

# Removal of Chloride Contaminants from Nitric Acid

## ELECTROLYTIC PROCESS USES PLATINUM ANODES

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Eldorado's refinery at Port Hope separates uranium from other components of the chemical concentrate feeds by a nitric acid digestion/solvent extraction technique. The waste liquid from extraction is high in free nitric acid impurities, and a plant process for the recovery of nitric acid from the extracted acid raffinate stream is used to effect a saving in nitric acid costs.

In this process, the acid raffinate is mixed with sulphuric acid to liberate the metal nitrates and the liquid is evaporated. The resulting metal sulphates are relatively easy to handle, and the ultimate disposal problem is simple. The path of the chlorides through the processing equipment is such that all the volatile chlorides ultimately enter the stainless steel fractionation column where nitric acid is concentrated. It has been found that during the extraction process nearly all of the chlorides present in the uranium concentrates follow the metallic impurities into the nitric acid raffinate.

From vapour-liquid equilibrium data on the HCl-HNO<sub>3</sub>-H<sub>2</sub>O system, it is indicated that the HCl concentration of the dilute nitric acid increases during continuous operation of the nitric acid concentrator. This accumulation of chlorides in nitric acid, resulting from inadequate removal facilities, causes rapid acceleration of the corrosion rate of the stainless steel concentrator.

There are three general methods of removing chlorides from nitric acid: (1) discard of a chloride-contaminated acid stream, (2) removal of chlorides by precipitation, and (3)

removal of chlorides by oxidation to chlorine. The third method offers the greatest economic advantage for the refinery. Chemical oxidants adapt themselves quite readily to the removal of chlorides from nitric acid, while in most instances chemicals such as potassium permanganate, potassium persulphate and sodium bismuthate are soluble in either water or nitric acid and are, therefore, conveniently handled. If ozone is considered, its gaseous state makes it extremely convenient. The choice of proper oxidants is dependent largely upon economic considerations.

The use of ozone requires a relatively large capital outlay for generating equipment. On the other hand, the use of other chemical oxidants requires little capital expenditure, but high chemical costs are inherent with these processes. Where a particular chemical oxidant is available at a low cost, this may show that method of chloride removal to advantage.

### Experimental Cells

Ozone oxidation equipment was installed during the original construction at the refinery. Subsequent years of operation have indicated the major disadvantages to be: (1) high maintenance costs, (2) high capital costs for the initial operation, and (3) lack of flexibility for treating a variable chloride load. Consideration of these disadvantages, along with the possibility of higher chloride levels in the refinery feed, prompted investigation of electrolysis as an alternative to ozonation.

The first experimental cell was constructed

on the chlorine-caustic bell jar design, using a carbon rod anode and a cylindrical stainless cathode, and was contained in a one-litre beaker. Nine volts were necessary to produce a reaction. The carbon anode began to flake and darken the acid with fine colloidal carbon. The reaction of this simple cell was sufficient to indicate that further development was worth while and platinum electrodes were the obvious choice. A second beaker cell was constructed with platinum electrodes; one side of each was imbedded in clear acrylic resin to eliminate the effect of the back of each electrode. With this cell, the effect of electrode spacing, current density, chloride concentration, nitric concentration and retention time were studied with respect to reaction rate.

At electrode spacings of less than one inch, a severe heating effect was noted and the nitric acid decomposed. At spacings of greater than one inch, the resistance of the solution became an important factor and the voltage efficiency was poor. The chloride removal efficiency of a cell operated at a fixed retention time and current density was relatively constant over a

wide range of chloride strengths. The current efficiency was increased only slightly with an increase in chloride concentration. An increase in the nitric acid strength decreased the chloride removal efficiency. The removal decreased from 80 to 70 per cent as the nitric acid strength increased from 20 to 30 per cent.

From a plot of the results of a beaker cell test, it was found that, at a given current density, the chloride concentration of the electrolysed solutions was an exponential function of the average retention time of the electrolyte between the electrode faces.

