

REMOVAL OF ORGANIC CARBON FROM BAYER LIQUOR

BY WET OXIDATION IN TUBE DIGESTERS

Dr. W. Arnsward, H.G. Kaltenberg, E. Guhl

Aluminium Oxid Stade GmbH, Postfach 5160,

2160 Stade, West-Germany

ABSTRACT

VAW has developed a method for the wet oxidation of organic carbon in Bayer liquor using molecular oxygen gas in tube digesters. This system has been used successfully for a number of years in the processing of tropical bauxites at a digestion temperature of 270° C in the plant of Aluminium Oxid Stade GmbH.

Previously, the highly efficient rotary drum red mud filtration system employed with its associated low liquor losses had led progressively to an organic carbon of 34 g/l before wet oxidation was started.

The plant results as well as the problems associated with the possible formation of explosive gas mixtures will be reported.

INTRODUCTION

The alumina plant of Aluminium Oxid Stade GmbH (AOS) in Stade started up in 1973 (Fig. 1). It operates according to the, at that time, latest VAW-know-how and has been modified further in the meantime. The actual production capacity is 0.7 million mt/y and is 100,000 mt more than originally designed. The alumina plant is a joint venture of 50 % each between Vereinigte Aluminium-Werke AG and Reynolds Aluminium Deutschland, Inc.

According to VAW-know-how (1), the Bayer-process includes in particular

- bauxite digestion in tube digester units at 270° C
- filtration of red mud
- filtration of the total hydrate after precipitation
- Lurgi fluid bed calcination
- same liquor concentration in digestion and precipitation (135 - 140 g/l Na₂O_{free}).

The plant has only a very small evaporation unit for salt separation.

On this basis, combined with a liquor productivity of approx. 68 kg Al₂O₃/m³ L to P, a very favorable energy consumption of less than 8.3 GJ/mt Al₂O₃ is attained.

Using the tube digester technology, practically all types of bauxite can be processed. In recent years these have been mainly Weipa, Gove and Boke bauxites with an organic C-content of partly over 0.2 %.

The environmentally favorable red mud filtration on drum filters, results in a well washed red mud, which contains only an average of 0.55 % Na₂O_{ws}. It can be deduced that with a high org. C-input, and only very small liquor losses, the org. C-concentration in the circuit liquor must be naturally rather high, to balance input and output. At AOS the org. C-concentration increased over the years up to 34 g/l, even though sodium oxalate and sodium carbonate were continually removed from the circuit and processed further by caustification.

The disadvantages of a rather high org. C-concentration in the circuit liquor of the Bayer process are generally known (2).

Tests to reduce this concentration by adding Polydamac (Nalco 8103) failed at AOS, as the tar-like products formed blocked the filter tissue and decreased the red mud filtration rate considerably.

For economic respectively environmental reasons bauxite-roasting as well as liquor purging are not practicable, so that the solution of the org. C reduction problem seemed to be, not only at AOS (3,4), possible through wet oxidation. The bases for wet oxidation in tube digester units were developed by VAW. (5,6).

The aim of the wet oxidation at AOS is to reduce slowly, over a long term -i.e. years - the organic C-content in the circuit liquor, and to monitor this effect analytically.

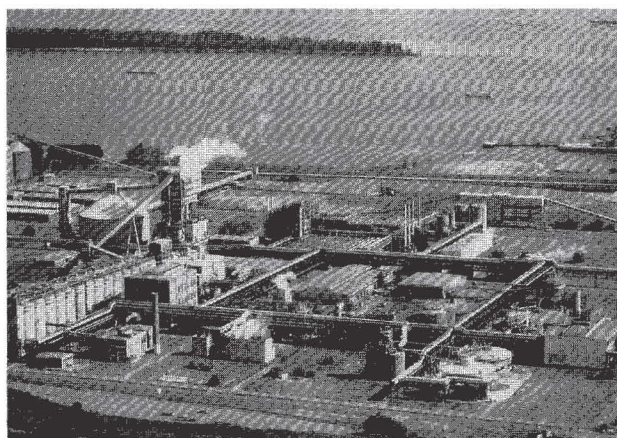


Fig. 1: Alumina Plant Stade

RISK POTENTIAL OF WET OXIDATION

At the end of the seventies the risk potential of wet oxidation is outlined as follows:

