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Recovery of Alumina from a surface - Treatment industry

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Abstract
Surface treatment industries are among the most polluting industries, they generate very basic effluents containing very high concentrations of metals. Spent liquor from the pickling of dies for the production of aluminum extrusions with caustic soda has been studied. These effluents are typically dewatered to reduce the volume of waste before to be land filling. In Europe, it is estimated that about at least 14,000m^3 of this residue is produced per year. The Recovery of alumina is important both environmentally by reducing the amount of sludge deposited and economically by obtaining alumina. Alumina is a material finding many applications in catalysis, manufacturing of ceramics, refractory. In recent years, a special attention has been focused on the preparation of (Al_2O_3) powders with high purity by various routes such as precipitation, sol-gel and hydrothermal methods. Among these methods, precipitation is the most commonly used method not only because it can produce high quality powders but also it is cheap. The precipitation of aluminum depends on several factors as temperature and pH . In this work the factor studied is the pH at 25°C. The aim of this work is to reach the point of maximum precipitation of aluminum to recovery the maximum amount of aluminum; the (H_2SO_4) is used. The X-ray diffraction and X-ray fluorescence analysis were used to study the characteristics of alumina and the titration curves are performed in laboratory. The purity of alumina obtained is nearly 60%, the spectra of alumina showed the presence of alumina in amorphous form.

Keywords: pickling batch-Aluminum hydroxide-precipitation-Alumina

1. Introduction
The extrusion of the aluminum billets [1] is a necessary step for aluminum production. This technology consists of pushing a hot cylindrical metal billet on within stainless steel die. In order to achieve good quality extruded products, the internal surfaces of the extrusion dies must be perfectly clean [2]. Pickling is probably one of the surface treatment operations among the best known. However, pikling term has a different meaning for all professionals [3].
In this work the meaning of pickling[4] is a cleaning the extrusion dies because after each pickling (one cycle) the matrixes of extrusions must be dismounted and cleaned to remove aluminum that has remained in the holes (2 Kg -3Kg Al per die), this step is necessary to ensure perfect quality profiles .This operation (600Kg Al per cycle) is done by soaking the dies for 7 hours in a concentrated NaOH solution (some 40% by weight) at a temperature approximately 70 °C[5].
This treatment brings aluminum into the solution as aluminates [5], according to the reaction:

$$2Al + 2OH^{-} + 6\ H2O \rightarrow 2\ Al\ (OH)_4^{-} + 3H_2 \quad (1)$$

As a consequence, a waste containing high amounts of aluminum is generated. In Europe, it is estimated that about at least 14,000m3 of this residue is produced per year [6] normally; the pickling solution is treated by neutralization in the profiling aluminum industry according to the following reaction:

$$Al(OH)_4^{-} \rightarrow Al(OH)_3 + OH^{-}(aq) \quad (2)$$

This method causes a continuous loss of resource materials (aluminum), as well as it results in generation of very large amounts of solid aluminum hydroxide residues [7] these residues are typically dewatered to reduce the volume of waste prior to being land filled.
Different works were demonstrated the possibility to recover of alumina from the wastewater of the profiling industries[8,9].In the work we'll study the possibility of alumina recovery from the waste effluents generated

during the cleaning of the extruder matrixes of the profiling aluminum industry by precipitation method to solve the pickling bath management.
The first step of experimental method is the dilution, followed by precipitation (maximum precipitation) the phosphoric acid is adding; the precipitate of aluminum hydroxide is filtered, the last step is calcinations [10, 11] to recovery of alumina. The method presents both economic (the use of alumina) [12, 13, 14] and environmental interests [15] and is an easy implanted solution to solve management problems of industrial waste.

2. Experimental

2.1. Materials

A representative sample (at the practical work conditions in the factory) of wastewater resulting from alkali washing of the extrusion dyes was collected by a Moroccan anodizing factory (Aluminium du Maroc). In the experimental procedure height purity of sulfuric Acid (H_2SO_4) and chloridric acid (HCl) is used, the experiments were realized with the diluted acids. The pH meter and magnetic stirrer were used to precipitation performed.

