Parameters	NaOH 50 g/l Al <sub>3</sub> <sup>+</sup> 50 g/l Additive 10 g/l Temp. 40-50 °C Time 2-3 min.	NaOH 70 g/l Al <sub>3</sub> <sup>+</sup> 100 g/l Additive 20 g/l Temp. 50-60 °C Time 5-10 min.	NaOH 100 g/l Al <sub>3</sub> <sup>+</sup> 150 g/l Additive 30 g/l Temp. 50-60 °C Time.15-20 min.
Types Of Additives	Gluconates Or Similar	Gluconates, Polyalcohols, Amine, And Complexing Heavy Metals	Polyalcohols, Amine, Fluidizers, Leveling Agents, And Complexing Heavy Metals
Notes	Not Indispensable	Medium Strength Complexing Agents Are Required	A Fluidizer Is Useful To Improve Rinsability
Application	Industrial Or Brushed Finish	Average Etched Finish	Highly Etched Finish

The Type 1 solutions are quite common in Asia where aluminum finishing is not achieved by varying the dipping times but rather by using a transparent electrophoretic coating process (E.D.) able to give a glossy, semi-glossy or matt effect, after the aluminum has been anodized and colored.

The Type 2 and 3 solutions are more commonly used in North America, South America and Europe where the caustic soda solution must eliminate the extrusion lines, giving the product an extremely white finish. The long dipping times lead to an increase in the dissolved aluminum which, combined with a proportional increase in free caustic soda, produces a highly concentrated, high viscosity solution. Under such conditions, to improve piece rinsability, the addition of a fluidizer and of a heated rinsing process is indicated. The reader who wishes to delve more deeply into the rather complex study of the functions and effects of the *additives* used in caustic soda solutions should see the manuals indicted in the bibliography (1,2).

In industry, a 20,000-liter tank of caustic soda can be used to treat an average of 4 batches per hour of approximately 100 m<sup>2</sup> each. Assuming we use a Type 2 solution, the dissolution rate is an average of 5 g/m<sup>2</sup> per minute of dipping. Assuming an average dipping time of 10 min per batch, the amount of aluminum dissolved into the tank, expressed in Kg/h, is given by the calculation below:

$$\frac{(4 \times 100) \times 5 \times 10}{1000} = 20 \text{ Kg/h of dissolved aluminium}$$

with a caustic soda consumption of:

$$(20/27) \times 40 = 29.6 \text{ Kg/h of caustic soda consumed}$$

Carefully observing the above-mentioned chemical reactions, it is clear that if we could in some way induce reaction (b), all the caustic soda, which had reacted with the aluminum, would revert back to free caustic soda in the solution.

This simple consideration has stimulated researchers to set up methods able to remove the aluminum from etching solutions and recover the caustic soda to be reused by the process.

### **3 – Methods To Recover And Recycle Etching Solutions**

There are two different methods for removing aluminum from the etching solution, thereby transforming the sodium aluminate present and releasing the caustic soda:

- 1) by chemical reaction,
- 2) by hydrolysis.

#### **3.1 – Removal Of The Aluminum By Chemical Reaction**

The most well known process of this type is the one that leads to the production of zeolites (12-14).

The advantage of this process is that it can be applied to any etching solution, or alkaline rinse water, containing aluminum in solution or in slurry. Therefore, it is effective, even in the presence of additives or aluminum complexing agents, which is contrary to the case for the methods indicated below at “point 3.2”.

The anodizer is free to formulate the etching solution to meet his own requirements since the presence and type of complexing agents have little effect on the zeolite production process.

The only drawback to this process is its operating cost; it is, therefore, only economically feasible if the zeolites produced can be sold. Indeed, these zeolites fully meet the quality parameters required by manufacturers of washing machine detergents, both in regards to type and quantity. Normal powder or tablet washing machine detergents contain between 15 and 30% of zeolite A.

Studies performed years ago by one of the authors (21), in co-operation with a well-known manufacturer in this field, confirmed that the zeolites produced by the elimination of aluminum from etching solutions perfectly meet the market requirements.

### 3.1.1 – What Are Zeolites?

Originally the term zeolite was used to indicate a family of natural minerals endowed with a particular property: ion exchange ion and reversible water absorption, hence the name zeolite or "stone that boils" (from Greek zeo = that boils and lithos = stone) (16).

From the structural point of view zeolites are classified as tectosilicates, the backbone of which is produced by the three-dimensional concatenation of tetrahedrons  $TO_4$ , each oxygen being shared by 2 octahedrons. T generally represents aluminum and silicon. The presence of trivalent aluminum in the place of tetravalent silicon yields a negatively charged structure and this must be compensated by cations. The zeolites, therefore, differ from other tectosilicates (i.e. feldspar) as they have a structure of canals and cavities containing compensation cations and water.

