



Review

Approaches for the treatment of waste streams of the aluminium anodising industry

E. Álvarez-Ayuso*

Department of Environmental Geochemistry, IRNASA, CSIC, Apto. 257, 37071 Salamanca, Spain

ARTICLE INFO

Article history:

Received 3 July 2008

Received in revised form 19 August 2008

Accepted 19 August 2008

Available online 23 August 2008

Keywords:

Aluminium
Anodising
Wastewaters
Recovery
Recycling

ABSTRACT

The aluminium anodising industry is an important industrial sector that invariably generates great amounts of different waste streams. Classical and especially new-developing technologies dealing with them are reviewed. Innovative methods are mainly based on engineering geochemical processes, looking for the recovery of resource materials and the reduction of emissions to the environment. These represent a promising alternative to the classical method (neutralisation process and anodising mud disposal) which is an end-of-pipe solution. Among the treatments recently proposed, there are the use of anodising mud in the manufacture of refractory bodies, and the synthesis of useful minerals from the wastewaters arising from the etching, anodising and brightening processes. The viability of the application of such methods in the treatment of waste streams of the aluminium anodising industry is discussed, pointing out the main shortcomings and benefits of each of them. For those methods appearing environmentally friendly the process cost and the actual marketability of the final products should be determinant on their near future applicability.

© 2008 Elsevier B.V. All rights reserved.

Contents

1. Anodising process	409
2. Conventional waste stream treatment	410
3. Alternative or co-operative techniques	411
4. Recycling processes	411
4.1. Recycling of anodising mud	411
4.2. Recycling of wastewaters	411
4.2.1. Wastewaters from the etching process	411
4.2.2. Wastewaters from the anodising process	412
4.2.3. Wastewaters from the brightening process	413
5. Conclusions	413
References	414

1. Anodising process

The anodising process is normally done in small and medium enterprises (SMEs) having one or two production lines. Aluminium is the most important material to be anodised, although, on a much smaller scale, magnesium, titanium, tantalum and niobium are also anodised. Aluminium items for the building industry, the transport sector and the machine manufacturing industry are those mainly

subjected to this process. A typical single production line consisting of 20–24 m³ baths can treat up to 1.5 × 10⁶ m² of displayed surface yearly. In 1999, an anodised aluminium surface of 190 × 10⁶ m² was produced in Europe [1]. Nowadays, an anodised aluminium surface close to 250 × 10⁶ m² is estimated to be produced annually within Europe, taking into account that an annual production rise about 3% was expected [1].

Anodising is an electrochemical process that physically modifies the surface of aluminium, accelerating its naturally occurring oxide coating. The anodising process forms a particularly structured and dense oxide layer that protects the underlying metal, offering properties such as substantial corrosion resistance, abrasion resistance

* Tel.: +34 923219606; fax: +34 923219609.
E-mail address: esther.alvarez@irnasas.csic.es.

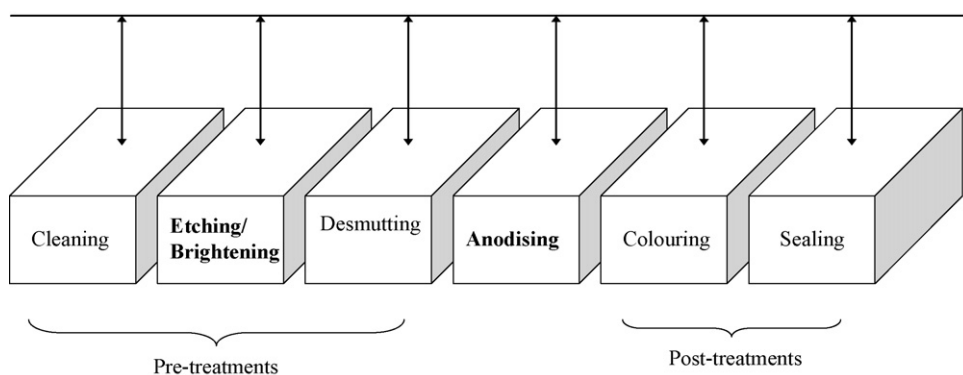


Fig. 1. Simplified process scheme of a typical anodising plant.

and electrical insulation. The sulphuric acid process is the most common method for anodisation due to the economic conditions, the satisfactory results obtained, and the means used to obtain them. It employs a 16–18% sulphuric acid concentration, a temperature of 18–20 °C and a current density of 1–2 A dm⁻². During anodising, some aluminium is lost to the bath solution in which the concentration is maintained below 15–20 g l⁻¹ for proper processing. This treatment yields coatings usually between 5 and 25 μm thick, depending on the end use of the anodised materials (decorative or/and protective). The whole process normally consists of several consecutive steps: cleaning, etching/brightening, desmutting, anodising, colouring and sealing (Fig. 1). All the pre-treatments are required to prepare the aluminium surface to be anodised, whereas only sealing is strictly required as a post-treatment to the satisfactory performance of the coating.