2.2 Procedure

2.2 2. Procedure for alumina recovery

The profiling aluminum industry uses a concentrated caustic soda to clean the internal surface of extruder matrixe to solubilise all aluminum that stood in the dies ,as $Al(OH)_4^-$species . Thus the pH of waste water effluent is very basic (pH=13, 95).
The waste effluent is diluted; the sulfuric acid is added until to maximal precipitation point of alumina.This step is followed by washing the precipitate with the distilled water and filtration. The last step is the hydroxide aluminum calcination in the furnace (1200°C), this step is necessary to recovery of alumina.

2.2.3. Principle of aluminum solubility:

Aluminum in the aqueous solutions at 25° is present in three forms $Al^{3+,}$
$Al(OH)_3$, $Al(OH)_4^-$ depending on the pH value (Figure 1)The reactions and formulas involved are:
$Al(OH)_3$ (s) --->Al^{3+} + $3OH^-$
$Ks_1 = [Al^{3+}][OH^-]^3$
$Al(OH)_3 + OH^-$ ---> $Al(OH)_4^-$
$Ks_2 = [Al(OH)_4^-][OH^-]$
After developing the formulas we get: $4pH = pKs_2 + 4pKe - pKs_1 + \log 3$

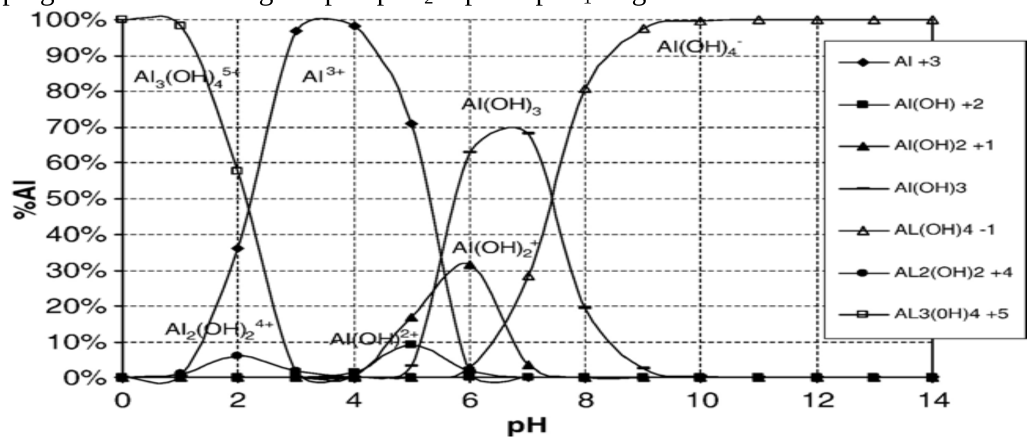

Figure 1: Speciation of aluminum in aqueous solutions at 25 °C [6]

The theoric pH value corresponding at the maximum precipitation of $Al(OH)_3$ is constant because it does not depend on aluminum concentration but it only depends on the values of pKe, pKs_1, pKs_2. These values are constant for a temperature 25 ° C.
In these experiments, a basic original effluent aluminum is diluted (dilution factor is 3) , the sulfuric acid (2N) is used to reach the pH value of 5,8(maximal precipitation).The temperature regulation at 25°C is necessary to keep the values pks_1, pKs_2, pKe constant.
Precipitation experiments were performed in a glass beaker, a pH meter with automatic recording device to temperature display is used , a volume of 10ml of effluent is diluted with distilled water 20ml, this solution is

titrated with H_2SO_4 (2N) (solutions are used diluted in order to keep the temperature constant 25 °C) with stirring.
These results are necessary to draw a titration curve of aluminum for obtaining the point of maximum precipitation and the curve of solubility product Ps depending on the pH: Ps = f (pH).
A comparison between the point of maximum experimental and theoretical precipitation is performed and the necessary volume of sulfuric acid to decrease the pH to down 5,8 is performed by titration curve and curve Ps=f(pH).The precipitate (Al $(OH)_3$) is washed by distilled water to eliminate the impurities, this step is followed by filtration and calcination in a furnace at 1200° during 2h.The characterization of alumina is carried out by X-ray diffraction (XRD) and X-Fluorescence analysis.

