

Improvement of Discharged Water Quality by Alteo Gardanne

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Abstract

Alteo Alumina in Gardanne, France, first operated in 1894, is the oldest alumina refinery in the world. It has met many challenges in its lifetime, a notable example being the move to the production of specialty aluminas in the 1990s. The most recent challenge, the need to significantly decrease the plant impact on the environment to follow regulatory evolution and improve community acceptance of the site, has perhaps been the most difficult and complex. The improvements made during the last 6 years have been spectacular. Specifically, in 2015 the “red mud” discharged from the plant had a solid bauxite residue content of 75g/L, pH 12.5, dissolved aluminium 400mg/L, dissolved arsenic 350µg/L, COD 200 mgO₂/L and BOD5 100 mgO₂/L. In 2021, water discharged from the plant has a solid content of less than 0.035g/L, pH 8.5, dissolved aluminium is less than 1 mg/L, dissolved arsenic is 40 µg/L, COD 50 mgO₂/L and BOD5 10 mgO₂/L. The various stages that made these dramatic improvements possible, and why these options were chosen at the time will be reviewed.

Keywords: Alumina production, Environmental performance, Bauxite residue, Waste water, Reduction of environmental impact.

1. Introduction

The environmental impact of alumina refineries, whether actual or perceived, poses a significant threat to the existence of the industry. Specific greenhouse gas emissions, although significantly lower than the downstream smelting of aluminium, will need to be reduced to meet ever tighter regulations as climate change will no doubt be the main driver for new policies. Other improvements need to be made on various emissions like NO_x or SO_x from steam production or calcination, while dusts from bauxite, alumina or bauxite residue need to be under better control.

The main issue that the industry faces however, is arguably the handling of the large quantities of bauxite residue (red mud) generated by the Bayer process. Several significant spills and incidents have raised awareness in the general public about this waste, and it is generally perceived as “hazardous”, although it is most of the time not the case for the solid part. The Ajka accident on the 4th of October 2010 [1], involving 10 fatalities, comes obviously to mind together with more limited and recent events.

Most, if not all, alumina refineries in the world have been under increasing pressure in the last 20 years to better manage their residue discharge stream and stored bauxite residue [2] to decrease hazards for local communities and environments. Significant investments and extra operating costs are necessary to comply with ever more challenging regulations. This weighs on a site’s balance sheet at best, and can put refineries out of business at worst. If the reduced discharge concentrations requested cannot be met, operating permits might not be renewed.

As most alumina production sites have been struggling with this for many decades, this paper documents what has been done at Alteo Gardanne, France, to very significantly improve the discharged water quality.

The Gardanne refinery was the first industrially operated Bayer process in the world, beginning operations in 1894. For most of its history it has been part of the Pechiney group, but since 2012 has been operated by Alteo, which has been recently acquired by UMS Group.

Along the way, several modernization stages and production increases have taken place, including a major step that took place in 1966. Since then, and for almost 50 years most of red mud has been discharged through a 55 km pipe to a discharge point 7 km offshore and 320 m deep into the Mediterranean Sea, as per Figure 1.

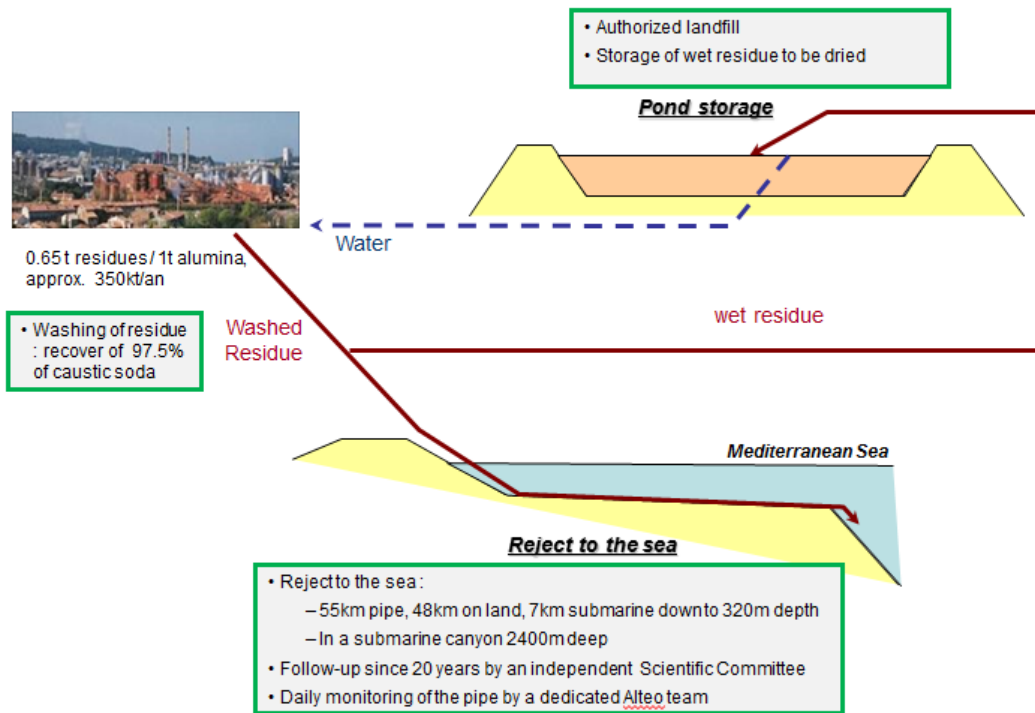


Figure 1. Pre-2008 management of bauxite residue and wastewater.