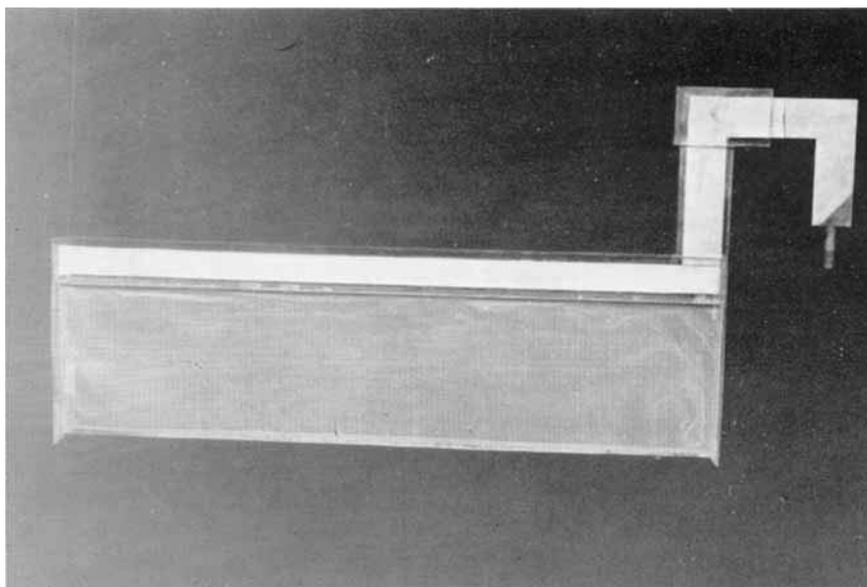
$$\log (\text{Cl}^-) = -kt$$

where  $t$  = residence time in minutes  
( $\text{Cl}^-$ ) = chloride concentration (mg/l)  
 $k$  = reaction rate constant

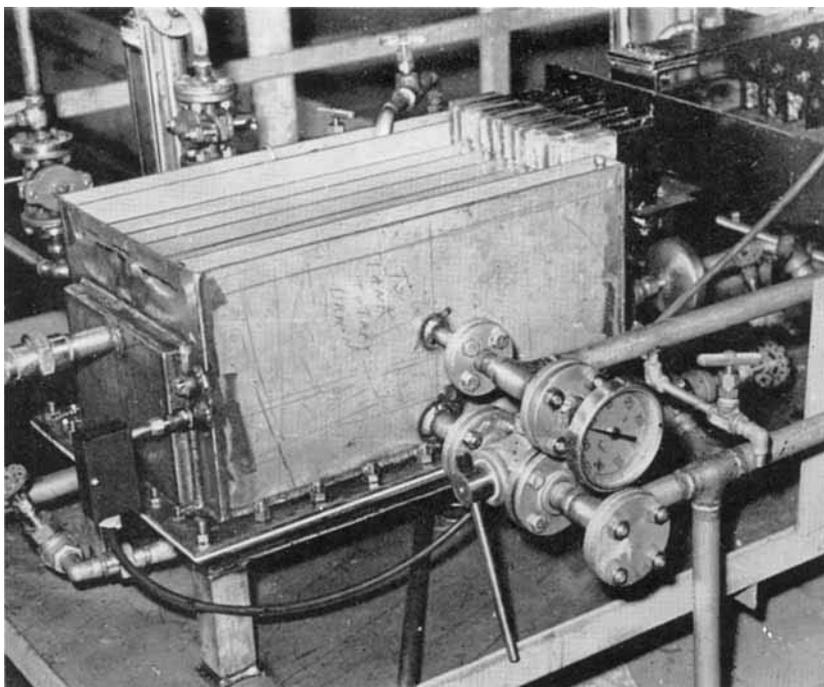
Solution agitation was important to the efficiency of the process, as electrode polarisation and the eventual chloride solubility were minimised by good agitation.

### Anode and Cathode Materials

Platinum was a satisfactory electrode metal electrochemically, but had the disadvantage of being expensive. No other material would



*One of the anodes used in the final design of the production unit. Constructed in Unimesh platinum by Johnson Matthey & Mallory Ltd., the anode is twenty-four inches in width by six inches in depth*



*The continuous flow cell, with six platinum anodes and five copper cathodes, for the removal of chlorides from nitric acid*

serve as an anode, but there were several possibilities for cathodes. The impressed potential should make the cathode passive and an investigation of cathode materials indicated as possible alternatives gold, carbon and copper.

Operations of batch cells with diffused air agitation removed 1.25 lb. of chlorine per day per square foot of anode at all acid strengths. The electrodes of continuous batch cells were constructed in a similar way to a storage battery and were connected in parallel with every other electrode an anode, each spaced one inch apart.