Cleaning is done in hot non-etching, alkaline detergent solutions, removing grease and surface dirt. Etching prepares the aluminium for anodising by chemically removing a thin layer of aluminium, and gives the aluminium surface a matte appearance. This treatment is performed in sodium hydroxide solutions with concentrations ranging between 50 and 200 g l⁻¹ at temperatures of 50–60 °C. Brightening is a chemical polishing of aluminium surface by treatment with a mixture of acids, nitric (3–6%), sulphuric (10–20%) and phosphoric (80–85%), resulting in a mirror-shiny surface; if a less reflective finish is required, a phosphoric–sulphuric acid solution not containing nitric acid may be used. The bath temperature is about 90–105 °C. Etching and brightening are alternative processes, giving different surface finishes (the former is the most widely applied). Desmutting removes, by dipping in an acid solution, unwanted surface alloy constituent particles not removed by

the etching process. After the desmutting process items are ready for being anodised. Freshly formed anodic coating is porous; in this condition it is at its hardest state, but it is also highly reactive. At this stage, the properties of the anodic coating may be modified by further chemical treatments. The most important of these are colouring and sealing. Anodic coatings are well suited to a variety of colouring methods, including adsorptive dyeing, using both organic and inorganic dyestuffs, and electrolytic colouring. Sealing closes the pores in the anodic coating, giving a surface resistant to corrosion and staining. It also prevents organic dyes from leaching out, and improves the light fastness. This is usually accomplished through hydrothermal treatment. Following each process stage, rinsing steps are performed in order to avoid contamination of process solutions.

2. Conventional waste stream treatment

Waste streams from the aluminium anodising industry arise mainly from the rinsing steps following the anodising and etching processes. Large amounts of acid and alkaline wastewaters are generated, respectively, from such processes. Their volume and pollutant concentrations depend mainly on the rinsing system applied. Numerous rinsing techniques have been developed in order to achieve the requisite cleanliness of the surface, and also to reduce water consumption to the ecological and economic reasonable minimum. The multi-stage counter-current rinsing system is the most widely applied due to its high efficiency (Fig. 2). Anyway, the composition of effluents is quite invariable. Thus, acid wastewaters mainly consist of sulphuric acid and aluminium, whereas alkaline streams are basically composed by sodium

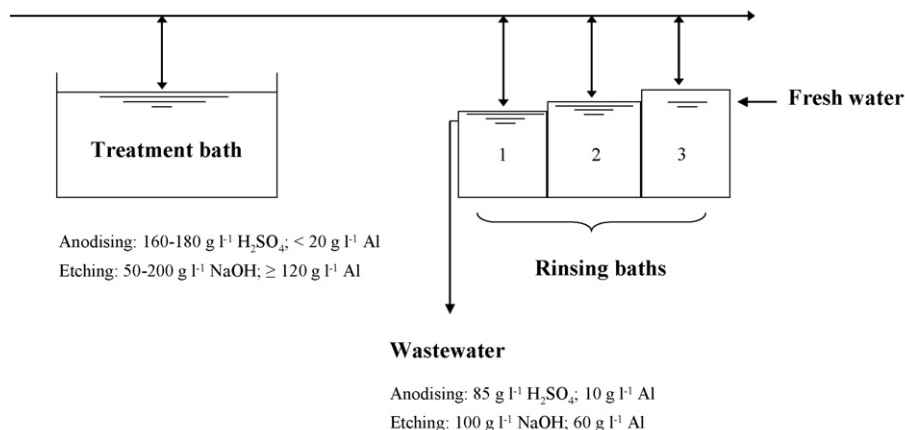


Fig. 2. Simplified scheme of a typical multi-stage counter-current rinsing system.

hydroxide and aluminium; their respective ratios being similar to those employed in the treatment baths. Moreover, very small amounts of other elements such as Si, Fe, Cu, Mn, Mg, Cr, Zn or Ti can also be present (their presence and concentrations are related directly to the compositions of alloys anodised).

A conventional and popular method for treating these waste streams is neutralisation by mixing them, requiring the incorporation of an additional neutralising agent (NaOH or lime) since the overall balance is generally acid. After this treatment, if the legal requirements for waste are fulfilled, the effluent is eliminated by direct discharge to the sewer, and the sludge (anodising mud) generated in such a process, containing mainly aluminium hydroxide and calcium sulphate, is sent to disposal. The neutralisation process causes a continuous loss of resource materials (aluminium, sulphuric acid and sodium hydroxide) which might otherwise have been recovered and recycled. Furthermore, the high sludge production (about 1×10^5 metric tonnes per year in EU countries [2]), and the increasing landfill closures and regulatory pressures on operating facilities to improve environmental conditions [3,4] cause increasing disposal costs which are difficult to confront by the SMEs of the anodising sector.