Since 2015 a major environmental transformation has taken place, with the achieved improvement in water quality summarized in Table 1. The improvement was done through several significant investments, as described in the following sections, including a preparatory stage from 2008 to 2015 with filter pressing a part of the residue flow.

Table 1. Improvement of water quality discharged in a sea trench

	2015	2021
pH	12.5	8.5
Suspended solids (mg/l)	75000	35
Dissolved Al (mg/l)	400	1
Dissolved As (mg/l)	0.35	0.04
COD (mg O ₂ /l)	200	50
BOD5 (mg O ₂ /l)	100	10

For reasons other than the success of the improvements reported here, Alteo is currently undergoing a transition to stop digesting bauxite and switch to an aluminium hydroxide feedstock, as the best way to continue serving our speciality alumina markets and customers.

2. Recovery of Solids from Bauxite Residue

A first filter press was set up in the Gardanne refinery in 2006. This allowed the gradual reduction in solid waste discharged to the sea according to our license to operate. Press filtration is recognized as a Best Available Technique for bauxite residue management [3]. Using filter presses for red mud management has 3 main advantages:

- Some soda is recovered from the mud and recycled to the process, while making the residue less caustic and more readily reused.
- The storage surface area needed in the bauxite residue storage area (BRDA) is reduced as volumes to be stored decrease.
- Handling dry residue, and dry storage significantly decreases the risk of spills and dam failures.

Filter presses achieve a maximum of 30% remaining moisture in the solids, sufficient to prevent liquefaction of the material during transport due to its thixotropic behavior. From 2006 to 2015, 100,000 tons of dry bauxite residue were produced per year, which was either stored in the BRDA or sold for reuse as Bauxaline®. The management of bauxite residue and wastewater changed as described by Figure 2.

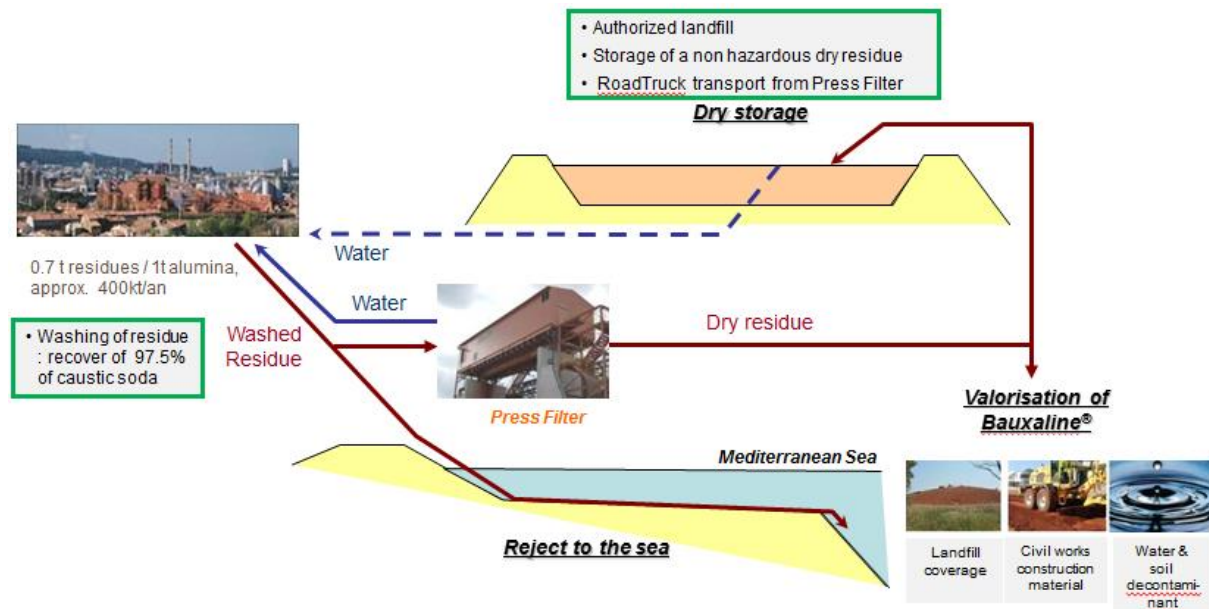


Figure 2. Management of bauxite residue and wastewater between 2006 and 2015.

