

Tube Digestion – Late Success of a VAW Technology

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Abstract

The Bayer process for leaching bauxite with caustic soda to produce aluminium oxide and the Hall-Héroult process for the extraction of aluminium using fused-salt electrolysis were decisive in providing the basis in 1888 for the production of aluminium on an industrial scale. Aluminium production is still based on these processes today. In the beginning, the introduction of these technologies was somewhat slow, there was a lack of suitable production equipment and a lack of markets for aluminium. Increased aircraft production resulting from the First World War created new demand and forced production to follow suit. This article describes the development of alumina production technology. The tube-digestion process, which Vereinigte Aluminium Werke A.G. (VAW) brought into industrial production as long ago as 1956, is now used in numerous modern alumina plants.

Keywords: Alumina plant, monohydrates, tube digester, high-temperature digestion, organics.

1. Historical Review

The extraction of aluminium was carried out for the first time in 1825 by the Danish chemist Hans Christian Oersted. He reduced aluminium chloride (AlCl_3) using potassium amalgam and extracted relatively pure aluminium particles.

In Germany, aluminium is associated with the name of Friedrich Wöhler. In 1821, Wöhler began studying chemistry under Gmelin in Heidelberg. Gmelin arranged for him to make a study visit to Berzelius in Stockholm. During his return journey, Wöhler visited Oersted in Copenhagen to find out more about the process for extracting aluminium. Oersted suggested that Wöhler should continue the work on aluminium because he himself was busy carrying out other research. The aluminium particles that Oersted gave Wöhler can be seen in the museum of the Institute for Chemistry in Göttingen.

Wöhler adopted Oersted's process. He used metallic potassium as the reducing agent and obtained pure aluminium in 1827. However, the cost of producing aluminium was higher than the price of gold so that industrial extraction was unattractive. Wöhler was appointed to the Chair of Chemistry and Pharmacy at the University of Göttingen in 1836. At the time, Göttingen was the hub for natural sciences and attracted students from all over the world, including Frank. F. Jewett from the USA from 1874 – 1875. He later became a professor at Oberlin College in Ohio, where he awakened the interest of one of his students, Charles Martin Hall, for the industrial extraction of aluminium – with success.

In 1886, Hall in the USA and Héroult in France applied for a patent for a process to extract aluminium using fused-salt electrolysis that they had developed independently at about the same time. Then in 1887 and 1892 Carl Joseph Bayer applied for patents for his inventions regarding the digestion of bauxite with caustic soda using the hydrothermal process that subsequently became known as the Bayer process. From 1864 onwards, Bayer had studied chemistry under Fresenius in Wiesbaden and then from 1869 – 1871 under Bunsen in Heidelberg.

These inventions provided the basis for the industrial production of aluminium and allowed aluminium's triumphal march to begin.

2. Development of Bauxite Digestion at VAW

When Vereinigte Aluminium-Werke A.G. (since 2002 Hydro Aluminium, although developments described were carried out exclusively at VAW), was founded in 1917 it was also assigned the task of producing the upstream and downstream products associated with aluminium production, with specific instructions to ensure that all raw materials used could be sourced within Germany. With this in mind, and given the scarcity of raw materials caused by the war, the Lautawerk in the Lusatia region was chosen as the location for an alumina plant, using the pyrogenic digestion of bauxite with soda and lime as the production process. The capacity was initially planned to be 36 000 tonnes a year but with the possible outcome of the war in mind it was limited to 24 000 tonnes. Commissioning proved to be extremely difficult; there was a whole host of so-called teething troubles, which were eventually solved.

It became necessary to increase the capacity for the first time in 1934. A decision to use the Bayer process for digestion had already been made because the question regarding raw materials appeared to have been solved with VAW's financial participation in Bauxit Trust A.G.. The superiority of the Bayer process was confirmed by tests carried out at the Lautawerk plant. The expansion was carried out in two stages and amounted to a total of 36 000 tpy. The expectations associated with the use of the Bayer process were fully met.

In keeping with the state of the art around about 1900, C.J. Bayer used an autoclave for his digestion process. Single-autoclave digestion remained standard practice until about 1940. However, despite the benefit of having a uniform residence time, the inadequate utilization of the plant (4 – 5 m³ per tonne of Al₂O₃ per day) was unsatisfactory. The workforce needed, the incomplete heat utilization and the difficult control of the method of operation constituted additional major disadvantages. An alternative approach was looked for from about 1930 onwards.

