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SULPHURIC ACID MANUFACTURE

- A. Scaling Problems in Connection with Waste-Heat Boilers  
B. Cathodic Protection of Sulphuric Acid Coolers

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A. Scaling Problems in Connection with Waste-Heat Boilers

Introduction

This report contains some information concerning the running of a waste-heat boiler, which is installed in the firm's sulphuric acid factory in Kalundborg.

In this factory the yearly maintenance costs for the electrostatic dust chambers were considerably high, because of the very hot gas from the heavily loaded ovens. This meant at the same time that the effectivity of the dust chambers was unsatisfactory. The allowed temperature in the dust chambers was actually the factor, which decided how much pyrites and sulphur we could roast in the ovens.

For the purpose of cooling the sulphurous gas from the ovens we therefore in 1957 installed a waste-heat boiler between the ovens and the dust chambers.

Our plant in Kalundborg has 4 pyrite ovens - Lurgi LC 7 - each with a daily capacity of 35 tons of pyrites and 1 sulphur oven with a capacity of 20 tons of sulphur.

From the purified sulphurous gas, 78% sulphuric acid is produced in a Hugo Petersen-tower system.

The waste heat boiler

The boiler is of the la Mont type and consists of two symmetrical halves of vertical boiler tubes, each half with a heating area of 145 m<sup>2</sup>. To each half there is a super-heater-section with a heating area of 45 m<sup>2</sup>.

The gas stream first meets the superheater, but a part of the hot gas is directly by-passed to the boiler section, so it is possible to maintain a constant temperature of the superheated steam.

The steam pressure is kept at about 40 atmospheres equi-

valent to a boiling temperature of approximately  $250^{\circ}\text{C}$  whilst the saturated steam is heated to  $400^{\circ}\text{C}$  in the super-heater.

As we had no need for the steam in our manufacturing process, the only way in which we could utilise it was in the making of electricity.

We therefore installed a condensation turbine, although we knew that the produced quantity of electricity would be very limited.

The two boiler halves have a common steam-and-water drum, and a common circulation pump. The feed-water is heated to  $200^{\circ}\text{C}$  in an economiser by the hot air from the cooling of the shafts in the pyrite ovens.

The speed of the  $\text{SO}_2$  gas through the boiler is about 10/m/sec.

#### Incrustation of the tubes

During the later years, Rio Tinto pyrites have mainly been burned in Kalundborg and for this pyrite the following analysis can be given:

Sulphur	48 - 49%
Iron	42 - 43%
Copper	0.6 - 0.7%
Arsenic	0.3 - 0.4%
Zinc	1.5 - 1.9%
Lead	0.90 - 1.25%
$\text{SiO}_2$	2.0 - 3.5%

The dew point of the oven gas was found to be abt.  $250^{\circ}$ . In spite of this a boiler pressure of 40 ato was chosen, because a higher pressure would mean a considerably more expensive boiler, and because we reckoned on being able to keep the boiler pipes reasonably clean by knocking them periodically.

However it was quickly shown that this was not the case. During the course of a few weeks there appeared a thick, hard incrustation on the boiler tubes several millimetres in thickness. It was not until this coating was about 10 mm thick, that the exterior of it became so warm that the condensation on the surface of the pipes stopped. By means of knocking the pipes, one was now able to prevent the coating getting any thicker.

No incrustation appeared on the super-heater tubes, where the steam was heated to approximately  $400^{\circ}$ . The dust was easily

tapped off here.

The composition of the boiler-pipe coating

An analysis of the deposit on the boiler tubes and of the dust from the super-heated tubes showed the following:

	<u>Super-heated tubes</u>	<u>Boiler tubes</u>	
		<u>entry</u>	<u>exit</u>
Gas temperature	abt. 600°	abt. 570°	abt. 430°
As .....	3.5%	31.4%	27.5%
Pb .....	29.3%	12.0%	8.4%
S-total .....	6.6%	7.2%	7.8%
" , converted into SO <sub>4</sub>	19.8%	21.6%	23.4%
SO <sub>4</sub> , water soluble	3.0%	15.3%	19.5%
Fe, "	0.7%	1.3%	1.6%
pH, 20 g/l H <sub>2</sub> O	2.8	1.5	1.4

The main part of the arsenic is to be found in a water-soluble and trivalent form, and it seems reasonable to assume that compounds of As<sub>2</sub>O<sub>3</sub> and H<sub>2</sub>SO<sub>4</sub> account for the hard coating on the boiler tubes.

Removal of the coating

The coating dissolves relatively easily in water, and we have not observed any signs of corrosion of the tubes during the five years the boiler has been in use.