By the end of 2015, discharge of bauxite residue solids to the sea was completely stopped. To do so, 2 additional filter presses were installed to dehydrate all of the 400,000 t of bauxite residue produced every year. These press filters are located directly at the BRDA, 4 kilometers away from the refinery. At the same time, to guarantee less than 35 mg/l of solids in the wastewater still discharged to the sea, a pressure filter process unit to minimise suspended solids was implemented. Details can be found elsewhere [4].

Management of bauxite residue and wastewater was then as per Figure 3.

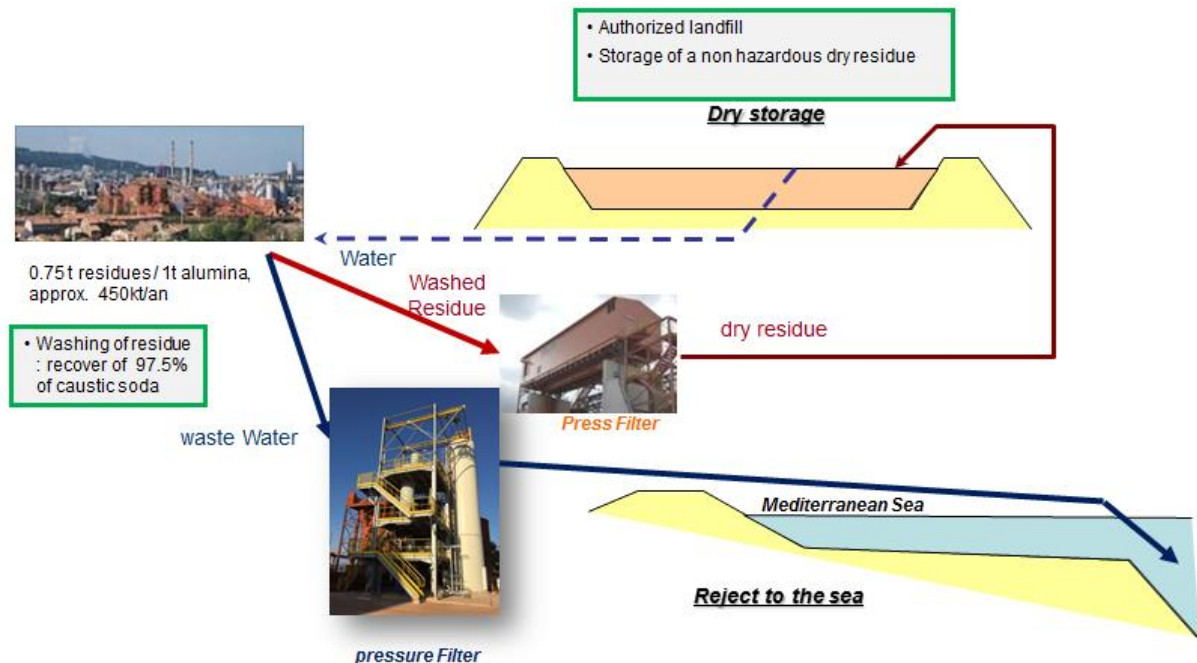


Figure 3. Management of bauxite residue and wastewater 2015-2019.

The implementation of these new operational stages had substantially reduced the environmental impact, with a 99.95% solid content reduction, and consequently a reduction of more than 99% in metals discharged at sea.

3. Decreasing pH and Dissolved Metals

Removing suspended solids obviously does not change the pH of the waste water and some metals are soluble at levels above the standards for discharge to fresh or sea water. Actual wastewater quality in 2016 was:

- high pH (typically between 12 and 12.4).
- high levels of aluminum (typically between 50 and 400 mg/L).
- high levels of arsenic (typically between 150 µg/L and 800 µg/L).

While water quality for a permit renewal was expected to be:

- pH < 9.5
- Aluminum content < 5 mg/l.
- Arsenic content < 50 µg/l.

3.1 First Improvements

Before any significant new investment, some improvements were already made with better process control. The aluminum and arsenic content of wastewater had been significantly improved in 2016 as shown Figure 4 through:

- Washer train and water balance efficiency, halving the average wastewater soda content.
- A new oxalate causticization unit implemented in the refinery in June 2016 and subsequently improved in April 2017.

Thanks to these changes, aluminum content was reduced by 5 to 10 times, but stayed generally over the expected maximum limit of 5 mg/l. Arsenic content decreased 20-fold and the average value was close to the expected limit. Nevertheless, this decrease was not sufficient to guarantee a concentration consistently lower than the limit.