3. Results and discussion

3.1. Chemical characterization of the original effluent

The chemical characterization of original effluent from the profiling aluminum industry is performed by Spectrometry Atomic Emission ICP AES (Ultima 2 - JobinYvon).
Table 1 shows the total metals (aluminum, chromium, copper, silicon, nickel and Zinc) concentrations present in the original basic suspension.
The free NaOH concentration is realized by volumetric analysis through titration with H_2SO_4 (1N), the dissolved aluminum concentration is carried out by two methods the volumetric analysis H_2SO_4 (1N) and Atomic Emission Spectrometry ICP (AES), as well as the pH, temperature and density are determinate in the laboratory (Table 2**)**. The pH values of all effluent are measured at a constant temperature 25 °C to avoid the change of the constant pKa.
The results of analysis show Table 1 that aluminum and sodium are the main elements present in the original effluent. Silicon is also present, as a minor element, and mainly in the colloid form. Copper, chromium nickel, Zinc are the minor constituents of original effluent.
At pH around 14 aluminum, copper, Zinc and Nickel are totally soluble [9]. In the case of sodium, all the total amount of sodium present in the wastewater (Table1) results from the sodium hydroxide added to the cleaning bath, the silicon present in the original effluent results from the aluminum alloys billets used in the profiling industry is (AL-Si 6060) between 0,30 wt.% -0,60 wt.%.

Table 1: Chemical composition of the original effluent

Constituent	concentration
Al	146 g/l
Si	96,350 mg/l
Cr	0 ,206 mg/l
Ni	0,008 mg/l
Zn	0,623 mg/l
Cu	0,042 mg/l
Na	900g/l

The Table2 summarizes, in particular, the main chemical parameters of the original solution. In the pickling process The concentration of Aluminum at form Al $(OH)_4^-$ specie (dissolved aluminum) increases and the rinsing caustic solution loses its activity .The results of Table2 demonstrate that the concentration of caustic soda is very high 7,3M and the concentration of aluminum in the effluent is 5,40M so this effluent is very concentrated and contains important amount of aluminum .

3.2. The Alumina recovery:

The proposed experimental of Alumina recovery is composed by three steps, the first step is a dilution (3 dilution factor) this is step is necessary for reducing the viscosity of basic effluent and the control of temperature (25°C). The second step is a neutralization of the basic effluent to down pH=5,8 (point of maximum precipitation) , the sulfuric acid is used because it is the cheapest acid [5] a volume 0,16 ml of concentrated sulfuric acid (95%) is necessary for decreasing the pH of the basic solution to 5,8 (6ml of H_2SO_4 (1N) , the precipitate recovery Al $(OH)_3$ is filtered and washed three times by dezioned water . The final step is the calcinations of the precipitate in a furnace at 1200° during 2h to recovery the alumina.

Table2: characterization of the original effluent

Parameter	value
pH	13 ,70
T°	25°C
Density	1,40
[NaOH]	321g/l
[Al]	146g/l

3.2.1 Aluminum precipitation:

The titration curve obtained at 25°C is shown in Figure 2, from these curves, three regions are distinguished :

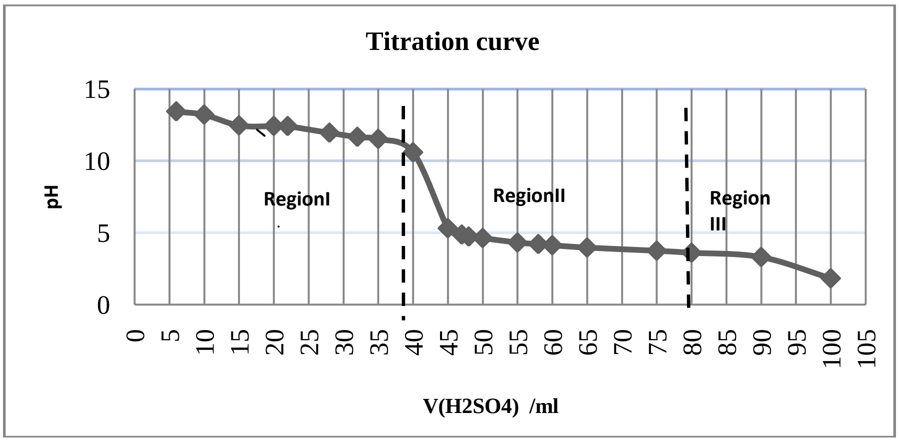

Figure 2: Titration curve obtained at 25°C by addition of H_2SO_4 (2N)