By heating the pipe-coating to 400-500° the main part of the arsenic becomes volatilized. We have taken advantage of this fact and have now and then used the following method of cleaning the tubes:

The circulation pumps are stopped. The steam and the water in the pipes is blown to the condenser, and the pressure in the tubes is reduced to 1 atm. Before this, the burning of pyrites and sulphur has been put back so much that the temperature of the gas in the boiler is abt. 500°C.

The boiler is allowed to stand a couple of hours without water, and the main part of the arsenic evaporates. The boiler is then gradually refilled with feed-water at approx. 200°C; at the same time care is taken that the pressure does not rise so high, that the safety valves blow. During this time, the

boiler tubes are knocked and due to the sudden changes in temperature the rest of the coating falls off in large flakes.

Although it can be said that this treatment of the boiler tubes is a rough one, it has, until now, only given good results, but unfortunately the effect of this de-coating only lasts a few weeks.

By burning 115 tons Rio Tinto pyrites and 15 tons sulphur, the normal steam production per hour is approximately 225 tons steam at 40 atmospheres and  $400^{\circ}\text{C}$ . From this is produced approx. 325 kWh.

We cannot boast that, by investing in waste-heat boiler, turbine and generator, we have managed to produce electricity cheaper than the the public electricity works. But through the achieved cooling of the gas the maintenance costs for the electrostatic dust chambers has been considerably reduced and their cleaning effect has been greatly improved. This cooling of the gas has at the same time allowed us to increase the amount of pyrites and sulphur, which can be burned in the ovens.

To avoid coating on the boiler tubes when burning a pyrite so rich in arsenic and lead as Rio Tinto pyrites, it would probably be necessary to use a boiling temperature of about  $300^{\circ}\text{C}$  equivalent to a steam pressure of about 88 atmospheres.

Instead of building a boiler for such a high pressure, it would undoubtedly be better to choose a pressure of about 40 atmospheres and just take the coating into account when calculating the boiler-heating area. Because of the scaling it would probably be an advantage if the boiler were placed nearest to the pyrite ovens, so the boiler tubes were exposed to the hottest part of the sulphurous gas. This on the other hand would mean that the superheater-sections should be enlarged, because of the smaller temperature difference between gas and steam. With a scaling-thickness on the boiler tubes of about 10 mm, we have found a transmission factor of approximately  $15 \text{ Kcal/h/m}^2/^{\circ}\text{C}$ .

## B. Cathodic Protection of Sulphuric Acid Coolers

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### Introduction

The problem of sea-water cooling of warm nitrous acid has been discussed many times by the technical ISMA meetings. The Danish Sulphuric Acid and Superphosphate Works has also worked with this problem and although we cannot claim to have solved it completely, it is our opinion that in carrying out a cathodic protection of the acid coolers, the annual repair costs will be considerably reduced.

### The sulphuric acid coolers

The following figures can be given as the normal working conditions of our sulphuric acid coolers:

Acid strength	78% - 80% $H_2SO_4$
" temperature, inlet	80 - 110°C
" " outlet	abt. 50°C
Nitrose content	4 - 6% $HNO_3$
Cooling water, salt content	1 - 2% NaCl

Our sulphuric acid coolers are built up of cast iron sections; each one being 28 m<sup>2</sup>. Each section contains 40 vertical pipes 2,4 metres in length and 80<sup>ø</sup>/65<sup>ø</sup> mm in diameter. The vertical pipes are placed in 4 rows, 10 in each row, and are connected by means of assembly boxes. There is only one input and output for each section. The sulphuric acid runs inside the pipes.

Approximately 70 of the above mentioned sections are necessary for the cooling of a production of 200 tons monohydrate per 24 hours with a maximum cooling-water temperature of 20°C. The annual maintenance costs for such a cooling system amount to between £2,500 - £4,000.

If the coolers are used as cascade coolers instead of submerged coolers, then the maintenance cost will be considerably increased.

At the same time, the submerged coolers present the possibility of using cathodic protection which we at first

carried out by means of zinc anodes.

#### Cathodic protection by means of zinc anodes

In order that the cathodic protection should be efficient it is necessary to use a current of approximately 50 mA per square meter. Therefore each cooler section requires

$$\underline{28 \times 0.050 = 1.4 \text{ A}}$$

This means that the annual zinc consumption should be about 15 kg as a current of 1 ampere per year theoretically amounts to a zinc loss of approximately 11 kg.

In practice, however, the loss is greater. It is due to the fact that it is impossible to attain the same current density over the whole of the cooler area, resulting in a local current density stronger than the 50 mA. Another thing is that the zinc anodes cannot be used up completely as they must have a certain area for working satisfactorily.

We chose a zinc anode measuring 320 x 220 x 30 mm and weighing 15 kg gross weight, inside which 2 pieces of iron were moulded making the installation of the anodes easier. Each cooler section uses 12 of these anodes, that is, a total weight of approximately 160 kg zinc. In this way it is possible to attain a reasonable life-time for the anodes and at the same time a suitable distribution of them over the cooler surface, thus securing the necessary current density.