The zeolites have the following chemical formula



where M is the compensation cation for valence n and  $y \geq 1$ .

In synthesis products, M is an alkaline or alkaline earth metal and, it is possible to obtain a wide range of zeolites by appropriately varying y.

Many zeolites exist in nature and among them the most well known, the clinoptylolites, have the following formula (17):



These zeolites are known for their capacity to absorb water and exchange ammonium ions which has led to widespread use in the zootechnical sector and in agriculture. Likewise the synthetic zeolites obtained by industrial reaction—adding sodium silicate to alkaline solutions containing aluminum—are also important. The most widely used of these zeolites is type A, commonly used by the detergent industry because of its ability to capture calcium ions. Indeed, thanks to this characteristic, for years now it has replaced phosphates in complexing water hardness. Figure 1 shows a diagram of the structure of zeolites A and Y (16) while Table 2 provides the composition of some zeolites (17).

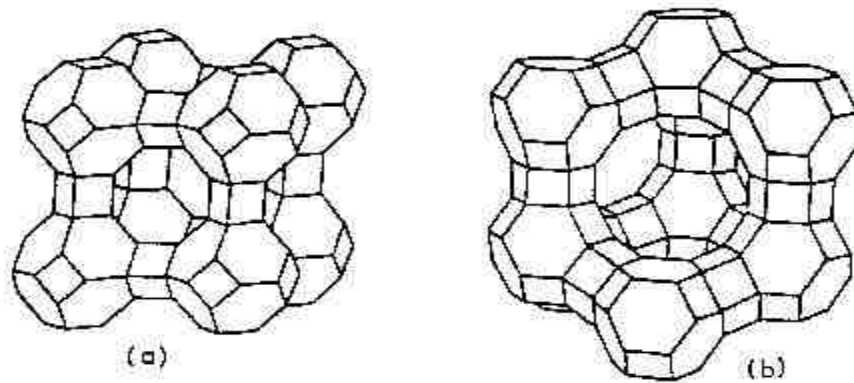


Fig. 1 - Crystallographic Structure of Zeolites "A" and "X" (Or "Y")

**Table 2 – Zeolite Compositions**

<b>Zeolite</b>	<b>Typical Formula</b>
<i>Natural</i>	$\text{Ca}_2[\text{AlO}_2]_4, (\text{SiO}_2)_8]^- \times 13\text{H}_2\text{O}$
Chabazite	$\text{Na}_8[\text{AlO}_2]_8, (\text{SiO}_2)_{40}]^- \times 24\text{H}_2\text{O}$
Mordenite	$(\text{Ca}, \text{Mg}, \text{Na}_2, \text{K}_2)_{4.5}[\text{AlO}_2]_9, (\text{SiO}_2)_{27}]^- \times 27\text{H}_2\text{O}$
Erionite	$(\text{Ca}, \text{Mg}, \text{Na}_2, \text{K}_2)_{29.5}[\text{AlO}_2]_{59}, (\text{SiO}_2)_{133}]^- \times 235\text{H}_2\text{O}$
Faujasite	$\text{Na}_6[\text{AlO}_2]_6, (\text{SiO}_2)_{30}]^- \times 24\text{H}_2\text{O}$
Clinoptilolite	
<i>Synthetic</i>	$\text{Na}_{12}[\text{AlO}_2]_{12}, (\text{SiO}_2)_{12}]^- \times 27\text{H}_2\text{O}$
Zeolite A	$\text{Na}_{86}[\text{AlO}_2]_{86}, (\text{SiO}_2)_{106}]^- \times 264\text{H}_2\text{O}$
Zeolite X	$\text{Na}_{56}[\text{AlO}_2]_{56}, (\text{SiO}_2)_{136}]^- \times 250\text{H}_2\text{O}$
Zeolite Y	

### 3.1.2 – How To Produce Zeolites

The main commercial process of the production of synthetic zeolites is the hydrogel process which uses an aqueous solution of sodium silicate, sodium aluminate and sodium hydroxide. A typical production diagram is given in Figure 2 (18), while Table 5 reports the operating parameters and

molar ratios of some important zeolites. Table 6 gives the material balance and chemical composition of zeolites A, X, Y (16).