During the digestion a waste gas is formed which contains beside nitrogen and methane mainly hydrogen. If oxygen gets to this waste gas, there is the danger of an oxyhydrogen explosion. This problem was discussed with the Authorities, whereby finally the following conclusions were reached:

1. The most unfavorable, and therefore the most dangerous gas mixture that can form is oxyhydrogen, i. e. the system hydrogen and oxygen.
2. Oxyhydrogen is explosive when the two following conditions exist together:
 - Oxygen concentration between 3 to 97 vol. %.
 - Ignition temperatures above 300° C.

Based on this knowledge oxygen was injected into the tube digester units at AOS during the period April 1979 to March 1982. The results were very satisfactory.

At the beginning of 1982 an explosion in a socket with a safety valve at the top stopped AOS's activities in the field of wet oxidation for a time. Below the safety valve an indefinable gas mixture had collected which exploded at a temperature of only 80° C. It must be assumed that there was either a self-ignition (phosphorus hydrogen) or a catalytic reaction (iron/iron oxide). Tests and considerations carried out over several years jointly with the Authorities concerned, led to the conclusion that wet oxidation can only be carried out from a safety point of view, if and when the waste gas mixture forming is always outside the explosion limits. For this the exact knowledge of the explosion limits of the three-component system hydrogen-oxygen-vapor is necessary. Fig. 2 shows the corresponding diagram for T = 110° C and P = 1 bar (7).

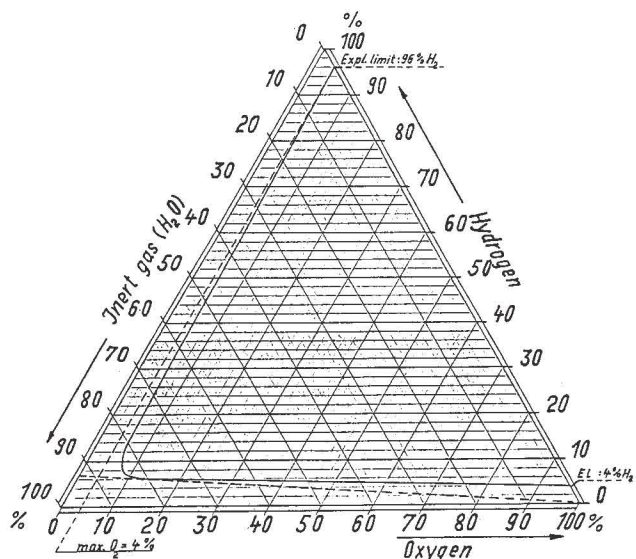


Fig. 2: Explosion limits in the system H₂-O₂-H₂O at P = 1 bar and T = 110° C

This illustrates the inertial effect of the vapor. One can recognize the following explosion limits:

- 84 vol. % for vapor
- 4 vol. % for oxygen.

Whereas pressures up to 50 bar practically do not influence the curves, the explosion limits increase slightly with higher temperatures, so that at 300° C the limiting values for oxygen are around 3 and 97 vol. % respectively.