3. Alternative or co-operative techniques

Different alternative or co-operative techniques are available for the treatment of waste streams of this industry [5,6]. Thus, the conventional treatment can be performed with ionic exchange inclusion. The difference is the use of ion-exchange resins to remove cations (Na^+ and Ca^{2+}) and anions (SO_4^{2-}). The effluent obtained can be reused for rinsing in the anodising plant. Membrane technologies such as reverse osmosis and electro dialysis can also be employed in the treatment of wastewaters arising from this industrial sector. Reverse osmosis provides purified water that can be returned to the anodising plant, and yields a wastewater solution that is more concentrated in impurities. This technique is applied to the sodium sulphate effluent generated after the neutralisation process where aluminium is precipitated in the hydroxide form. This treatment allows decreases in the volumes of calcium sulphate sludge and wastewater to be treated. Mono or bipolar electro dialysis can be used to obtain sodium hydroxide and sulphuric acid solutions from concentrated sodium sulphate solutions (15–25%). The main drawback of such alternative or co-operative techniques comes from an economic standpoint. These processes are capital and operating-cost intensive; this is why their use is very limited. Among them, ion-exchange resins are the most popular, but their application is mainly restricted to the regeneration of anodising bath.

4. Recycling processes

4.1. Recycling of anodising mud

Different applications for the anodising mud have been attempted. These include the use of valuable materials from it derived as well as the use of the whole waste after being subjected to some previous treatments. Sodium aluminate and aluminium sulphate are the main chemicals obtained from the anodising mud, finding application as glue for paper production and as a flocculation agent in wastewater purification processes, respectively [7–9]. On the other hand, the incorporation of this waste in several matrix materials such as concrete, glass and ceramics has been also suggested, mainly as a way of inertizing it [10,11]. However, the high water content of anodising mud (up to 85 wt.%) and its gel-like consistency make hard the obtaining of homogeneous mixes

with the other raw materials, and increase the drying shrinkage of resulting bodies. Furthermore, anodising mud previously dried at 100°C exhibits a strong agglomerated structure that also hinders the achievement of a good mixing with the other raw materials. As a consequence, the final products display decreasing mechanical properties and increasing water absorption values. These shortcomings make such applications spurious, not consuming more than 20% of the generated anodising mud [2,12].

More recent and successful recycling ways have been proposed for this waste. Thus, its use as the main compound in alumina (Al_2O_3), mullite ($3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$), mullite-alumina and cordierite ($2\text{Al}_2\text{O}_3 \cdot 5\text{SiO}_2 \cdot 2\text{MgO}$) refractory bodies has been suggested. Alumina, mullite and alumina-mullite-based materials show high thermal inertness, electrical insulating properties, and strong mechanical strength as main properties, being suitable for applications such as electrical resistance supports, crucibles and sample holders, furnace furniture and rolls, and mechanically resistant elements [13–15]. Cordierite, in addition to its refractoriness and electrical insulating properties, is characterised by its low thermal expansion. Accordingly, cordierite-based materials have found favour as honeycomb supports for catalytic converters in automobiles, as furniture for self-cleaning ovens and in industrial heat exchangers for gas turbines [16–21]. With this aim, several studies have been conducted to design feasible compositions, using the sludge alone or mixed with natural/commercial raw materials such as sand, ball clay, kaolin, talc and diatomite [2,22–28]. These studies demonstrate the potential to recycle the anodising mud in the production of the just mentioned refractory materials. Three factors show to be the main responsible for the final properties of resulting materials. These are: (a) the physical state of the sludge (as-received, dried or calcined), (b) the nature of the other components used in the formulations, and (c) the shaping technique adopted to consolidate the products (dry pressing, extrusion or slip casting). After optimisation of such factors, products with interesting thermomechanical characteristics comparable to those of materials from natural sources or chemical reagents can be derived. The main drawback of this anodising mud recycling method is the high-energy consumption required in some cases when a high pre-calcination temperature is needed to the good performance of sintered products. Moreover, cordierite-based materials cannot be safely used above 1200°C .

4.2. Recycling of wastewaters

Even if the anodising mud could find its way to the market through some of the addressed recycling methods, these are far from absorbing the whole production. Therefore, systems focused on the reduction in anodising mud generation are required. In this way, selective treatments of wastewaters before the neutralisation process have been studied. These are based on the recovery and reuse of primary resources, and on the restriction of emissions to the environment. With this aim, several geochemical engineering processes have been proposed for both alkaline and acid wastewaters. Table 1 summarises the main characteristics of more recent methods suggested in this regard.

4.2.1. Wastewaters from the etching process

Three different methods have been developed for the direct treatment of etching wastewaters. These include the application of caustic regeneration systems, and the recovery of materials through the synthesis of valuable minerals.