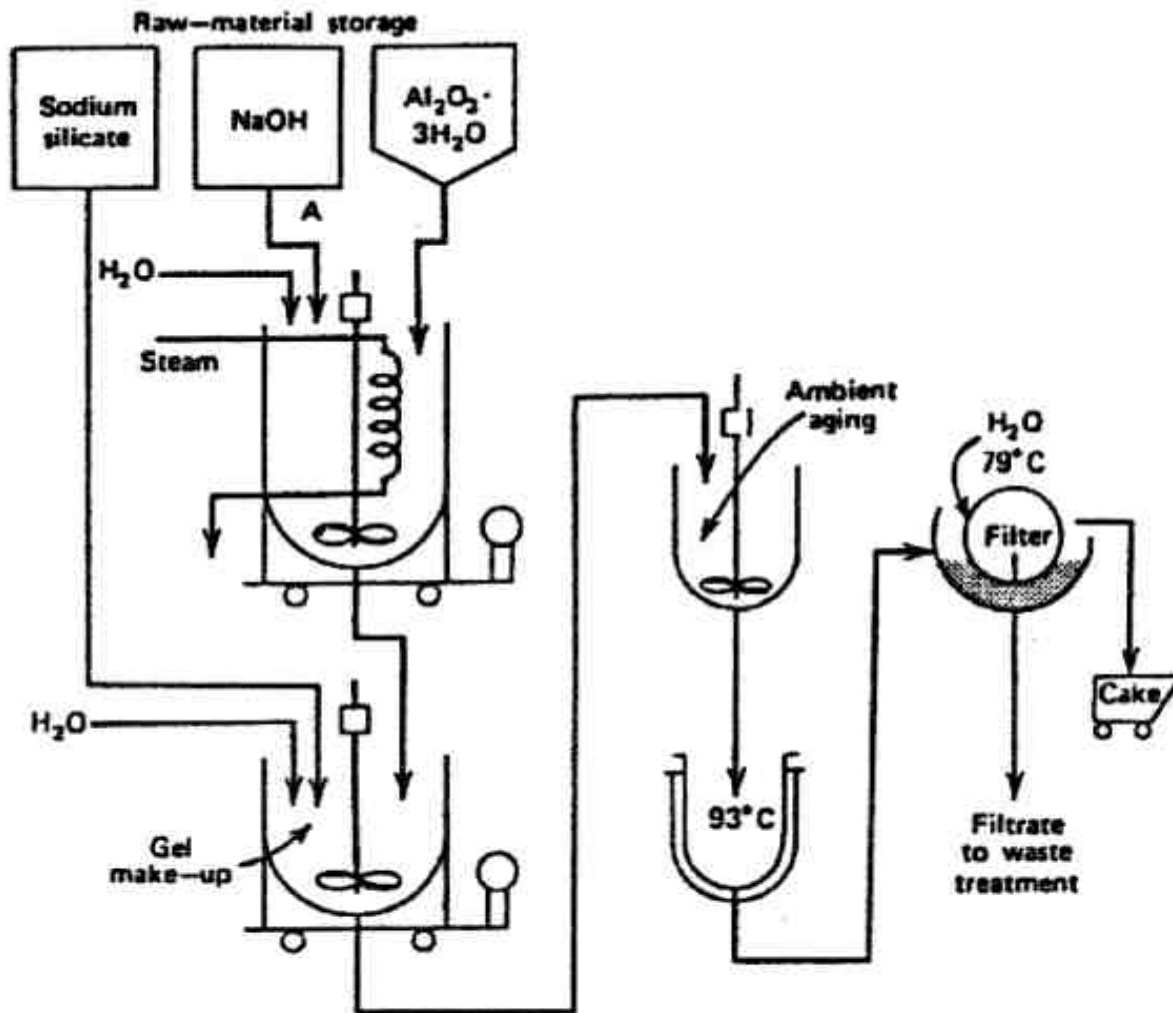


Fig. 2 Hydrogel process. Process flow sheet for the manufacture of zeolite type A, X and Y from reactant hydrogels (15)



**Table 3 – Some Synthetic Zeolites Prepared From Sodium Silicate-Silicate Gel**

Zeolite Type	Typical Composition mol/mol Al <sub>2</sub> O <sub>3</sub>			Reactants	Reactant Temp °C	Zeolite Product Composition mol/mol Al <sub>2</sub> O <sub>3</sub>		
	Na <sub>2</sub> O	SiO <sub>2</sub>	H <sub>2</sub> O			Na <sub>2</sub> O	SiO <sub>2</sub>	H <sub>2</sub> O
<b>A</b>	2	2	35	NaAlO <sub>2</sub> , NaOH, Nasilicate	20-175	1	2	4.5
<b>X</b>	3.6	3	144	NaAlO <sub>2</sub> , NaOH, Nasilicate	20-120	1	2.0-3.0	6
<b>Y</b>	8	20	320	NaAlO <sub>2</sub> , NaOH, coll. SiO <sub>2</sub>	20-175	1	3.0-6.0	9