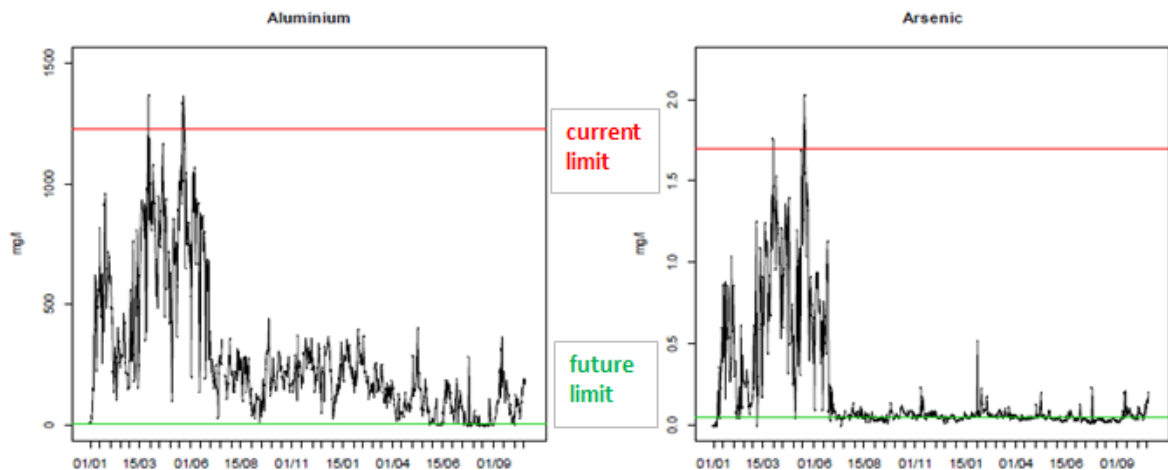


Figure 4. Aluminum and arsenic content in wastewater 2016-2017.

3.2. Neutralization Method Selection

Different treatments were considered to further reduce dissolved metals:

- acid neutralization (HCl, H₃PO₄, H₂SO₄, mixed acids)
- lime precipitation
- MgCl₂ neutralization and precipitation
- CO₂ neutralization

In spite of it being a weak acid, carbon dioxide was selected, mainly because of a general compatibility with the Bayer process:

- the precipitated solids can be mixed with bauxite residue without changing its chemical properties (still non-hazardous waste);
- the sodium carbonate recycled to the Bayer process could be easily removed by a typical causticization process;
- the treated water presents no corrosion risk for the steel wastewater pipe to the sea.

On the other hand, sulfuric, phosphoric or hydrochloric acids have associated drawbacks:

- acid anions are not removed by usual Bayer process treatments, such as causticization;
- it is not possible to mix the precipitated solid with bauxite residue due to their chemical properties, since these precipitated solids are classified as hazardous waste and as such, must be disposed of in a specific waste storage area.

Lime was not selected because there is no effect on pH and it requires excessive water consumption. MgCl₂ treatment is effective for aluminum, arsenic and pH reduction but generates large amounts of sludge (hydrotalcite), with associated handling issues.

3.3 CO₂ Neutralization Process Design

3.3.1 Principle

By decreasing the pH of the wastewater, impurities such as aluminum and arsenic naturally precipitate. The precipitated solid, named 'CO₂ sludge', is separated from the treated water by settling using specific flocculants. The color of the 'CO₂ sludge' varies from white to pink depending on the percentage of bauxite residue particles in the wastewater.

The 'CO₂ sludge' could be eventually recycled into the Bayer process, in the last washer, where it could settle with the red mud and subsequently be sent to the filter press and to the bauxite residue disposal area.

3.3.2 Pilot Plant Description

A pilot plant had been in operation for more than one year in cooperation with an environmental engineering consultant and a carbon dioxide supplier. As shown in the below picture, the pilot plant consisted of:

- One neutralization tank (170 L) in which the wastewater is fed at about 500 L/h.
- One recirculating loop (2000 L/h) in which carbon dioxide is injected (up to 2 kg/h).
- One agitated coagulation tank and one agitated flocculation tank (140 L each).
- One conical-bottomed cylindrical settler with rake (surface 0.2 m²).

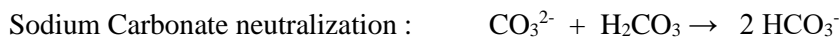
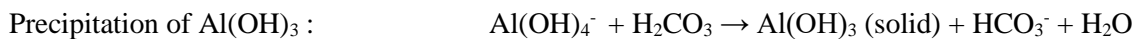
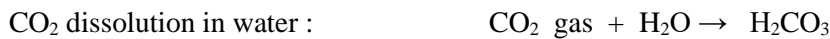
The carbon dioxide injection was set in accordance with the pH target (measured in the neutralization tank).



Figure 5. Carbon dioxide neutralization pilot plant.