Caustic regeneration is a well-known technology, and has been used in some countries for several years [29]. Such a system, based on the Bayer process, consists of the transformation of sodium aluminate into aluminium hydroxide (or alumina trihydrate). The

Table 1
Summary of most recent methods suggested for the treatment of aluminium anodising waste streams

Waste streams	Geochemical treatments (synthesis of minerals)	Additional sources	Optimal conditions	Applications proposed	References
Etching	Zeolites (4A, 13X, Y, HZSM5)	Amorphous silica or sodium silicate	4A (T: 80 °C; t: 3 h) 13X (T: 80 °C; t: 6 h) Y (T: 95 °C; t: 15 h) HZSM5 (T: 125 °C; t: 24 h)	Detergent industry and catalysts	[30–33]
	Dawsonite	Sodium bicarbonate	NaHCO ₃ /Al: 3; T: 30–150 °C; t: 2–24 h	Fire retardant, ceramic industry and absorbent of flue gases	[35]
Anodising	Ettringite	Calcium aluminate + calcium oxide	Sulphate <0.1 M; pH ≈12; T: 60 °C; t: 4 h	Specific plasters and sorbent material	[45]
	Hydrotalcite-like compounds	Magnesium oxide	pH ≈8	Polymer stabiliser	[54]
Brightening	Magnesium phosphates	Magnesium oxide ¹ or low grade-magnesium oxide ²	¹ t ≥ 1 h; ² t ≥ 6 h and [Mg] ≈4 [Mg] _{stoichiometric}	Soil fertiliser	[58]

procedure is rather simple: the etching solution is pumped into a reactor where it is stirred and kept at the proper temperature; then, aluminium hydroxide seeds are added to enhance crystallization. After several days of aging the aluminium hydroxide begins to precipitate, resulting in an increase in the free sodium hydroxide content in solution. At this point, the aluminium hydroxide is filtered out and can be reused for different industrial purposes, and the recovered sodium hydroxide solution can be returned to the etching tank. The main drawback of this system is the fact that it can only be applied when aluminium is present in the form of sodium aluminate. This means that the system is only effective in the absence of aluminium complexing additives (gluconates, polyalcohols, amines, etc.) and with low concentrations of dissolved aluminium (30–50 g Al l⁻¹). The excellent matte finishing of aluminium, which is generally desired by most aluminium finishers, can only be achieved when the soluble aluminium content in the etching bath is allowed to rise to well over 120 g l⁻¹. Such high concentrations can only be reached when using aluminium complexing additives.

Geochemical engineering processes aimed to recover source materials from etching wastewaters through the synthesis of secondary minerals have been focused on the production of zeolites and dawsonite (NaAl(OH)₂CO₃). The synthesis of 4A, 13X, Y and HZSM5 zeolites using different sources of silicon (amorphous silica, sodium silicate and Si-containing solutions obtained from fly ashes) has been studied [30–34]. The interest in these zeolites mainly lies in their possible marketable applications either as a component of detergents or as catalysts. The feasibility of synthesising the mentioned zeolites has been proven using either amorphous silica or sodium silicate as silicon suppliers. The physico-chemical properties of synthesised zeolites (high cation exchange capacity, specific surface area and whiteness, and low particle size), together with their particularly low content in trace metals, make them useful for the mentioned industrial uses, especially as water softeners in the detergent industry. Conversely, the use of Si extracts from fly ashes fails in the obtaining of a single pure zeolite phase with industrial interest; at the most suitable conditions just a 4A-X zeolite blend was synthesised using this silicon source. As a consequence of the treatment of etching wastewaters via the described geochemical process a residual solution is generated. This is mainly composed by sodium silicate and hydroxide. Such composition allows its reuse in new syntheses of zeolites. Alternatively, this could be subjected to the typical neutralisation process. In this case, it is worth mentioning that the volume of waste solution to be neutralised is greatly reduced by the previous stage of zeolite synthesis.

The synthesis of dawsonite has been also proposed as a way to deal with the etching waste streams of the aluminium anodising industry [35]. Dawsonite and dawsonite-type compounds show interest for their behaviour of antacids and fire retardants [36], for being often employed in the preparation of new ceramic

materials made of alumina [37–39], and also for their use as absorbents for industrial flue gases [40]. The feasibility of synthesising this mineral from the etching wastewaters was studied as a function of NaHCO₃/Al molar ratio (1–10), crystallization temperature (30–150 °C) and reaction time (2–48 h) using supersaturated NaHCO₃ solutions. It was found that a NaHCO₃/Al molar ratio of 3 is optimal to obtain dawsonite as a single phase, whereas crystallization temperature and reaction time only have influence on the mineral crystallinity. Almost 100% of the aluminium present in the etching waste streams is recovered in the form of dawsonite when the suitable NaHCO₃/Al molar ratio is used to synthesise dawsonite as the only crystalline product. In such conditions, the aluminium concentrations remaining in solution after synthesis comply with the legal requirements of discharge established by the European Committee for Surface Treatment [6]. Therefore, this treatment appears as a really interesting alternative to manage the etching waste streams, especially if the carbonate required to synthesise dawsonite could be supplied in a way to lower the cost of the process (e.g., by CO₂ bubbling). One must bear in mind that different processes and patents have been proposed and registered for the synthesis of dawsonite [40–44] as this mineral displays numerous important industrial applications, and so this is an important marketable mineral.

4.2.2. Wastewaters from the anodising process

The synthesis of two different minerals with different industrial and/or environmental applications has been proposed for the direct treatment of anodising wastewaters; these are ettringite and hydrotalcite-like compounds.