**Table 4 – Typical Material Balance For The Hydrogel Production Process (a)**

Raw materials	Zeolites		
	A	X	Y
Sodium Silicate (B)	1350	2000	--
SiO <sub>2</sub> , Powder (C )	--	--	1450
Alumina Trihydrate (D )	575	500	340
Caustic, 50% NaOH	870	1600	1400
Water	3135	7687	5300
<i>Gel Composition, Mol Ratio</i>			
Na <sub>2</sub> O	2.04	4.09	4.0
Al <sub>2</sub> O <sub>3</sub>	1	1	1
SiO <sub>2</sub>	1.75	3.0	10.6
H <sub>2</sub> O	70	176	161

- a) To produce 1000 Kg, dry basis,
- b) 9.4% Na<sub>2</sub>O, 28.4% SiO<sub>2</sub>
- c) 95% SiO<sub>2</sub>
- d) 65% Al<sub>2</sub>O<sub>3</sub>, 35% H<sub>2</sub>O

### 3.1.3 – How To Obtain Zeolites From The Etching Solutions

No matter what the specific concentrations and additives used, any etching solution can produce zeolites if treated with the right amount of sodium silicate and left to age at the right temperature (13,14,15, 19,20).

By adequately filtering and rinsing the resulting precipitate to eliminate the excess alkalinity, it is possible to recover a great deal of caustic soda and nearly totally remove the aluminum from the solution treated.

Table 5 gives an experimental example of this treatment (21).

**Table 5 – Production Of Zeolite From An Industrial Etching Solution**

<i>Volume Treated</i>	<i>5 Liters</i>	
<b><i>Composition Of The Initial Solution</i></b>	<b>Concentration (G/L)</b>	<b>Total (G)</b>
Free Caustic Soda	55	275
Dissolved Aluminum	120	600
Complexing Agents	15	75
<b><i>Volume Recovered</i></b>	<b><i>4.5 Liters</i></b>	
<b><i>Composition Of The Recovered Solution</i></b>	<b>Concentration (G/L)</b>	<b>Total (G)</b>
Free Caustic Soda	70	315
Dissolved Aluminum	4.2	18.9
Complexing Agents	12	54
<b><i>Characteristics Of The Zeolite A</i></b>	<b>Produced</b>	<b>Theory</b>
Quantity (G)	2975	3000
Zeolite/Aluminum Ratio	4.96	5.0 (A)
<b><i>Composition (%)</i></b>		(B)
Aluminum (Al <sub>2</sub> O <sub>3</sub> )	27.8	28
Sodium (Na <sub>2</sub> O)	16.7	17.0
Silica (SiO <sub>2</sub> )	33.5	33.0
Water (H <sub>2</sub> O)	22.0	22.0

Notes

(a) the theoretical value is obtained by simple mathematical calculation of the values reported in Table 4.

(b) the composition reported is the one accepted by detergent manufacturers.

The detergent manufacturers prefer to receive zeolites in the form of a stable slurry, the characteristics of which are reported in Table 6. In fact, even when powdered or granulated detergents are being produced, the process normally passes through a fluid mixture where all components are added; after this phase the mixture is dehydrated.

It is not difficult to fall within the parameters indicated in the table as the particle size distribution of the final product, and its exchange capacity, are determined by the physical parameters of the preparation (i.e. temperature, stirring type, length of aging). Contamination is prevented by the use of additives and/or complexing agents, generally already in the starting solution.

**Table 6 – Characteristics Of Zeolites In The Form Of Slurry**

<b>Appearance</b>	<b>Stable Fluid Slurry</b>
Zeolite A Content (1 h at 800° C)	50%
Exchange Capacity (at 24° C)	170-180 mg CaO / g of Anhydrous Zeolite
Brookfield Viscosity	200-1000 cps
Freezing Point	0.5° C approx.
Particle Size	
Average Size	2.5-3.5 micron
% larger than 10 micron	max. 5%
% smaller than 1 micron	max. 2%
Possible Contaminants (in the dry product)	
Iron (Fe)	< 50 ppm
Nickel (Ni)	< 1 ppm
Chromium (Cr)	< 1 ppm
Cobalt (Co)	< 1 ppm
Arsenic (As)	< 3 ppm
Titanium (Ti)	< 5 ppm

### 3.2 Aluminum Removal Through Sodium Aluminate Hydrolysis

The transformation of sodium aluminate into aluminum hydroxide (or alumina tri-hydrate) is one of the basic processes of the aluminum industry and is known as the Bayer process. During the preparation of alumina, the bauxite is attacked by the caustic soda solution (50%) at a pressure of 4.6 atm. The hydrate oxide dissolves as meta-aluminate ( $\text{NaAlO}_2$  or  $\text{NaAl(OH)}_4$ ) and the pressure is essential for insolubilizing the silicon as silicon aluminate. After filtering to eliminate the silicates, the iron and the titanium bioxide, which are nearly always present in the original mineral, the solution is

diluted and treated with crystallized  $\text{Al}(\text{OH})_3$ . Generally, after 3-4 days, 60% of the pure hydrate precipitates. Then, after being concentrated, the residual liquid is reused to treat new bauxite.