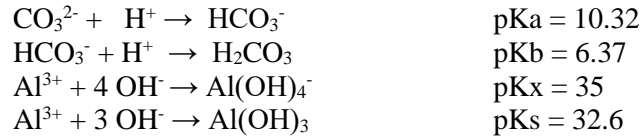
3.3.3 Main Results

To estimate carbon dioxide consumption, a simplified approach is to consider that the major species of Bayer wastewaters are caustic soda (sodium hydroxide or NaOH), sodium aluminate (NaAl(OH)₄) and sodium carbonate (Na₂CO₃). When injecting carbon dioxide the following reactions occur.



Other dissolved metals, such as arsenic, have no significant impact on the carbon dioxide consumption. Consumption of carbon dioxide may be estimated using electro neutrality and mass balances and considering the following pK values:





The carbon dioxide consumption can be calculated by using these constants linked to the chemical reactions estimated by this approach. For instance, to reach a pH of about 8.3 (first equivalence), the consumption is:

$$Q \text{ CO}_2 \text{ kg/h} = (2 \times [\text{Na}_2\text{O}_{\text{total}}]_{\text{g/L}} / 62 - [\text{Na}_2\text{O}_{\text{cbtd}}]_{\text{g/L}} / 62) \times 44 \text{ g/mol} \times \text{Waste Water flowrate m}^3/\text{h}$$

which gives, for 2 g $\text{Na}_2\text{O}_{\text{total}}$ /L, 10 % $\text{Na}_2\text{O}_{\text{cbtd}}$ and a feed flowrate of 500 L/h, a resulting carbon dioxide flowrate of 1.3 kg/h. $\text{Na}_2\text{O}_{\text{cbtd}}$ refers to sodium carbonate concentration analyzed with caustic soda and alumina. Figure 6 compares this calculation to the real carbon dioxide flowrate for different targeted pH.

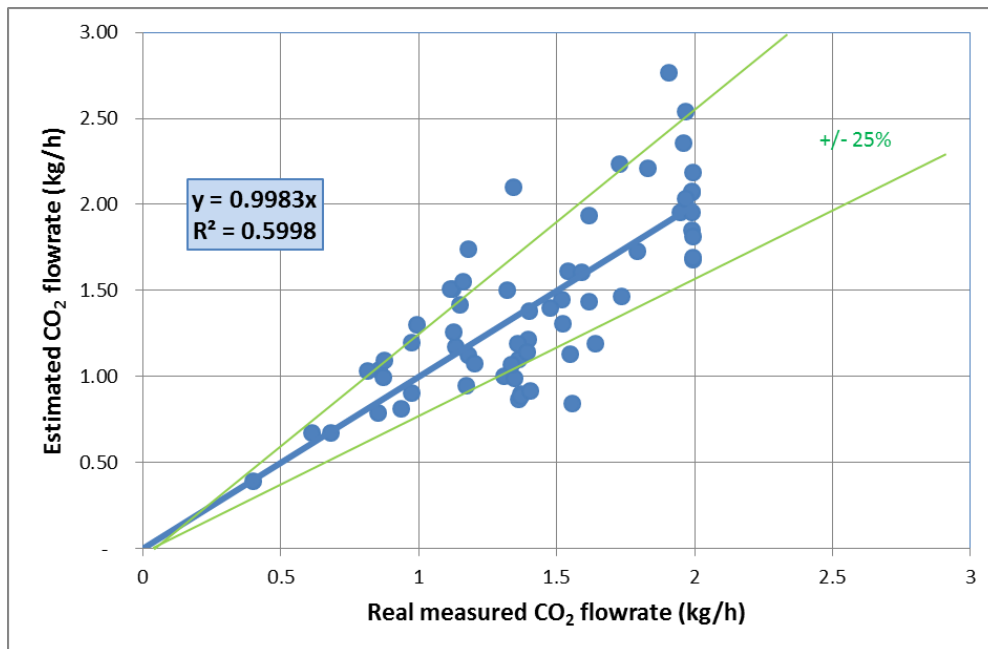


Figure 6. Comparison between estimated and measured CO₂ flowrate.

Considering measurement uncertainties of 10 %, the correlation is quite good and confirms a high carbon dioxide dissolution efficiency. The carbon dioxide supplier indicates regular efficiencies up to the 90 - 95 % range.

3.3.4 Flocculation, Settling and Mass Balance

The flocculants used are a very high molecular weight polymer at a concentration of 10 to 15 ppm (dry powder / waste water). Laboratory settling rates are between 30 to 40 m/h and turbidity less than 2 NTU.

The white 'CO₂ sludge' produced by the neutralization of filtered wastewater has a solid content from 20 to 30 g/L. Its flowrate is from 5 to 10 % of the wastewater's, depending on the alumina content. Some coagulants were tested, in particular ferric chloride, but none improved the quality of treated water. Some species in the Bayer liquor may already play the role of coagulant aid.

3.4.3 Aluminum and arsenic reduction

Dissolved aluminum and arsenic concentrations in the treated water were less than the expected environmental regulation limits, when the pH was below 8.5. Figure 7 shows the concentration of treated water in the pilot (logarithmic scale, the green line is the limit of the environmental regulations), depending on the pH targeted in the neutralization tank.