WET OXIDATION IN TUBE DIGESTER UNITS

Based on our knowledge today, tube digester units with a retention time stretch and a combustion of the waste gases which are discharged from the vapor heat exchangers, are for wet oxidation very suitable and safe in operation. (Fig. 3)

The following items should be particularly pointed out:

- The oxygen is injected into a tube filled with the suspension flow. Because of the turbulence and the missing of any dead space there is no separation.
- The dissolution and reaction conditions are most favorable for the oxygen as a result of the high temperature (270° C) and high turbulence.
- The vapor chamber of the vapor heat exchangers is small. There is no dead space in the system.
- The continuous control of the discharged waste gas from the vapor heat exchanger 1, and of the total waste gas with respect to its oxygen content has proved successful and safe in operation.
- By special measures it is guaranteed that in the case of failure of a unit, while fully in operation (electricity failure), the allowed oxygen limiting value in the waste gas of only 1 % is not exceeded.

Wet oxidation was taken up again, with only one unit to start with, in January 1989. Currently oxygen is injected at a rate of 100 m³/h into two of the four tube digester units. The suspension flow of each tube digester is around 300 to 340 m³/h/unit. The operation is without problems.

A number of unit parameters - some measured redundantly - have to be met before the oxygen injection can take place. The continuous control of the waste gas in respect of its oxygen content - which has to be below 1 vol. % - was a challenge for the technicians, which was solved successfully. Thus, the dead time is only 12 minutes between oxygen injection and the waste gas analysis, if the oxygen has been injected into the heated up suspension.

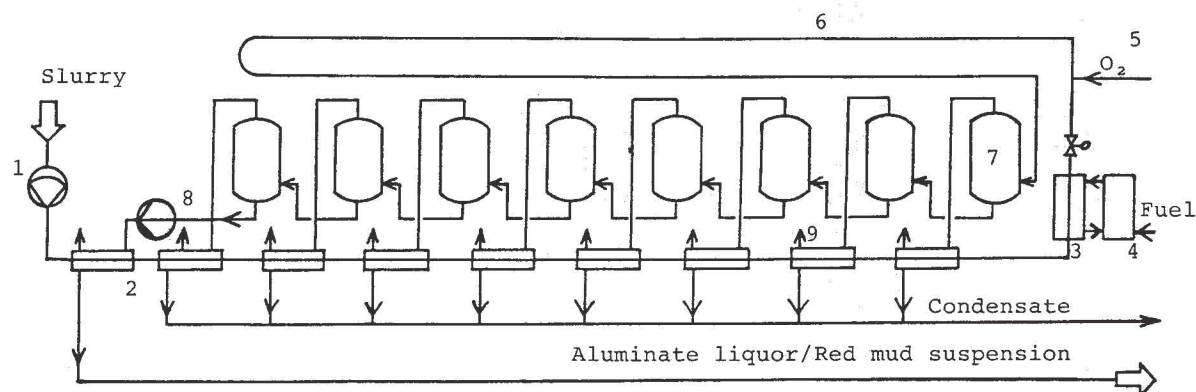


Fig. 3 Scheme of a Tube Digester

1 Diaphragm piston pump, 2 Tube reactor - vapour heat exchangers -, 3 Salt heat exchanger, 4 Salt heater, 5 Oxygen addition, 6 Retention time stretch, 7 Flash Tanks, 8 Centrifugal pump, 9 Waste gas outlet to combustion

RESULTS

The operating results of the two oxidation periods show:

1. Corrosion

When injecting oxygen at the beginning of the tube digester units into the cold suspension with a concentration of approx. 8 g/l NaCl, pit corrosion appeared. Subsequently the oxygen injection was transferred to the hot part of the unit. Since then, in spite of frequent controls, no corrosion signs have been observed up to now.

2. Increased Waste Gas Development

The waste gas increases in units with oxygen injection from about 6 to 19 m³/h. As the hydrogen concentration increases from 55 to 85 vol. %, the additional waste gas amount consists mostly of hydrogen.

3. Energy Saving

The positive thermal effect for the oxidation of org.-C compounds is around 14 KJ/g oxygen. This corresponds with a temperature increase of approx. 1.5° C in the suspension. At a constant digestion temperature this results in equivalent energy saving.