Researchers (3-12) have seen that the Bayer process can be applied to normal etching solutions as long as they do not contain substances that complex aluminum; that is, if it is present in the form of sodium aluminate.

The mechanism is quite simple: a part of the solution is brought into the reactor where it is stirred and kept at the proper temperature; then  $\text{Al}(\text{OH})_3$  is added and this acts as a crystallization generator. After a few days of ageing the aluminum hydroxide begins to precipitate resulting in an increase in the free caustic soda content in the solution. At this point, the aluminum hydroxide is filtered out and the recovered solution is returned to the etching tank. An accurate balance of each flow permits a continuous process.

More recently a process called Epal (22) has been presented which does not require the use of a reactor since the sodium aluminate hydrolysis reaction takes place directly in the etching tank.

A typical diagram for the recovery of caustic soda through sodium aluminate hydrolysis is given in Figure 3. The quality of the aluminum hydroxide produced in this manner is excellent and can be used as a source of alumina 'as it is' or it can be transformed into aluminum salts.

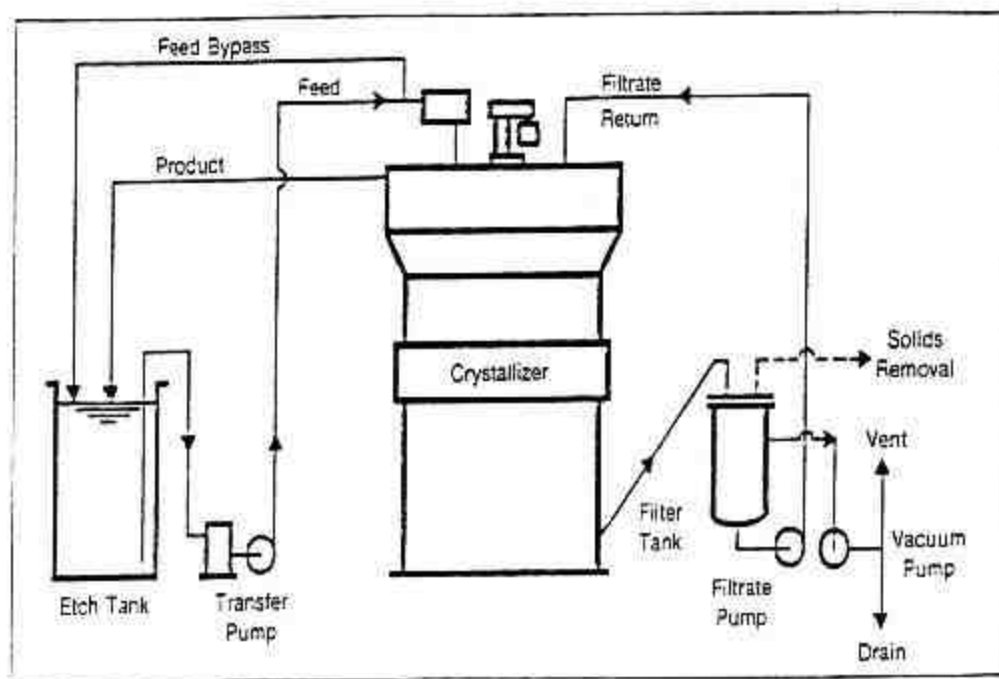


Fig. 3 Flow sheet for the soda recovery system of Ecotec

One drawback to this type of treatment is the fact that complexing additives cannot be used, requiring the use of low aluminum content etching solutions.

Starting from this consideration, the authors sought to verify whether it is possible to apply a caustic soda recovery system utilizing the “Bayer Process” in plants where the dissolved aluminum content and free caustic soda in the tank is high as a result of the use of complexing additives.

## 4 – Our Research

Before starting our tests, we posed a preliminary question: what is the maximum aluminum concentration reached in a 20,000 liter etching tank used to treat 400 m<sup>2</sup> of aluminum per hour? The aluminum concentration in the solution would stop increasing when the amount progressively being dissolved is counterbalanced by that carried over into the rinse water. A Type 2 solution (Tab. 1), used on material for windows and doors, causes a carry over of approximately 0.5 liter/m<sup>2</sup>.