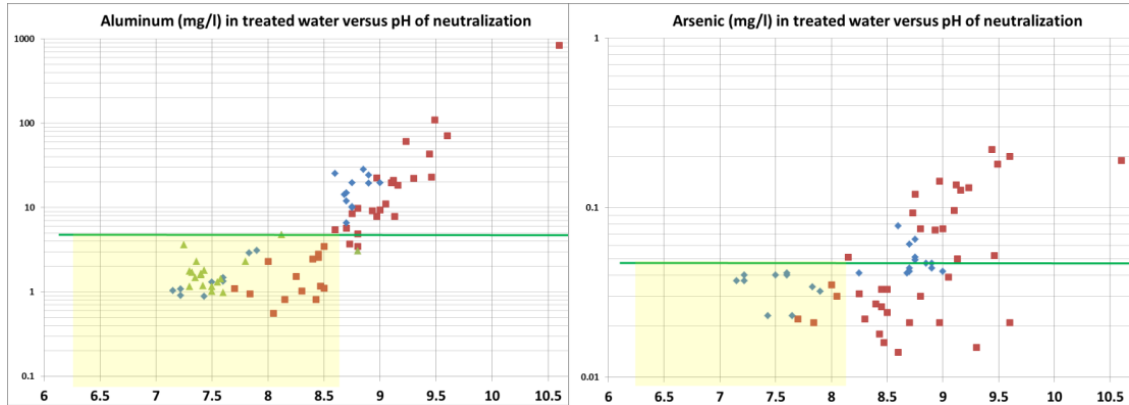


Figure 7. Aluminum and arsenic concentration of CO₂ treated water versus pH.

Other impurity concentrations are also reduced with this process: selenium, molybdenum, vanadium and chromium, but these concentrations are already below environmental regulations' limit, as analyzed with ICP-AES (Alteo Laboratory).

3.3.5 'CO₂ sludge' Components

A typical analysis of 'CO₂ sludge' is shown in Table 2. As expected, the major components are alumina, mineral carbon, calcium and sodium, while some traces of arsenic are detected. The dried 'CO₂ sludge' components are mainly Bayerite (Al(OH)₃) and some Dawsonite (Na Al CO₃ (OH)₂) as shown on the following XRD spectrum (obtained with synthetic soda liquor).

Table 2. Analysis of dried 'CO₂ sludge'.

Total Carbon	3.40%	Fe ₂ O ₃	0.20%
TOC	0.90%	V	0.01%
Loss in ignition	52.40%	As	0.01%
Al ₂ O ₃	46.00%	Se	0.001%
Na ₂ O	0.70%	Sn	0.001%
CaO	3.00%	Mo	0.001%
SiO ₂	0.30%	Zn	0.0003%

3.3.6 Recycling of 'CO₂ sludge' into the Last Washer of the Bayer Process

Tests were conducted to check the opportunity to recycle 'CO₂ sludge' into the last washer. These three requirements need to be fulfilled;

- low influence on settling of Bayer mud,
- solubility of CO₂ mud as low as possible in the last washer,
- limited impact on the quality of bauxite residue.

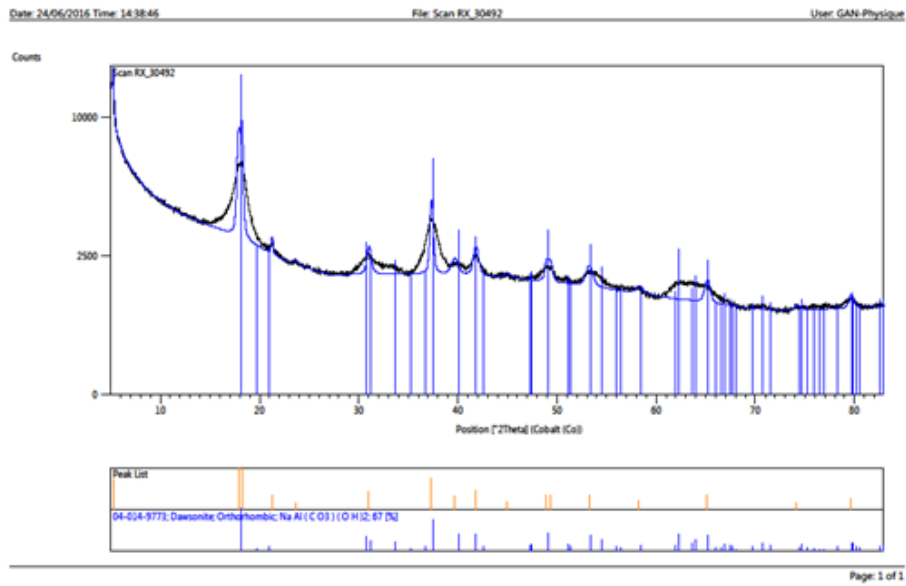


Figure 8. XRD spectrum of dried 'CO₂ sludge'.