The synthesis of ettringite (3CaO·Al₂O₃·3CaSO₄·32H₂O) has been proven to be a possible way to deal with the acid wastewaters of the aluminium anodising industry [45]. This process allows to reduce in a high degree the emissions to the environment and to recover at the same time resource materials as a useful mineral. Ettringite is an important crystalline component of Portland cement, and may constitute the principal matrix former of sulphoaluminate cements, showing characteristics such as superior sulphate resistance, rapid hardening, early sustainable strength, expansion and self-stressing [46–48]. On the other hand, ettringite possesses the ability to behave as a host for metallic pollutants to immobilise both cationic and anionic ions through sorption and phase mixing [49]. Ettringite appears, therefore, as a valuable material for remediation of contaminated sites, waste immobilisation in cementitious materials and wastewater treatment [50–52]. The synthesis of ettringite from the waste streams arising from the anodising process was shown to be achievable by slight heating of wastewater suspensions containing calcium oxide and calcium aluminate (sources of calcium and aluminium); the latter also acting as a promoter of ettringite precipitation. The optimal conditions to perform this synthesis are high alkalinity (pH ≈12) and sul-

phate concentrations below 0.1 M. Hence, wastewaters should not be concentrated above this value to avoid additional water consumption. Following this process, about 90% of the aluminium initially present in the wastewater solutions can be recovered in the form of ettringite when the suitable conditions of synthesis are employed. The residual solution derived from the described process could be reused in new syntheses as a source of both aluminium and alkalinity. The synthesis of ettringite appears, therefore, as an alternative, low-cost method to treat the acid anodising wastewaters.

The feasibility of synthesising the $\text{Mg}^{2+}\text{-Al}^{3+}\text{-SO}_4^{2-}$ -hydrotalcite type compound from the acid wastewaters of the aluminium anodising industry was firstly shown by Álvarez-Ayuso and Nugteren [53] using Mg-salts as sources of this element, as is usually done in the synthesis of hydrotalcite-type compounds. Nevertheless, even if the synthesis of this mineral from these waste streams could represent an interesting option to manage them, the incorporation of nitrates in the mentioned process represents the inclusion of an additional pollutant, restringing greatly the actual application of this geochemical treatment. Afterwards, the process was proven using MgO as a source of magnesium [54]. The main requisite to perform this synthesis is to keep the solution pH at values ≥ 8 . The use of MgO to supply the required magnesium appears as a really good alternative. First, the introduction of counterbalance anions into the solution is avoided. This prevents the solution from being polluted with such anions. Secondly, MgO dissolves easily in acid medium, thereby increasing the solution pH, and so decreasing the amount of alkalinity required to perform the process of synthesis. Following this geochemical process, almost 100% of the aluminium initially present in the wastewater solution is recovered in the form of the desired compound, remaining in the final waste solution aluminium concentrations that comply with the legal limit currently in force in most EU countries. This clay mineral is useful as catalyst and polymer stabiliser [55–57]. Taking into account the characteristics of some reagents (wastewater solutions) used in the described process, the hydrotalcite-type compound synthesised from it could find its way to the market mainly as polymer stabiliser.

4.2.3. Wastewaters from the brightening process

Although the volume of wastewaters produced from the brightening process is much more reduced than those from the anodising and etching processes, their treatment has also been a subject of study. A geochemical engineering process based on the sequential precipitation of phosphates and sulphates (the main components of these acid waste streams) has been proposed [58]. In a first step, phosphates are removed after the incorporation of MgO, giving rise to the formation of magnesium phosphates, either bobierite ($\text{Mg}_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$) or newberyite ($\text{MgHPO}_4 \cdot 3\text{H}_2\text{O}$), depending on the specific source of magnesium employed in the precipitation process. The former is the dominant product when using analytical grade MgO, and the latter when low-grade MgO is employed. Low-grade MgO requires more time and about four times the stoichiometric amount of magnesium for the reaction to proceed. In spite of these disadvantages, its use is recommended from an economic standpoint. In a second step, sulphate is recovered in the form of gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) by means of the addition of lime to the remaining waste solution. The magnesium phosphates obtained in this way have been proposed to be useful as soil fertilisers. Nevertheless, their actual application should be tested in order to assure that no-side adverse environmental consequences could be derived from this use. Concerning gypsum, this mineral is produced in huge amounts from the desulphurisation processes applied in coal-combustion power plants. In some countries (e.g., The Netherlands) this by-product is employed in the wallboard manufacture or in

the cement industry. Conversely, in other countries with natural deposits of gypsum (e.g., Spain) this by-product is used in a great proportion as a landfill material in mine reclamation or just sent to landfills for its disposal. Therefore, the application of the gypsum arising from the process just described could be quite limited.