Under such conditions, supposing the treatment time is 10 min, we have:

Dissolved Aluminum:  $(400 \times 5 \times 10)/1000 = 20 \text{ Kg/Hour}$

Volume of Etching Solution Carried Over:  $0.5 \times 400 = 200 \text{ Liters/Hour}$

From this it follows that 20 Kg of aluminum are carried away in the 200 liters of solution if the aluminum concentration in that solution is

$$20 \times 1000 / 200 = 100 \text{ g/l}$$

Starting from this result the following was studied:

- a) The stability of the caustic soda solution with at least 100 g/l of dissolved aluminum.
- b) The variable quantity of free caustic soda in the total absence of any additive.
- c) The change in the rate at which aluminum dissolves in some of these solutions as operating temperature is changed.
- d) The ability of the additives to slow down or prevent sodium aluminate hydrolysis.
- e) The effect of the addition of some additives selected from among those, which did not negatively affect the precipitation process.
- f) The solution stability and dissolution rate.

All the tests were performed starting from a mother solution obtained by dissolving pieces of aluminum, ASTM 6063 alloy, the standard material used for aluminum window frames and a material that is, therefore, subjected to anodizing. A solution was obtained having the following composition:

Free Caustic Soda	200 g/l	Dissolved Aluminum	200 g/l.
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After filtration to eliminate the heavy metals, this solution was clear and stable in time. The various test solutions were prepared from this mother solution by simply diluting and, if necessary, adjusting the caustic soda and dissolved aluminum concentrations.

#### 4.1 – Stability Of Caustic Soda And Aluminum Solutions

Solutions of a defined concentration and totally free of additives were kept at the indicated temperature, checking how many days passed before an evident white precipitate began to form, indicating the onset of sodium aluminate hydrolysis. The results are presented in Table 7.

The data shown in Table 7 indicate that solution stability increases as:

- a) The Free Caustic Soda / Dissolved Aluminum Ratio Increases
- b) The Storage Temperature Increases

**Table 7 – Stability Of The Etching Solutions At Different Temperatures**

Composition	T = 15° C	Note
NaOH 60 g/l Al <sub>3</sub> <sup>+</sup> 100 g	Precipitated after 2 days	--
NaOH 70 g/l Al <sub>3</sub> <sup>+</sup> 100 g	Precipitated after 4 days	--
NaOH 80 g/l Al <sub>3</sub> <sup>+</sup> 100 g	Precipitated after 10 days	--
NaOH 90 g/l Al <sub>3</sub> <sup>+</sup> 100 g/l	Precipitated after 15 days	--
NaOH 100 g/l Al <sub>3</sub> <sup>+</sup> 100 g/l	Precipitated after 25 days	--
NaOH 110 g/l Al <sub>3</sub> <sup>+</sup> 100 g/l	Precipitated after 30 days	--
NaOH 120 g/l Al <sub>3</sub> <sup>+</sup> 100 g/l	Precipitated after 40 days	--
NaOH 150 g/l Al <sub>3</sub> <sup>+</sup> 150 g/l	No precipitate after 60 days	Highly viscous solution

**Table 8 – Rate Of Aluminum Dissolution In Caustic Soda Solutions (\*)**

Composition	T = 50° C	T = 60° C	T = 70° C
NaOH 50 g/l Al <sub>3</sub> <sup>+</sup> 50 g/l	5.5	8.9	20.2
NaOH 100 g/l Al <sub>3</sub> <sup>+</sup> 100 g/l	5.7	9.3	20.5
NaOH 150 g/l Al <sub>3</sub> <sup>+</sup> 150 g/l	5.3	8.1	21.0
NaOH 70 g/l Al <sub>3</sub> <sup>+</sup> 100 g/l	4.2	7.3	15.9
NaOH 120 g/l Al <sub>3</sub> <sup>+</sup> 100 g/l	6.4	11.9	27.0

(\*) the rate at which aluminum dissolves is expressed in (g/m<sup>2</sup>) / min.

## 4.2 – Dissolution Rate

The data for these tests are given in Table 8 and were obtained as follows:

The solutions used were obtained from the above-mentioned mother solution by diluting and reportioning by adding caustic soda and/or dissolving additional aluminum. Five liters of each test solution were used. For each test a sample ASTM 1050 aluminum alloy sheet of 4 dm<sup>2</sup> was used after degreasing and weighing. The dipping time was 20 min. In all cases the test temperature was easily maintained ( $\pm 1^\circ$  C) vs. the indicated value. After carefully rinsing and neutralizing in a conventional neutralization solution, the sample was once more weighed and left to air dry.