The flow of 'CO₂ sludge' was estimated in the range 5 to 40 m³/h. The last washer is fed between 100 and 120 m³/h of residue slurry. So the 'CO₂ sludge' flow rate represents 5 to 25 % of the total feed of the last washing stage.

Settling tests were conducted with up to 4 times the amount of concentrated CO₂ mud (about 150 g/L) to exaggerate the effects. The maximum proportion expected in industrial operation (25%) corresponds to 5% of concentrated 'CO₂ sludge'. Both 'pink CO₂ mud' and 'white CO₂ mud' were tested. As shown Table 3, the settling rate is only slightly affected by the 'pink CO₂ mud' and is lower with the 'white CO₂ mud'. Turbidity is not affected for the expected mix under industrial conditions, but degrades when the proportion of 'CO₂ sludge' significantly increases. These tests confirmed the possibility to recycle 'CO₂ sludge' into the last washer.

Table 3. Settling tests in the last washing stage with various ratios of 'CO₂ sludge'.

% CO ₂ mud (by volume)	%	0%		pink CO ₂ mud'						white CO ₂ mud'		
		0%	0%	5%	5%	10%	10%	20%	20%	5%	10%	20%
Settling speed	m/h	1.09	1.8	3.5	2.52	0.33	3.6	0.11	1.31	0.39	0.34	0.31
Mud volume after 1h	mL	310	300	330	470	510	450	670	550	470	520	570
Mud volume after 20h	mL	260	270	310	340	410	410	560	520	300	370	470
Turbidity of overflow after 1 h	NTU	4.64	3.04	4.65	5.51	24.6	14.2	115	66.6	4.4	14.2	31.6
Turbidity of overflow after 20 h	NTU			3.2	3	8.9	6.9	20.6	16.4	4.2	6.8	9.8

Leaching tests were conducted by washing 10 g of concentrated CO₂ muds in 100 mL of a synthetic soda liquor at 2, 5 and 10 g/L as Na₂O (variation range of the last washer of Gardanne plant). No dissolution of aluminum was detected. About 25 % of arsenic is dissolved in the washer liquor, with dissolution greater with more concentrated liquor. For selenium and molybdenum, the dissolutions are 40 % and 20 % respectively. These low dissolution ratios allow recycling of the 'CO₂ sludge' into the last washer.

To check this last point, 10 % by volume of ‘CO₂ sludge’ produced in the pilot plant was mixed with last washer red mud to obtain the expected industrial ratio. This mix is filtered up to 70 % of dry solid content, close to the industrial press filter performance in the bauxite residue storage area. This mixed and filtered future residue is subject to the normalized leaching test (EN 12457-2). This involves contacting 100g of mud with 1 liter of water and then analyzing the leached water. The comparative leaching tests of the then bauxite residue with future residue showed that the future residue would still be classified as a ‘non-hazardous waste’.

3.4 Full Scale CO₂ Neutralization Plant

Based on the pilot plant principles and results, a full-scale CO₂ neutralization plant was designed and built. The equipment was commissioned and operation started on the 1st of March 2019.

A general view of the equipment can be seen in Figure 9, and the way the main wastewater parameters, specifically pH and metals content, changed from there.



Figure 9. CO₂ neutralization plant.

It can be readily seen in Figure 11 that dissolved aluminium decreased in March 2019 following the startup of the plant, and increased again during two episodes that year when the neutralization plant was stopped for some minor adjustments. Arsenic stabilized at a satisfactory level given the regulatory limits the plant is subject to. Nevertheless, BOD₅ was, as expected, unaffected and at a level largely exceeding the upcoming new limit of 30 mgO₂/l. That was to a lesser extent also true for COD. A further polishing stage was then necessary.

4. Biological Treatment

Excessive BOD₅ and COD levels were still exhibited by the wastewater, and the decision was made to add a biological treatment plant to deal with remaining excessive organic compounds. Although arguably these parameters would not have created an environmental issue as the discharge point is located 320m deep into the sea, complying with the regulation was absolutely necessary.

BOD₅ and COD are due to the presence of organic compounds, mainly oxalates and humates. In the solution designed by our partner, a global water treatment and environment group, these compounds are digested by a bacterial biofilm building up on small plastic beads floating in flowing wastewater. A large biomass is gradually produced and excess biomass is steadily released. After coagulation and flocculation, a settler and a thickener allow the extraction of a concentrated sludge, which then joins the upstream red mud flow to be filter pressed.

After running a pilot plant for a year, our partner built a full-scale plant able to treat wastewater at a flow rate of 270 m³/h, downstream of the neutralization plant, as a lower pH is needed for the microorganisms to thrive. As seen in Figure 10, two large tanks contain the biomass generation system. Operation of the plant then started on the 22nd of July 2020. Improvement of key parameters can be seen Figure 11.