5. Conclusions

Among the different systems proposed for the treatment of waste streams of the aluminium anodising industry, the classical procedure based on the neutralisation process and the subsequent sludge disposal represent an end-of-pipe solution. This aspect, together with the increasing disposal taxes, and the high cost of other alternative or co-operative techniques already available for their implementation, has provoked the proposal of new possible routes that would lead to sustainable solutions to manage the waste streams concerned. These entail the recovery of resource materials, and the reduction of emissions to the environment. Among the treatments recently proposed, there are the use of anodising mud in the manufacture of refractory bodies, and the synthesis of useful minerals (zeolites, dawsonite, ettringite, hydrotalcite-like compounds, magnesium phosphates and gypsum) from the wastewaters arising from the etching, anodising and brightening processes. Concerning the former methods their viability is mainly dependent on their cost; those requiring high calcination temperatures, and therefore high-energy consumption, must be discarded. Among the zeolites whose synthesis has been found to be feasible from the etching streams (4A, 13X, Y and HZSM5), only those with application in the detergent industry (4A, 13X) are actually worthy. The use of zeolites synthesised in this manner as catalysts in industrial processes must be rejected; products with no impurities are compulsory for catalytic processes. Dawsonite is a really interesting mineral to be synthesised also from the etching streams whenever the process occurs using a low-cost source of carbonate. The treatments suggested to deal with the anodising wastewaters seem feasible from an economic point of view. The main limitation of the ettringite synthesis lies in the sulphate concentration limit required for the reaction to proceed. Its implementation is, therefore, dependent on the specific rinsing system applied in each anodising industry. Promising is also the hydrotalcite-like compound synthesis. The marketability of this product as polymer stabiliser appears quite feasible. Anyway, further research is required to assure that the corresponding required specifications are accomplished. Additionally, the viability of the synthesis and the marketability of the final product should be tested using low-grade MgO. The feasibility of solutions proposed for the treatment of the brightening wastewaters is mainly dependent on the actual applicability of synthesised magnesium phosphates as soil fertilisers (not investigated so far), and on the location of anodising industries.

In general, it seems that selective treatments of wastewaters before the neutralisation process could be the best option to achieve the goal of sustainability pursued. First, this would allow a great reduction in anodising mud generation, which is nowadays the main concern. Secondly, the objective of recycling of primary materials would be achieved. Furthermore, in this way the manufacture of refractory bodies could absorb in an important proportion the reduced production of anodising mud, approaching the ideal target of zero discharges to the environment. To do so, the different stages of this integral approach must be performed successfully. The main tasks to perform are to optimise the synthesis processes, to bring the synthesised products to current market specifications, and to establish engineering factors for the scaling up of processes. Developing such technology both economic and environmental benefits may be obtained.