Tower digestion represented a move away from the use of a suspension; it used the digestion solution to leach out solid chunks of bauxite. Although the mode of operation was only semi-continuous, it brought with it major process benefits, which resulted in significant steam savings. The process was tried out at the Lautawerk plant from 1934 onwards and used on a large-scale from 1938 onwards at the Lippewerk plant in Lünen. It had to be abandoned however, because the bauxite chunks broke down on digestion and this led to difficulties in emptying the towers. In addition, it was only possible to process lumpy bauxites. Connecting the individual autoclaves in a continuous series was therefore investigated for fine bauxites. A test unit with a capacity of 0.25 m³/h was operated at the Lautawerk plant from 1935 to 1938. Production units went into operation at the Lippewerk plant and the Nabwerk plant in Schwandorf in 1940 and 1941, respectively.

This technique managed to establish itself once pumps could be found that could convey the strongly abrasive suspension against the digestion pressure (the level of which depends on the temperature). Only piston pumps are suitably reliable for this. It was only after the Second World War that these were sufficiently well-developed for autoclaves in series to find general use. The level of control engineering that had been achieved by then was also contributory because it enabled the number of workers to be reduced significantly.

There are drawbacks to both types of autoclave:

- High investment costs, above all at high temperatures,

- susceptibility to failure resulting from wear of stuffing boxes and valves,
- susceptibility to corrosion,
- the need for elaborate control units,
- low turbulence in the autoclaves.

Problems with the autoclaves meant that ideas for alternatives were soon developed. Professor Müller proposed using a tube for digestion (Prof. Wolf Müller, Vienna, DRP Patent 579114, 1928). The suggestion could not be implemented at the time however, because the known reaction times meant it would have been necessary to have a tube that was more than ten kilometres long and for which there were no pumps available for the associated pressures. Tube reactors had already become established in many areas of organic chemistry and, despite considerable reservations, this encouraged investigations into its possible use for bauxite digestion once again at a later date. The practical testing in plants of differing sizes led to findings that opened up good prospects for tube digestion.

Dr. Fritz Otto Bayer, a son of Carl Joseph Bayer, worked at VAW's Lautawerk plant from 1934 to 1940 amongst other things on the continuous digestion of bauxite.

VAW tried to free itself from the use of bauxite as the raw material by developing the sulphuric acid/alumina process on an industrial scale. Based on the results of laboratory and field tests, aluminium oxide was produced on a large scale in a test facility using this process at the Lautawerk plant from 1940 onwards. Calcined clay was digested using sulphurous acid and this allowed aluminium oxide to be obtained from an indigenous raw material. Production did not exceed 4000 tonnes a year because of the obstacles imposed by the war. Even though the technical difficulties had been overcome, for economic reasons the process was not used again after the war.

In 1956, VAW continued the development of the tube-digestion process at its Nabwerk plant under the direction of Dr Klaus Bielfeldt. The process, which had taken ten years to develop, was used commercially for the first time for a 20 000 tpy capacity upgrade in 1966.

Tube digestion was also used at the Lippewerk plant to allow economic processing of difficult-to-digest monohydrate bauxites from Greece.

The AOS plant, a 600 000 tpy oxide plant with a completely new design based on the VAW tube-digestion process, started operation in 1973.

Essentially, three bauxite digestion processes have been used in the aluminium industry since the Second World War:

- (1) Autoclave digestion using a dual-stream process
- (2) Autoclave digestion using a single-stream process
- (3) Tube digestion using a single-stream process.

The bauxite available determines the choice of digestion process:

- Autoclave digestion is preferred for easily digestible trihydrate bauxites ($\text{Al}(\text{OH})_3$), such as hydrargillite (gibbsite), which occurs predominantly in the tropics.
- The tube-digestion process is preferred for difficult-to-digest monohydrate bauxites (AlOOH), such as boemite from the Mediterranean region or diaspore, which is the main mineral in Russian and Chinese bauxites.

The dual-stream process referred to in (1) is characterized by a large number of heat exchangers in which the digestion liquor is first heated up using vapour from the pressure-reducing units in

lines that operate in parallel, and together with the bauxite suspension then heated by process steam to digestion temperatures of up to 240 °C in several large-volume autoclaves. This digestion process was developed for readily soluble trihydrate bauxites but can also be used for boehmitic bauxite.