Figure 10. Biological treatment plant.

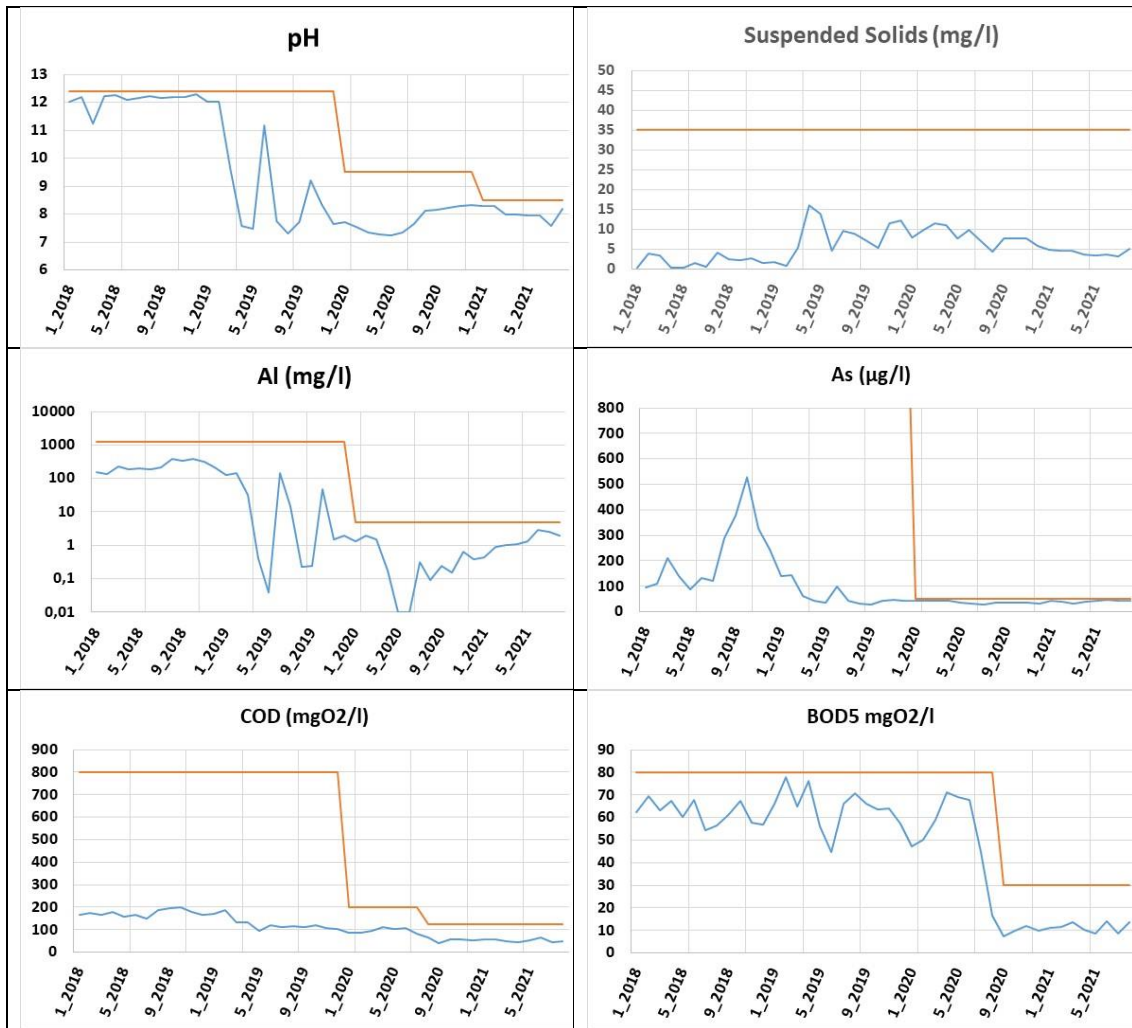


Figure 11. Wastewater quality changes, monthly averages. Red lines are regulatory limits.

5. Conclusions

The Gardanne alumina refinery environmental transformation journey began over two decades ago although it has accelerated since 2015. Wastewater quality discharged at sea improved dramatically as below:

	2015	2021
pH	12.5	8.5
Suspended solids (mg/l)	75000	35
Dissolved Al (mg/l)	400	1
Dissolved As (mg/l)	0.35	0.04
COD (mg O ₂ /l)	200	50
BOD ₅ (mg O ₂ /l)	100	10

It took a lot of dedication, energy and money to achieve this result. In-house R&D proved necessary as off the shelf solutions often did not exist. Enlightened by this experience, we believe we can help others to reach their own environmental targets, faster and more cheaply, and have created a consultancy called “Alteo Technologies” to do so. The team gathers our experts from the Bayer process, water treatment processes, BRDA management and bauxite residue reuse.

8. References

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