4. Removal of Org. Carbon

Fig. 4 shows the development of the org.-C content in the L to P at AOS. A steady increase up to 34 g/l, which was only stopped during the oxygen injection between 1979 and 1982, can be recognized. Only after restarting the wet oxidation in 1989, the reduction of the org. C concentration in the L to P has begun. Fig. 5 shows that this results in a removal of the org. C-content in the total liquor circuit.

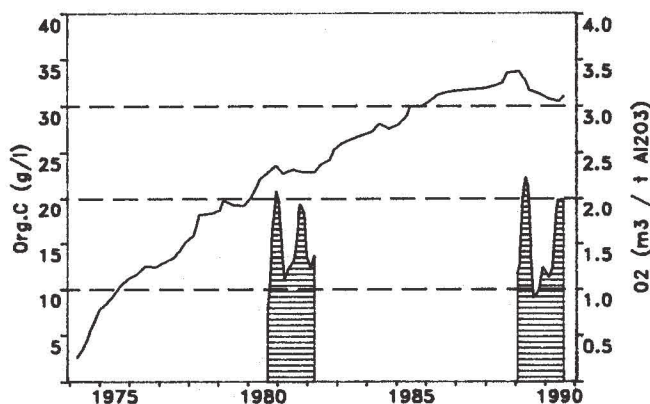


Fig.4 : Org. Carbon in L to P and Oxygen Addition

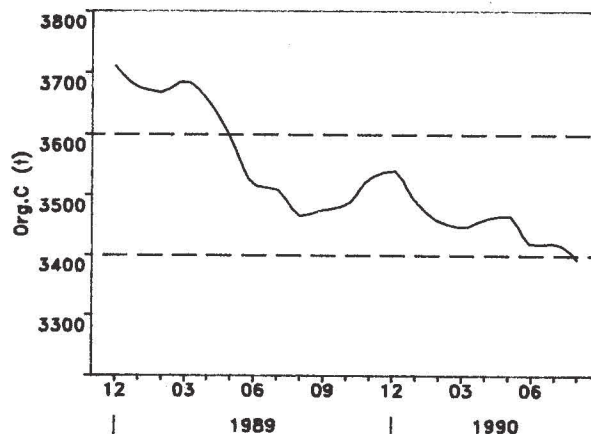


Fig.5 : Org. Carbon in the Circuit

When starting up each wet oxidation period the quick reduction of the coloring substances (humates) in the liquor (Fig. 6) was noticeable. The whiteness of the hydrate has also been improved. At the same time up to 250 m³/h unit of oxygen could be injected.

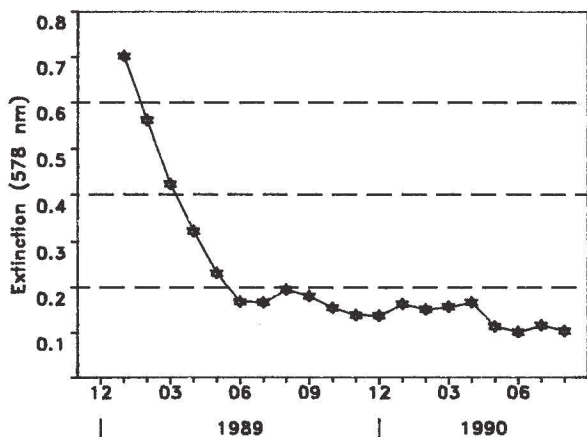


Fig. 6 : Extinction of Spent Liquor (578 nm)

The qualitative and quantitative analytical control of the liquor circuit over a period of many years showed in respect to the low-molecular organic compounds (acetate, succinate and formate), an almost constant relation to the org. C in the liquor, although this was increasing steadily. Due to the wet oxidation and the subsequently reduced org. C in the liquor, it seems that the percent acetate content of the liquor rises slightly, whereas that of the formate becomes less. The respective values for the L to P are shown in Fig. 7.