References

- [1] M. Kalmar, Proceedings of the European Surface Treatment of Aluminium, ESTAL, Istanbul, 2000, pp. 98–132.
- [2] M.J. Ribeiro, J.A. Labrincha, Properties of sintered mullite and cordierite pressed bodies manufactured using Al-rich anodising sludge, *Ceram. Int.* 34 (2008) 593–597.
- [3] Council Directive 1999/31/EC of 26 April 1999 on the landfill of waste.
- [4] Council Decision 2003/33/EC of 19 December 2002 Establishing Criteria and Procedures for the Acceptance of Waste at Landfills Pursuant to Article 16 of and Annex II to Directive 1999/31/EC.
- [5] W.J. McLay, F.P. Reinhard, Waste minimization and recovery technologies, *Met. Finish* 98 (2000) 817–850.
- [6] BAT Reference Document, Surface Treatment of Metals and Plastic Materials using Electrolytic or Chemical Process, European Committee for Surface Treatment, European IPPC Bureau, 2002.
- [7] R.J. Brook, Concise Encyclopedia of Advanced Ceramic Materials, Pergamon Press, New York, 1991.
- [8] P. Pajunen, Chemical recovery for aluminium finishers, in: Workshop on Cleaner Production in the Metal Finishing Industry, Taipei, 1999.
- [9] C. Iranzo Blasco, Procedimiento de fabricación de sulfato de aluminio y sus derivados a partir de lodos de hidróxido de aluminio procedentes de las plantas de anodizados, Spanish Patent 2,176,064 (2002).
- [10] J.A. Perez, R. Terradas, M.R. Manent, M. Seijas, S. Martinez, Inertization of industrial wastes in ceramic materials, *Ind. Ceram.* 16 (1996) 7–10.
- [11] D.A. Pereira, J.B. Aguiar, F.P. Castro, M.F. Almeida, J.A. Labrincha, Mechanical behaviour of Portland cement mortars with incorporation of Al-rich salt sludges, *Cement Concrete Res.* 30 (2000) 1131–1138.
- [12] D.A. Pereira, D.M. Couto, J.A. Labrincha, Incorporation of aluminium-rich residues in refractory bricks, *Ceram. Forum Int.* 77 (2000) 21–25.
- [13] I.A. Aksay, D.M. Dabbs, M. Sarikaya, Mullite for structural, electronic and optical applications, *J. Am. Ceram. Soc.* 74 (1991) 2343–2358.
- [14] M. Mizuno, Microstructure, microchemistry, and flexural strength of mullite ceramics, *J. Am. Ceram. Soc.* 74 (1991) 3017–3022.
- [15] S.M. Naga, D.A.A. Aziz, Effect of alumina/clay ratio on the properties of doped electrical alumina porcelain, *Br. Ceram. Trans.* 101 (2002) 129–132.
- [16] S. Sundar, V.S.S. Vepa, A.M. Umarji, Effect of substitution of Ca on thermal expansion of cordierite ($Mg_2Al_4Si_5O_{18}$), *J. Am. Ceram. Soc.* 76 (1993) 1873–1876.
- [17] E. Schmidbauer, P.W. Mirwald, Electrical conductivity of cordierite, *Mineral. Petrol.* 48 (1993) 201–214.
- [18] R.N. Das, C.D. Madhusoodana, K. Okada, Rheological studies on cordierite honeycomb extrusion, *J. Eur. Ceram. Soc.* 22 (2002) 2893–2900.
- [19] A.G.T. Martinez, M. Camerucci, G. Urretavizcaya, A.L. Cavalieri, Behaviour of cordierite materials under mechanical and thermal biaxial stress, *Br. Ceram. Trans.* 101 (2002) 94–99.
- [20] D.U. Tulyaganov, M.E. Tukhtaev, J.I. Escalante, M.J. Ribeiro, J.A. Labrincha, Processing of cordierite based ceramics from alkaline–earth–aluminosilicate glass, kaolin, alumina and magnesite, *J. Eur. Ceram. Soc.* 22 (2002) 1775–1782.
- [21] M.A. Camerucci, G. Urretavizcaya, A.L. Cavalieri, Sintering of cordierite based materials, *Ceram. Int.* 29 (2003) 159–168.
- [22] J.M.F. Ferreira, S.M. Olhero, Al-rich sludge treatments towards recycling, *J. Eur. Ceram. Soc.* 22 (2002) 2243–2249.
- [23] M.J. Ribeiro, D.U. Tulyaganov, J.M. Ferreira, J.A. Labrincha, Recycling of Al-rich industrial sludge in refractory ceramic pressed bodies, *Ceram. Int.* 28 (2002) 319–326.
- [24] M.J. Ribeiro, J.C.C. Abrantes, J.M. Ferreira, J.A. Labrincha, Predicting processing-sintering-related properties of mullite-alumina ceramic bodies based on Al-rich anodising sludge by impedance spectroscopy, *J. Eur. Ceram. Soc.* 22 (2004) 2243–2249.
- [25] M.J. Ribeiro, D.U. Tulyaganov, J.M.F. Ferreira, J.A. Labrincha, Production of Al-rich sludge-containing ceramic bodies by different shaping techniques, *J. Mater. Process. Tech.* 148 (2004) 139–146.
- [26] M.J. Ribeiro, D.U. Tulyaganov, J.M. Ferreira, J.A. Labrincha, High temperature mullite dissolution in ceramic bodies derived from Al-rich sludge, *J. Eur. Ceram. Soc.* 25 (2005) 703–710.
- [27] M.J. Ribeiro, S. Blackburn, J.M. Ferreira, J.A. Labrincha, Extrusion of alumina and cordierite-based tubes containing Al-rich anodising sludge, *J. Eur. Ceram. Soc.* 26 (2006) 817–823.
- [28] J.A. Labrincha, C.M. Albuquerque, J.M. Ferreira, M.J. Ribeiro, Electrical characterisation of cordierite bodies containing Al-rich anodising sludge, *J. Eur. Ceram. Soc.* 26 (2006) 825–830.
- [29] H. Verheul, How social networks influence the dissemination of cleaner technologies to SMEs, *J. Cleaner Prod.* 7 (1999) 213–219.
- [30] J. Dufour, A. La Iglesia, V. Gonzalez, J.C. Ruiz-Sierra, Viability of the use of pickling baths from aluminium surface treatment for synthesizing low Si/Al zeolites, *J. Environ. Sci. Health A* 32 (1997) 1807–1825.