The single-stream autoclave process referred to in (2) is characterized by a large number of autoclaves arranged in series, whereby the number of autoclaves increases with increasing digestion temperature and increasing residence time.

Digestion temperatures in these plants reach up to 250 °C. Liquors of higher alkali concentration are usually used to increase the production capacity and yield, and the plants are connected to an energy-intensive steam-supply station. A single-stream autoclave process is preferred for use with trihydrate bauxites.

The tube-digestion process referred to under (3) displays characteristics of both autoclave systems. However, it leads to considerably lower energy consumption and operates continuously. Tube digestion was developed for use with monohydrate bauxites but can also be used with trihydrates.



Figure 1. AOS Stade alumina plant.

The digestion temperature is 280 °C at an operating pressure of approx. 11 MPa and a design pressure of 12 MPa. The maximum digestion temperature depends on the type of bauxite used. A temperature of 280 °C is used for monohydrates.

The incrustation (scale) that takes place with time is taken into account by means of an intermediate increase in the salt inlet temperature from about 300 °C to about 400 °C. The heat exchanger is cleaned hydromechanically to remove titanate-containing crusts at higher temperatures and by acid treatment to remove silicate-containing crusts at lower temperatures. The time between cleaning operations depends on the composition of the bauxite used. For the bauxites used by VAW, an intermediate acid treatment was carried out after about 200 operating hours and an acid treatment with hydromechanical cleaning of the salt heat exchanger and cleaning of the pressure-reducing unit after about 4 000 hours of operation.

Reciprocating diaphragm pumps are used to feed the bauxite suspension into a tube digestion plant. Likewise, for adding lime.

The flow velocity in the digestion tubes is chosen so that there is no sedimentation of red mud even if the bauxite is coarsely ground; it is 2 – 3 m/sec.



Figure 2. AOS diaphragm pumps.

The process steps occurring during tube digestion are:

Bauxite milling: Relatively coarse grinding can be used here to save energy and reduce wear. The specific values depend on the milling properties of the bauxite.

Separation of sand and red mud: Coarse-grained bauxite produces coarse-grained red mud. About 10 – 15 % can be separated out as sand before the red mud is fed into the thickener. This reduces the burden on the thickener and the red mud filter.

Thickener: A high digestion temperature can improve sedimentation if the red mud has poor sedimentation characteristics. This leads to better utilisation of the thickeners.

Evaporation plant: Vapour condensate from the pressure-reducing unit of the tube digester is used for the washing process during alumina production instead of the condensate from evaporation plants that is normally used. The lower concentration of digestion liquor typically used in tube digestion means strong liquor is not produced. This leads to a further reduction in the size of the evaporation plant.

Boiler house: The use of heat transfer salt instead of steam heating and the use of salt heating plants instead of a high-pressure boiler house leads to better use of primary energy. In addition, the low-pressure boiler house still needed to supply steam to the alumina plant can be installed with a significantly lower power output than would be necessary with autoclave plants because of the reduced evaporation capacity required.

The change of molten salt temperature between 300 °C and 400 °C can be used as a scaling control parameter.

Tube digesters were originally designed for difficult-to-digest monohydrate Greek bauxites from Delphi and Eleusis. There are no limitations on the bauxite composition because of the high digestion temperatures in the tube reactor. They have been used to process bauxites from Australia, Africa, South and Central America, Europe and Asia.



Figure 3. AOS tube-digestion plant.

The benefits of the tube-digestion process compared with the use of autoclaves to process monohydrate bauxite are:

- **Low energy requirement:** The high turbulence during digestion favourably affects heat transfer and material transfer. This results in a lower liquor requirement and a reduced heat requirement for the process. The use of salt as the heat transfer medium achieves a high degree of primary-energy utilization and thus low energy consumption. Under comparable conditions, the total energy requirement for tube digestion is 40 % lower than it is when autoclaves are used.
- **Low investment:** Digestion yields are already sufficiently high at a low lye (caustic soda) concentration, for example at the precipitation concentration, and thus evaporation plants are not needed to produce strong liquor. The high digestion temperature allows large quantities of condensate to be produced by flash evaporation, which depending on the type of bauxite and quantity of red mud can suffice to meet the process's washing-water requirement completely. Evaporation units to produce wash water can thus be dispensed with. The use of salt as the heat-transfer medium means the tube-digestion process does not require any high-pressure steam. Savings associated with evaporation compensate for the considerable investment needed for the digestion system.
- **High plant availability:** The availability of the plants is about 90 %. Together with operating data for upstream and downstream activities, plant utilization is designed to be 85 %. At Aluminium Oxid Stade, utilization is practically 92 %.
- **Inline removal of organics:** The inline removal of organics has been achieved by the injection of oxygen.