Region I: (pH between13,42 and 10):the pH decrease progressively until the value 10,58,this region is characterized by the high solubility of Aluminum and the aluminates ion Al $(OH_4)^-$ dominance .

Region II : (pH between 10 et 4) presence of a bearing, the pH value decreases from 10.58 to 4. This region represents the region of the lowest aluminum solubility and thus aluminum was massively removed from the solution, forming initially a very viscous gel due to intense condensation phenomena and then an extremely viscous pulp consisting principally of an amorphous solid material. The results of experiments obtained in the laboratory demonstrated than the volume of sulfuric acid causing maximum precipitation (solid gel) is 45 ml, which corresponds to a pH value of 5.6 Figure 2 , after this volume the addition of sulfuric acid causes a beginning of redissolution of the precipitate and pH decreasing.

Region III: pH is bellow to 4 the pH starts to decrease and we see the total and net redissolution of the gel formed, the aluminum hydroxide Al $(OH)_3$ was transformed into Al $^{3+}$.

Curve Ps=f(pH)

The concentration of aluminum value of the original effluent allowed us to define the corresponding pH values of total redissolution in acidic and basic aqueous solution respectively 3.03 and 13.60.

The PH value corresponding a maximal precipitation is not depending of aluminum concentration, this is almost 5, 8 (see precipitation of aluminum part introduction).For a pH value between 3.03 and 5.8 the formula is: Ps = -9.7 + 3 pH ,and to a pH value between 5.8 and 13.60 is the formula: Ps = 13-pH .The results obtained are shown in the curve below (Figure3). These results demonstrated than the lower solubility of aluminum is obtained at pH= 6 ,at this pH the aluminum is present at species form $Al(OH)_3$ (precipitate), this pH value is almost the pH value of maximal precipitation obtained in the titration curve (Figure2) pH=5,3 .At a pH below 3 the solubility of aluminum is zero, the aluminum is present in its soluble form Al $^{3+}$, this value is nearly the same value of 3.74 pH obtained in the titration curve (the total redissolution). The aluminum solubility decreases to a pH value between 4 and 10 until total redissolution at pH values 3 and 13.

The results obtained by the titration curve (experimental method) are confirmed by the curve Ps = f (pH) (theoretical method). Thus we can conclude that the pH value corresponding to the point of maximum precipitation of original effluent is between 5.3 and 6.

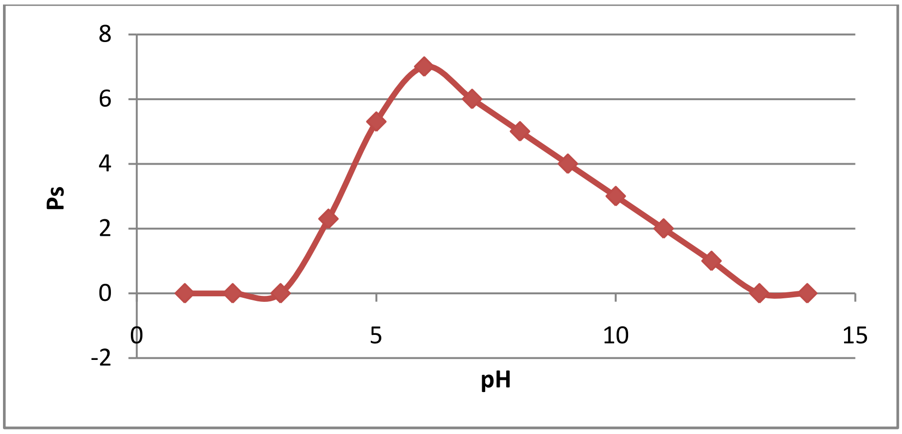

Figure 3: The solubility Ps=f (pH)