The weight loss was expressed in g/m<sup>2</sup> per minute of dipping. The data in the table indicate that the dissolution rate increased with an increase in the:

- a) Temperature
- b) Free-soda / Dissolved Aluminum Ratio (and not simply with an increase in the free caustic soda content)



### 4.3 – Effect Of Additives On Aluminate Hydrolysis

In order to formulate an additive able to improve aluminum finishing without preventing the recovery and recycling of the caustic soda solution, we evaluated some of the most common additives used in etching tanks.

Since the treatment, which will be assumed in § 5 is applied to a hypothetical *static* rinse tank (i.e., without the input of any water except that needed to maintain the correct level), the tests were performed using a solution *more diluted* than the general etching tank.

In practice, the solution used had the following composition:

Free Caustic Soda	40 g/l
Dissolved Aluminum	40 g/l
Additives	1 - 20 g/l.

The test was performed at 40° C, under mechanical stirring and using a closed container to keep evaporation losses to a minimum. For all the samples, 30 g/l of  $Al_2O_3 \times 3H_2O$ , was added as the precipitation generator.

The aluminum and free caustic soda concentrations were checked an average of 60 hours later and two opposite situations were found:

- a) hydrolysis did not occur, and the caustic soda and aluminum contents remained unchanged;
- b) hydrolysis had taken place, while the dissolved aluminum had dropped to 11-15 g/l and consequently the free caustic soda content had increased proportionally to approximately 80 g/l, the result being practically stechiometric.

The results obtained were not particularly affected by the concentration used and made it possible to draw up Table 9.

When the products did not appear to have any negative effect, the stability in the operating solution:

NaOH	100 g/l
$Al_3^+$	100 g/l

was checked both under hot (55 °C) and cold (15 °C) conditions.

**Table 9 – Effect Of Some Chemical Products On Sodium Aluminate Hydrolysis**

<b>Chemical product</b>	<b>Effect</b>	<b>Notes</b>
sodium gluconate	Negative even at low concentrations	
amine	Has no effect, even at high concentrations	
sodium nitrate	Has no effect, even at high concentrations	
sodium thiosulfate	Has no effect, even at high concentrations	
sodium phosphate	Has no effect	Cannot be used because the operating solution becomes a gel as it cools
sodium fluoride	Has no effect	Cannot be used because the operating solution forms a precipitate
phosphonates	Have no effect	For obvious commercial reasons, the numerous products tested are not indicated
heavy metal salts	Have no effect	Poorly soluble in the operating solution
group VI A metal salts	Have no effect	
sorbitol	Negative	
anionic surfactants	Have no effect	

The data in Table 9 enabled us to formulate a new additive. Information is available upon request.

## 4.4 – Our Results

Using the new additive formulation, the following etching solution composition was formulated:

Free Caustic Soda	80 - 120 g/l
Dissolved Aluminum	100 - 120 g/l
New Additive	10 - 30 g/l
Temperature	55 - 60 °C

The main characteristics of which are presented in Table 10.

**Table 10 – Characteristics Of The Etching Solution Prepared With The New Additive**

	<b>Parameters</b>	<b>Notes</b>
<b>Operating Temperature</b>	60° C	indicative interval: 50 - 70° C
<b>Aluminum Dissolution Rate</b>	5 g/m <sup>2</sup> x min.	indicative interval 4 - 9 g/m <sup>2</sup> x min.
<b>Average Etching Treatment Time</b>	10 min.	10 - 20 min.
<b>Appearance</b>	clear solution	brown color
<b>Caustic Soda Recovery</b>	possible both in the main tank and in the subsequent static rinse tank	
<b>Stability</b>	stable solution even at T = 15° C for more than 10 days	Suggested storage temperature T > 25° C

The above solution is suitable for recycling by precipitating the aluminum hydroxide. However, given the high dissolved aluminum concentration and the high alkalinity (which cannot be reduced without compromising the aluminum finishing), it is advisable to check whether a recovery treatment can be achieved in the rinse downstream of the etching tank.

#### 4.5 – A New Caustic Soda Recovery System

Given that there are at least two rinses—downstream of the etching tank and upstream of the acid neutralization tank—it is therefore possible to transform the first into a “static rinse”; that is, without the input of any water except what is strictly required to maintain the correct level and drawing this water from the second rinse. In this manner, and with the proper control design and mechanism, the aluminum content in the static rinse tank can reach and be maintained at 30-40 g/l of dissolved aluminum, which is a level suitable for the installation of our closed –loop recovery system.

Maintaining the temperature in this tank at approximately 40°C, the materials coming from the etching tank are thoroughly rinsed and a residence time of a few minutes can enhance the final finish on the aluminum.

