Efficiency of Platinum Gauzes in the Manufacture of Nitric Acid

A METHOD FOR DETERMINING THE FREQUENCY OF PICKLING

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In an ammonia oxidation plant for the manufacture of nitric acid the rhodium-platinum alloy catalyst gauzes must be pickled at intervals to remove accumulated impurities such as iron oxide and so to avoid a reduction in catalytic efficiency. This article outlines a method recently devised to determine the optimum frequency of pickling required to ensure consistent operation at high efficiency.

The largest contribution to the costs of operating a modern nitric acid plant is made by the cost of liquified ammonia. Because of this, it is incumbent on plant operators to reduce to an absolute minimum all ammonia losses at each stage of the process. One stage at which significantly less than 100 per cent efficiency is generally obtained is the oxidation of the ammonia to nitric oxide over the rhodium-platinum gauze pad. Conversion efficiencies are generally about 94 to 95 per cent, but vary with the age and condition of the platinum alloy gauzes and may drop to 90 per cent if precautions are not taken to maintain a high level of gauze activity. Pickling the gauze pad in hydrochloric acid to remove impurities carried over in the feed gas (mainly iron oxide scale) must therefore be carried out as frequently as production requirements permit in order to maintain the gauzes in their active state and to prevent an economically undesirable drop in conversion efficiency.

Because the determination of ammonia oxidation efficiency is highly dependent on the analytical methods used in measuring gas concentrations, and since these are not always easy to keep constant, apparent converter efficiencies may vary with time, making it difficult to decide on the optimum time at which a gauze should be pickled. This article reviews work that has been undertaken by Imperial Chemical Industries Limited, Nobel Division, to examine the cumulative sum (cusum) technique when applied to converter efficiency determination (1). The nitric acid plant used for these tests operates with the converters at atmospheric pressure and with the subsequent absorption stages at 3 to 4 atmospheres pressure. The plant has been described elsewhere (2).

Analytical Methods for Determining Converter Efficiencies

The efficiency of the ammonia oxidation is measured by the chemical determination of the ammonia concentration in the feed gas and the nitric oxide concentration in the gas immediately below the platinum alloy gauze pad. Ammonia is generally determined by titration with standard acid, and the oxides of nitrogen by back-titration with standard acid after absorption in an aqueous alkali solution. Two analytical methods were compared during the initial experiments:

Method 1

In the first instance, about 4 litres of the ammonia/air mixture were drawn off above the gauze pad during a period of about fifteen minutes, and ammonia titrated simultaneously with the sampling. Hydrogen peroxide was used for the nitrous gas oxidation.

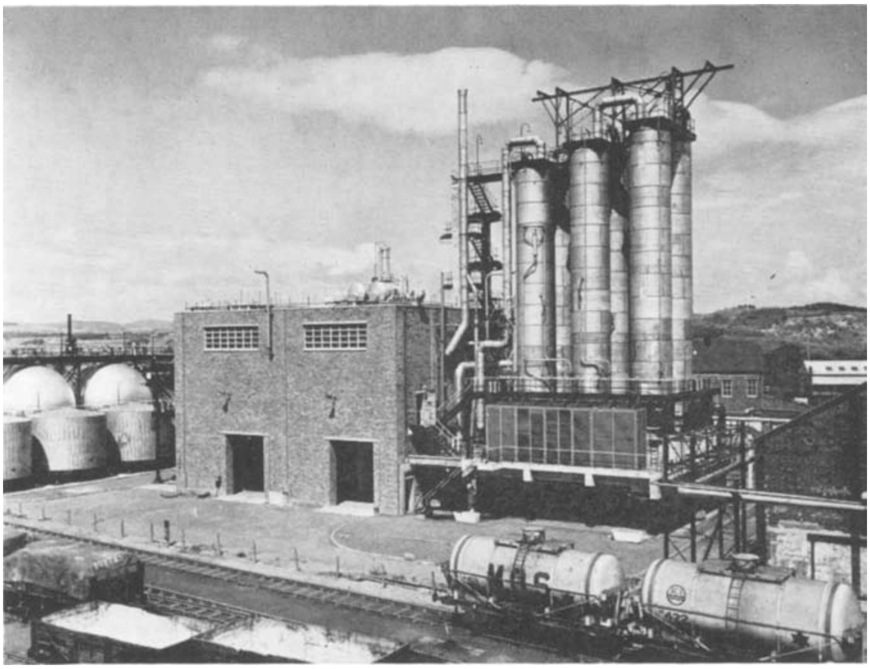


Fig. 1 The nitric acid plant of the Nobel Division of Imperial Chemical Industries Limited at Ardeer in which the investigations on the frequency of catalyst gauze pickling were conducted. The use of the cusum method has enabled the plant to increase significantly its overall efficiency