	1982	1985	1988	1989*	1990*
org. C g/l	22,8	28,2	31,4	30,2	28,4
therefrom % C as					
Sodiumacetate	30,7	29,6	29,5	31,0	32,9
Sodiumsuccinate	8,0	7,7	7,2	7,6	7,7
Sodiumformate	4,3	4,7	4,6	3,6	3,1

* period of oxygen addition

Fig. 7: Organic carbon content of spent liquor and the contribution of some components

With the help of HPLC and UV-detection a further 15 % of the total org. C can be determined (for instance hydroxybenzoic acids). Neither the composition nor the concentration of this part changed significantly as a result of wet oxidation.

Based on many years' operating results regarding the formation of oxalate and carbonate, an increased amount of oxalate and carbonate is noticeable with wet oxidation. If this additional formation takes place from -CH₂-chain links, then 95 % of the used oxygen is required. Out of this amount 28 % is required for the additional oxalate formation, and 72 % for the carbonate formation.

Even though no statement can be made in detail on the reaction between oxygen and org. C, it is very important that the oxygen is used under AOS operating conditions for the formation of salts which can be removed from the liquor circuit. The current oxygen amount is sufficient to oxidize around 20 % of the org. C input by bauxite to CO₂, assuming aliphatic C-chains.

5. Costs of Wet Oxidation

A preliminary cost estimation based on the current situation shows:

Wet Oxidation	0.70 DM/mt Al ₂ O ₃
Credit through energy saving	- 0.25 DM/mt "

	0.45 DM/mt Al ₂ O ₃
	=====
Expenses for lime for recycling the Na ₂ O from the separated salts by caustification	0.90 DM/mt Al ₂ O ₃ **

** This cost corresponds nearly with the marginal costs

6. Effects of the Wet Oxidation on Operation

Time of operation up to now is still too short for quantitative statements. Also, besides wet oxidation, further changes were carried out at the plant, which influence the Bayer process positively.

However, we recognize already in operation improvements in the areas of

- Oxalate solubility (3.2 → 2.9 g/l L to P)
- Hydrate filtration
- Liquor productivity
- Grain size development of the hydrate.

CONCLUSION

As the removal of org. C compounds from the liquor circuit by wet oxidation in tube digester units is planned to be done over an extended period, it is at this time only possible to give a report on initial experience. This should be completed later.

References

- (1) Arnswald, W., "VAW-Technology for Alumina-Production According to the Bayer-Process." Productivity and Technology in the Metallurgical Industries, Ed. by M. Koch and J.C. Taylor, The Minerals, Metals & Materials Society 1989. pp. 843 - 853.
- (2) Zöldi, J., Solymár, K. and Fehér, H., "Organic removal and its effect on precipitation and Alumina quality", International Alumina Quality Workshop, Gladstone, Queensland, Australia, in September 1988. pp. 24. - 37.
- (3) Foster, B.J. and Roberson, M.L., "Removal of HMW organic compounds by partial wet oxidation", Light Metals 1988. pp. 79 - 85.
- (4) Ziegenbalg, S., Solymár, K., Löwe, D., Ufer, H., "Naßoxidation organischer Beimengungen in Betriebslaugen der Bayer-Technologie-Ergebnisse der technologischen Entwicklung", Neue Hütte 34,2, Februar 1989. pp. 43 - 48.
- (5) Brandt, W., Memmel, K.-J. et al, unveröffentlichte Ergebnisse, Vereinigte Aluminium Werke AG, Georg-von-Boeselager-Straße 25, D-5300 Bonn 1.
- (6) Brown, N., "Kinetics of copper-catalysed oxidation of Bayer liquor organics", Light Metals 1989. pp. 121 - 130.
- (7) Conrad, D., "Untersuchung des Explosionsbereichs im Dreistoffsystem $H_2-O_2-H_2O$ ", Bundesanstalt für Materialforschung und -prüfung, Unter den Eichen 87, D-1000 Berlin 45, April 1988.