This specialized recovery system is designed to continuously withdraw a part of the static rinse solution, sending it on to the reactor (crystalizer) where an equal volume of a solution, enriched with free caustic soda and depleted of dissolved aluminum, is returned to the etching tank, after reducing the volume through evaporators and other mechanical means, to keep the volumes balanced. This keeps the level and composition of the solution in the etching tank stable. The volume lost from the first rinse is recovered by this continuous system, which withdraws solution from the second rinse, where an adequate flow of water is maintained to ensure that the incoming treated material is thoroughly rinsed before it reaches the downstream acid neutralization tank.

The treatment flow chart of this specialized recovery system is shown in Fig. 4

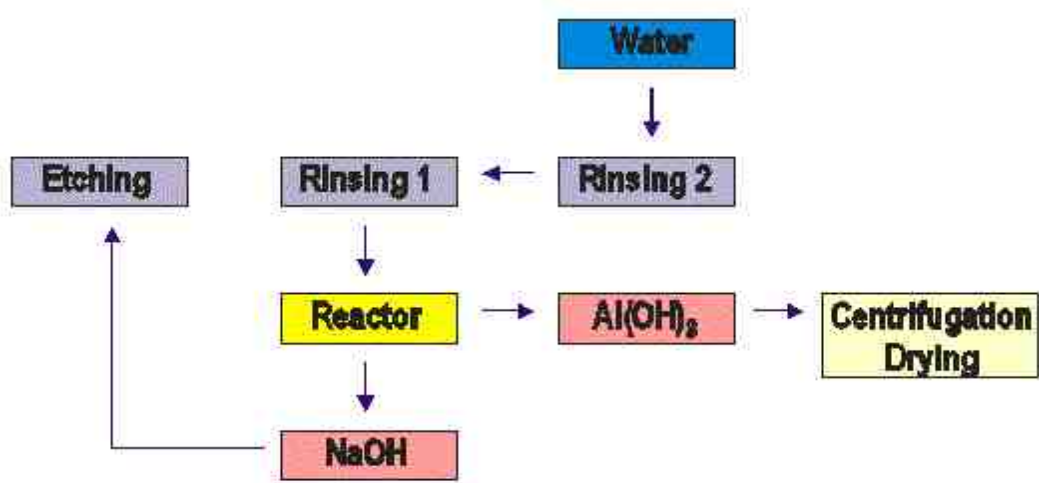


Figure 4.

## 5. Conclusions

When the need to achieve an etched finish requires the use of a caustic soda solution with a high level of aluminum content, this specialized caustic soda recovery system, which is mechanical and chemical in nature, can be applied to the first rinse tank, which is then kept in a “static” condition by this specialized process.

This significantly reduces the amount of aluminum entering the effluent waters, and achieves an effective caustic soda recovery process. This is accomplished without, in any way, modifying the composition of the etching tank, as this would inevitably compromise the finishing of the aluminum.

## Bibliography

1. Wernick S, Pinner R, Sheasby P.G.; The Surface Treatment and Finishing of Aluminum and its Alloys, ASM Int.l Metal Park, Ohio USA
2. Brace A.; The Technology of Anodized Aluminum 2<sup>nd</sup> ed.; Interall Publ. Modena Italy
3. Patent USSR 686751, 1997
4. **Verbitskaya I.L.**; Vodostabzh. Sanit. Tekh., 1979, **4**, 24
5. Patent USSR 810854, 1979
6. Brown C.J.; Plat. Surf. Finish. 1982 **69**(6), 102-105
7. Dejak M.; Plat. Surf. Finish. 1984, **71**(4), 30-32
8. Berry L.; Product Finish (Cincinnati) 1988, **52**(7) 92-5
9. Gu Z.; Daindu Yu Huanbao 1988, **8**(4), 30-1
10. Pajunen P.; 3<sup>rd</sup> World Congr. Cyprus 1997, (Conf. Proc.) Vol. II, 229-39
11. Lancey Int.; Tech. Bull. 3601
12. Patent USA 5091046, 1992
13. Patent Japan 8348490 B, 1975
14. Patent Japan 8222994, 1973
15. Patent Japan 80144415, 1979
16. **Guth J.L., Caillet P.**; Jour. Chim. Phys. 1986, **83** (3), 155-75
17. **Breck D.W., Anderson R.A.**; Kirk\_Othmer Enc. of Chem Techn., 2<sup>nd</sup> Ed. J. Wiley NY 1981
18. **Breck D.W.**; Zeolites Molecular Sieves, Struct., Chem. and Use J. Wiley & Sons Inc: NY 1974
19. Patent Japan 83167425, 1982
20. Patent Japan 8430716, 1984
21. **Strazzi E.**; Unpublished data (1985)
22. Epal – trade mark by CM – Oberflächentechnik AG (Switzerland)