### **Continuous Flow Cells**

Three sizes of flow cells were constructed, one containing electrodes totalling 16 square inches, another of 24, and a semi-industrial cell of 3.75 square feet to observe the scale-up effect on the design of much larger cells. The small continuous flow cell contained platinum anodes of perforated sheet and a solid plati-

num cathode to act as a baffle to the acid flow. The removal rate of the smallest cell was 0.30 lb. chlorine per day per square foot. The low efficiency compared to a batch operated cell was assumed to be due to the flow short-circuiting the cathode and baffle. A larger cell, containing 24 square inches of electrode, was then constructed. This cell, operated at 175 amp per square inch, removed 0.48 lb. chlorine per square foot of anode per day. The platinum cathodes were changed to solid copper. The cell removal of chlorides was increased to 0.65 lb. chlorine per square foot per day and the improvement was attributed to the copper cathode reducing the hydrogen polarisation voltage. At a temperature of 120°F and 30 per cent acid, the copper sheet was attacked by the acid solution. The heat build-up was minimised by the cooling produced by the air agitators and was not considered a problem in the design of larger cells.

Flow-cell tests indicate that a better rate of chloride removal is possible if the electrodes

are positioned with their longer dimension in the horizontal plane. Bubble resistance seems to increase if the vertical dimension is longer than the horizontal; the electrode width to height ratio should be at least 2 to 1.

The semi-industrial cell containing 3.89 square feet of electrode surface was made up of five copper cathodes and six platinum mesh anodes each spaced one inch apart. Cell operation on acid strengths up to 23 per cent nitric removed 0.75 lb. chloride per square foot of anode. With acid strengths greater than 23 per cent the copper cathodes were attacked. This occurred at a temperature of 120°F and it was assumed the energy going into heat was too great to be removed by air diffusion. Water tubes were placed between each of the electrodes in vertical banks of five tubes. Cooling water passed through the tubes removed sufficient heat to allow copper cathodes to operate in 35 per cent acid without attack.

Design data obtained from the operation of three sizes of continuous flow cells were

sufficient to construct a large industrial model. This cell was composed of six anodes, each 24 inches wide by 6 inches deep, constructed in platinum Unimesh by Johnson Matthey & Mallory Ltd., Toronto, and five copper cathodes of similar size.

Water cooling tubes were necessary to operate the cell with nitric acid strengths up to 35 per cent. The current efficiency of a large cell was 30 per cent and the power cost was \$1.60 per pound of chlorine removed, compared with \$7.00 for the ozone process. The industrial cell has been operated three months without requiring maintenance.

In any plant concentrating a nitric acid contaminated with chlorides by a fractionation process, electrolysis is competitive with ozone oxidation for the removal of the chlorides. The capital expenditure is \$1,000 per pound of chlorine removed per day, or about 30 per cent of the cost of the ozone process, and the operating cost is about 25 per cent. The amortisation period is estimated to be 10 years.

## Synthesis of Penicillin Derivatives

### HYDROGENATION WITH PALLADIUM CATALYST

An important advance in medical treatment, made possible by the synthesis of penicillin derivatives of greater antibiotic activity than those produced naturally, has recently been announced by Beecham Research Laboratories Ltd.

The first major step in a long programme of research was the isolation of the common nucleus of the penicillin compounds, 6-amino penicillanic acid, which has the simple basic structure of the penicillins without any side-chain other than one hydrogen atom. From this compound it became possible to produce an immense number of penicillins that could not be obtained from the natural mould by the introduction of substituent groups into the side-chain of existing penicillins, or in other words, into the amino group of 6-amino penicillanic acid. Very broadly, the replacement of one hydrogen in the simple side-chain of the penicillin nucleus by one of a wide range of aminoacyl groups can yield a variety

of derivatives, some of which possess activities against a wider range of infections than did earlier preparations. Others of the range are either more readily absorbed orally than the older penicillins or are lethal to certain strains of staphylococci that have hitherto destroyed penicillins by producing a substance called penicillinase.

In the course of preparing these synthetic penicillins, the 6-amino penicillanic acid is coupled with the desired amino-substituted carboxylic acid having its amino group protected, and the protective group is then removed by catalytic hydrogenation. This last procedure must be carried out under conditions sufficiently mild to avoid attack on the penicillin nucleus with subsequent loss of antibiotic activity, and it has been found that, with a palladium catalyst on an inert support such as barium carbonate, this reaction can successfully be carried out at room temperature and atmospheric pressure.