Method 2

In the second method, 0.8 litres of the feed gas were taken off during thirty seconds, and the oxygen remaining in the residual air was used for the oxidation of the nitrous gas sample.

The Cumulative Sum Technique

It is not always possible to determine at daily intervals the data required to plot a cumulative sum chart for the converter efficiencies. A corrected cusum was calculated therefore for each of the two analytical methods described. The datum is the conversion efficiency below which it had been decided that gauze pickling would be carried out.

The differences between these duplicate determinations of conversion efficiencies and the datum line were calculated and their arithmetic mean (x) was taken. These values

Example of the Construction of a Cusum Chart
(Based on a Datum of 93 per cent)

Day	Conversion Efficiency (per cent)		Difference from Datum		Mean x	Corrected Cusum
0	97.3	97.9	4.3	4.9	4.6	4.6
5	97.6	98.2	4.6	5.2	4.9	28.35
12	93.3	94.1	0.3	1.1	0.7	47.95
19	95.6	96.4	2.6	3.4	3.0	60.90

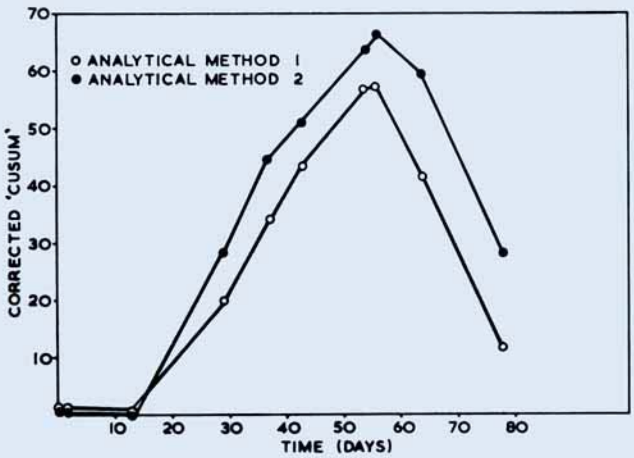


Fig. 2 A cusum plot for one of the ammonia converters, based on a datum of 94 per cent. This shows that to maintain a conversion efficiency equal to the chosen datum it is necessary to pickle the rhodium-platinum gauzes after approximately eighty days

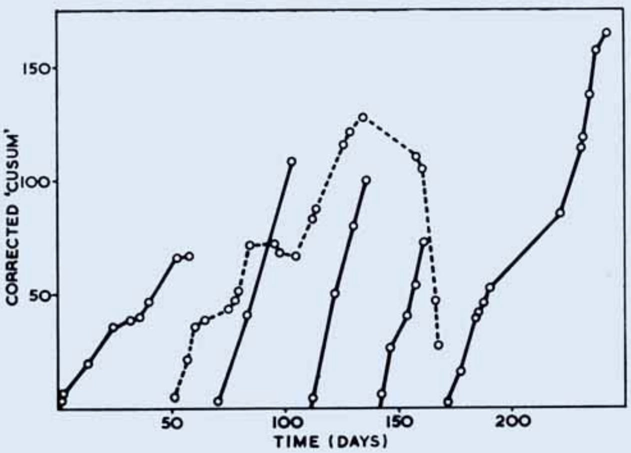
would normally be added to each other, and plotted daily to give a cusum chart. Since this was not always possible, the arithmetic mean of the successive values of x was calculated and multiplied by the time interval in days. The results were added to each other to give a corrected cusum chart. This method enables such a chart to be compiled with results obtained at irregular intervals and the results were found to be almost identical with similar charts obtained using data from regular, daily determinations. The example given in the table was based on a datum of 93 per cent.