3. Developments Undertaken by Other Alumina Producers

Work has been carried out on the continuous tube-digestion process at Aluterv in Hungary since the middle of the 1960s. The alumina plants in Ajka, Mosomagyarovar and Almasfüzitő were equipped with tube digesters to process monohydrate Hungarian bauxites economically. The total capacity in Hungary was 900 000 tpy.

In the 1980s, Aluterv granted a licence for tube digestion to the Ziar nad Hronom aluminium smelter in Slovakia. This plant was sold to Iran in the mid-1990s and commissioned by experts from the Chinese company NFC-Chinalco in Jajam/Mesched in 2003.

A further tube digestion plant for 300 000 tpy was erected in Nikolaev/Ukraine in the 1980's. This plant is operated by Rusal.

Aluterv granted a licence for a replica of the tube digester to Kaiser Engineers, who were installing a 200 000-tpy alumina plant Mokpo, South Korea.

4. Plants Based on the VAW Tube-Digestion Process

In the 1980s, VAW decided to close Tube Digestion Unit No. 6 in Lünen for economic reasons. The plant was sold to China Great Wall Corp. in Zhengzhou, Henan, where it was erected again. After start-up, there were problems with the service life of the pump membranes, but these could be solved. The plant is operating successfully with China's very hard, monohydrate bauxites. According to the project manager, Prof Li Yuan, there are now 12 tube digesters based on the VAW process operating in China.

The Chinese engineering company NFC has built two alumina plants based on the tube-digestion process, each with an annual capacity of 600 000 tonnes, in Tan Rai and Thanh Nien in the Central Highlands in Vietnam. The first unit started operation in 2014, the second was commissioned in 2015.

In 2002 VAW awarded a licence to Rio Tinto Alcan and provided expertise to build a tube digester for the Yarwun alumina plant in Gladstone in Central Queensland, Australia. The plant went into operation in 2005 with an annual output of about 1.4 million tonnes. The capacity was expanded to 3.4 million tpy in 2012.

In 2009, Ma'aden Aluminium of Saudi Arabia (75 % state-owned, 25 % Alcoa) decided to use VAW tube digestion for the difficult-to-digest monohydrates from the Az Zabirah deposits. The alumina plant was completed and commissioned in 2014.

Also in 2014, Emirates Global Aluminium decided to build an alumina plant based on VAW tube digestion alongside the 1.4 million tpy aluminium smelter in Abu Dhabi. The plant is scheduled to go into operation in 2017 with an annual production of 2 million tpy, with plans to eventually increase to six million tonnes a year.



Figure 4. Tan Rai alumina plant, Vietnam.



Figure 5. Yarwun alumina plant, Australia.

5. Summary

Since the Second World War, global aluminium production has shown a dramatic increase from about five million tonnes in 1960 to some 40 million tonnes in 2014. This has been achieved by upscaling the amperage from 50 kA to up to 600 kA in new smelters. About 80 million tpy of alumina are needed to produce 40 million tpy of aluminium.

On the alumina side, autoclave technology has reached economic and technical limits. It is not possible to increase the size of the reaction area in autoclaves arbitrarily. In addition, the availability of readily digestible trihydrate bauxites is declining. The digestion temperature has to be increased to 250 – 300°C to achieve economic efficiency with an increasing fraction of monohydrates. Here autoclaves have their limitations and tube digestion is an option. Since 1956, VAW has developed this technology to the production stage. A number of alumina plants built in the past 20 years operate using VAW tube-digestion technology.

At about the same time as the development of the tube-digestion process, VAW began to develop rotary tubular-kilns in cooperation with Lurgi to replace the calcination of aluminium hydroxide to aluminium oxide with a more energy efficient process. A successful process was developed with fluidized-bed calcination. Fluidized-bed calcination plants are now built and marketed by Outotec (formally Lurgi) and have achieved a dominant position in the global market.

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