- [31] J. Dufour, V. Gonzalez, A. La Iglesia, Optimization of 4A zeolite synthesis as recovery of wastes from aluminium finishing, *J. Environ. Sci. Health A* 36 (2001) 1257–1269.
- [32] J. Dufour, V. Gonzalez, A. La Iglesia, Synthesis of 13X zeolite from alkaline waste streams in the aluminium anodizing industry, *Ind. Eng. Chem. Res.* 40 (2001) 1140–1145.
- [33] A. La Iglesia, M.V. Gonzalez, J. Dufour, Zeolite synthesis employing alkaline waste effluents from the aluminum industry, *Environ. Prog.* 21 (2002) 105–110.
- [34] N. Moreno, X. Querol, F. Plana, J.M. Andres, M. Janssen, H. Nugteren, Pure zeolite synthesis from silica extracted from coal fly ashes, *J. Chem. Technol. Biotechnol.* 77 (2002) 274–279.
- [35] E. Álvarez-Ayuso, H.W. Nugteren, Synthesis of dawsonite: a method to treat the etching waste streams of the aluminium anodising industry, *Water Res.* 39 (2005) 2096–2104.
- [36] C.J. Serna, J.L. White, S.L. Hem, Nature of amorphous aluminum hydroxycarbonate, *J. Pharm. Sci.* 67 (1978) 324–331.
- [37] K. Hayashi, S. Toyoda, K. Nakashima, K. Morinaga, Optimum synthetic conditions of ammonium aluminum carbonate hydroxide (AACH) as starting material for α -alumina fine powders, *J. Ceram. Soc. Jpn.* 98 (1990) 444–449.
- [38] M. Giannos, M. Hoang, T.W. Turney, Thermally stable aluminas for high temperature applications, *Chem. Lett.* 8 (1998) 793–794.
- [39] J.G. Li, T. Ikegami, J.H. Lee, T. Mori, Y. Yajima, Synthesis of Mg–Al spinel powder via precipitation using ammonium bicarbonate as the precipitant, *J. Eur. Ceram. Soc.* 21 (2001) 139–148.
- [40] P. Bénézech, D.A. Palmer, L.M. Anovitz, J. Horita, Dawsonite synthesis and reevaluation of its thermodynamic properties from solubility measurements: implications for mineral trapping of CO_2 , *Geochim. Cosmochim. Ac.* 71 (2007) 4438–4455.
- [41] P. Van Der Heem, Dawsonite, U.S. Patent 4,221,771 (1980).
- [42] R.L. Altman, Synthesis of Dawsonites, U.S. Patent 4,356,157 (1982).
- [43] G. Herold, Process for Producing Dawsonite, US Patent 5,078,983 (1992).
- [44] X. Zhang, Z. Wen, Z. Gu, X. Xu, Z. Lin, Hydrothermal synthesis and thermodynamic analysis of dawsonite-type compounds, *J. Solid State Chem.* 177 (2004) 849–855.
- [45] E. Álvarez-Ayuso, H.W. Nugteren, Synthesis of ettringite: a way to deal with the acid wastewaters of aluminium anodising industry, *Water Res.* 39 (2005) 65–72.
- [46] S. Hu, H. Yang, S. Liu, D. Chen, D. Dollimore, Kinetic analysis of the hydration of $3CaO \cdot 3Al_2O_3 \cdot CaSO_4$ and the effect of adding $NaNO_3$, *Thermochim. Acta* 26 (1994) 129–140.
- [47] Q. Zhou, F.P. Glasser, Thermal stability and decomposition mechanisms of ettringite at $<120^\circ C$, *Cement Concrete Res.* 31 (2001) 1333–1339.
- [48] F. Goetz-Neunhoffer, J. Neubauer, P. Schwesig, Mineralogical characteristics of Ettringites synthesized from solutions and suspensions, *Cement Concrete Res.* 36 (2006) 65–70.
- [49] M.L.D. Gougar, B.E. Scheetz, D.M. Roy, Ettringite and C–S–H-portland cement phases for waste ion immobilization: a review, *Waste Manage.* 16 (1996) 295–303.
- [50] R.B. Perkins, C.D. Palmer, Solubility of ettringite $Ca_6[Al(OH)_6]_2(SO_4)_3 \cdot 26H_2O$ at $5\text{--}75^\circ C$, *Geochim. Cosmochim. Ac.* 63 (1999) 1969–1980.
- [51] Q. Zhang, F. Saito, Sonochemical synthesis of ettringite from a powder mixture suspended in water, *Powder Technol.* 107 (2000) 43–47.
- [52] M. Zhang, E.J. Readon, Removal of B, Cr, Mo and Se from wastewater by incorporation into hydrocalumite and ettringite, *Environ. Sci. Technol.* 37 (2003) 2947–2952.
- [53] E. Álvarez-Ayuso, H.W. Nugteren, Synthesis of a $Mg^{2+}\text{--}Al^{3+}\text{--}SO_4^{2-}$ -hydrotalcite type compound from the acid wastewaters of the aluminium-anodizing industry, *Clay Clay Miner.* 53 (2005) 11–17.
- [54] E. Álvarez-Ayuso, H.W. Nugteren, Emission reduction of aluminium anodising industry by production of $Mg^{2+}\text{--}Al^{3+}\text{--}SO_4^{2-}$ -hydrotalcite type compound, *Chemosphere* 62 (2006) 155–162.
- [55] E. Suzuki, Y. Ono, Aldol condensation reaction between formaldehyde and acetone over heat-treated synthetic hydrotalcite and hydrotalcite-like compounds, *B. Chem. Soc. Jpn.* 61 (1988) 1008–1010.
- [56] E. Dumitriu, V. Hulea, C. Chelaru, C. Catrinescu, D. Tichit, R. Duran, Influence of the acid-base properties of solid catalysts derived from hydrotalcite-like compounds on the condensation of formaldehyde and acetaldehyde, *Appl. Catal. A: Gen.* 178 (1999) 145–157.
- [57] F. Kovanda, D. Kolousek, R. Kalouskova, Z. Vymazal, Starting production of synthetic hydrotalcite in the Czech Republic, *Chem. Listy* 95 (2001) 493–497.
- [58] J.M. Chimenos, A.I. Fernández, A. Hernández, L. Haurie, F. Espiell, C. Ayora, Optimization of phosphate removal in anodizing aluminium wastewater, *Water Res.* 40 (2006) 137–143.