The corrected cusum for the fifth day, for example, was obtained by taking the mean of 4.6 and 4.9 multiplied by the time interval in days and added to the original 4.6.

The Cusum Method in Use at Ardeer

Fig. 2 illustrates a cusum plot for one of the plant's ammonia converters, but in this instance a datum of 94 per cent had been chosen. From day 12 to day 50 this burner operated at a conversion efficiency greater than 94 per cent, and from day 50 to day 78 at less than 94 per cent.

Fig. 3 If it is possible to pickle the rhodium-platinum gauzes when the cusum plot has just passed through its peak the converter efficiency will be maintained at a value considerably in excess of the datum, in this case 94 per cent. The dotted line is a typical cusum plot for one converter; the other curves were obtained by pickling the gauze pad at intervals of one to two months



To maintain a conversion efficiency equal to the datum already chosen it is therefore necessary to pickle the gauzes after approximately eighty days' service.

It is obvious that if it is possible to pickle when the cusum plot has just passed through its peak, the converter efficiency will be maintained at a value considerably in excess of the datum. The dotted line in Fig. 3 is a typical cusum plot for the number two burner; the other curves are obtained by pickling the gauze pad at intervals of one to two months. The cusum plots in Fig. 3 show that the conversion efficiency can be maintained at a value above the datum, in this case 94 per cent.

Use of the cusum method for determining the optimum time for pickling the converter gauze pads has enabled the Ardeer nitric acid plant to increase significantly its overall nitrogen efficiency.

References

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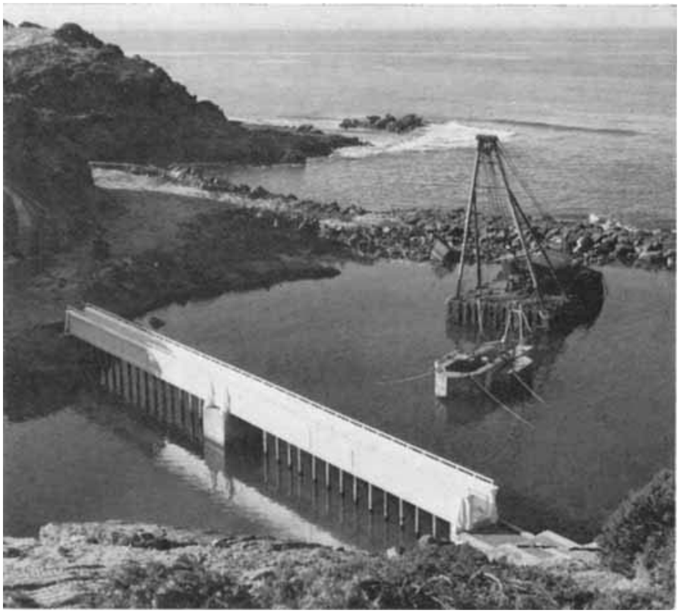
2 D. T. Austin and J. G. Sloan, *Ind. Chem.*, 1961, **37**, 159; J. G. Sloan and H. C. Staats, *Platinum Metals Rev.*, 1961, **5**, 54

Platinised Titanium Anodes in a Sea Return System

A new 200 kV d.c. power link between the Italian mainland and Sardinia feeds electricity produced from Sardinian low-grade coal into the Italian grid via Corsica, the circuit comprising overhead conductors and submarine cables in one direction and the sea itself in the other. The sea return shows considerable cost savings but requires an efficient and durable anode system to feed the current into the sea.

Conventional anode materials would be subject to relatively rapid corrosion and would require considerable space; platinised titanium anodes were therefore chosen, and Marston Excelsior Limited were asked to design a suitable anode system to take full advantage of the properties of platinised titanium and to ensure that voltages near the anodes would not exceed defined values.

Various design systems were evaluated, taking into account the contours of the sea bed, the geometrical arrangement of anodes in various arrays, current flow and other factors, using a computer for the calculations. The system finally selected comprised an in-line array of thirty cylindrical anodes, with an average spacing of one metre, suspended vertically in the sea from a platform above the high water level.



The anode installation at the Italian mainland end of the 200 kV power link (Photograph by courtesy of The English Electric Co Ltd)