3, 2.2. Alumina recovery

The characterization of Alumina is performed by XRD patterns and X Fluorescence spectroscopy. The purity of Alumina obtained by precipitation at 25°C and calcination at 1200°C in furnace during 2h is determined by the X Fluorescence analysis as shown in Table 3. The result shows that the purity of alumina recovery is almost 60%, the major impurities are the sodium, sulphates and silicates with values respectively 19%, 15,1%,2,14%. The sodium oxide present (Na_2O) as a major element 19% results from the caustic soda added to the clearing bath by against the value of the sulfide (SO_3) 15% results from the sulfuric acid added to produced the maximal precipitation and the silicon value (SiO_2) 2,14 % results from the Aluminum alloy. The silicon is the major constituent of Aluminum alloy. The content of minor impurity is almost 10% (eg. iron, magnesium, chromium, nickel), these all elements are constituents of the aluminum alloy (minor constituents of aluminum alloy).

Table 3: Alumina recovery Results by X fluorescence

Element	Concentration%	Element	Concentration%
Al_2O_3	55,700	Fe_2O_3	0,196
Na_2O	19	Cr_2O_3	0,059
SO3	15,100	K_2O	0,024
SiO2	2,190	NiO	0,024
Mg O	0,494	P_2O_5	0,018

The XRD diagrams in Figure 4 shows that at a lowest temperature 25°C and for pH =5,3 totally amorphous phase was formed [8] .The spectrum of alumina resulting is amorphous, this result is explained by the non-compliance of the calcination temperature (malfunction of the furnace) , The resulting precipitate was calcined at a temperature of 900 °C instead of 1200 °C, for obtaining the alumina in its crystalline form , the temperature should be 1200°C.

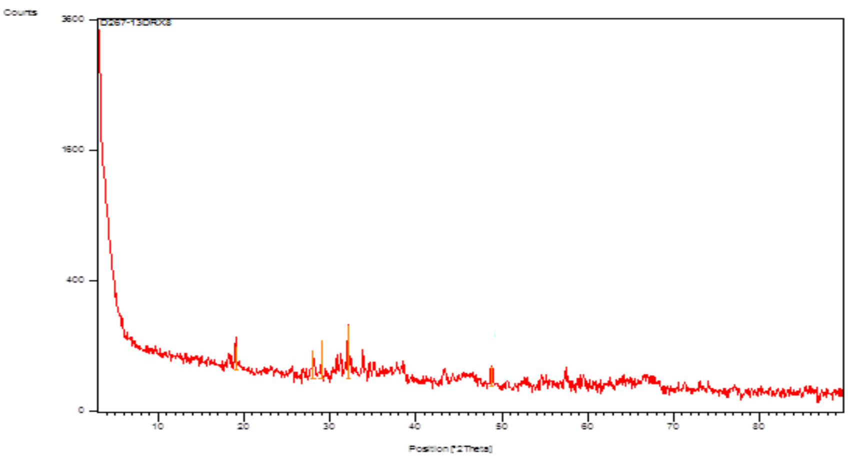

Fig 4: the Alumina recovery spectrum by rayon X diffraxion

Conclusion

In this work we were able to recover the alumina from a pickling bath of aluminum alloys by the method of precipitation at 25 °C.

The comparison between the theoric value of maximal precipitation point of aluminum was confirmed by the experimental results of titration curves and curve Ps=f(pH),the maximal precipitation point is obtained for pH value between 5,3 and 6.The X Fluorescence analysis of alumina demonstrated that the purity of alumina recovery was almost 60%, the spectrum of alumina carried out by rayon X diffraction is amorphous, and these results can be explained by the low temperature of precipitation [8] or by the non conformity of the calcination temperature .

The process performed during this study presents both economic (alumina) and environmental interests (setting discharge of sludge) and is an easy implanted solution to solve management problems of industrial waste. This method shows how a waste can save money not only by the recovery of alumina but by the elimination of treatment cost and the alumina recovery can be used as an adsorbent, a catalyst or a refractory material.

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