The placing of the anodes is shown on the drawing on the following page.

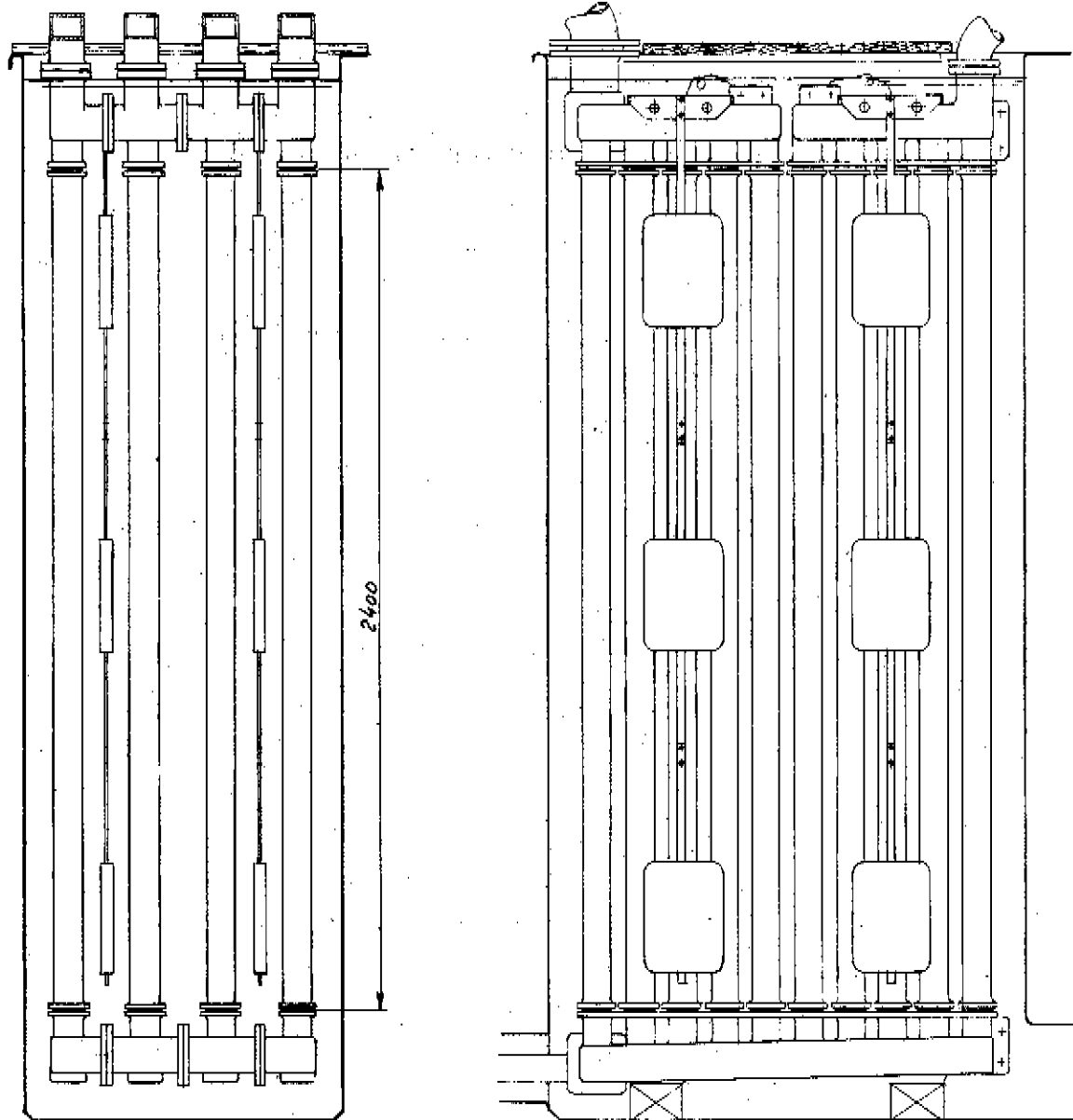
#### The provisional findings

By means of a  $\text{Cu}/\text{CuSO}_4$  electrode the potential was periodically measured in various positions in the coolers. According to this electrode the protection potential of the cast-iron is  $\pm 850$  mV, and this potential was achieved quite quickly with the above mentioned placing of the anodes. Directly opposite these, the potential is approximately  $\pm 1000$  mV whereas in the extreme end of the cooler farthest away from the anodes it is about  $\pm 850$  mV.

A small amount of hydrogen is given off at the cathode and the remaining  $\text{OH}^-$  ions gradually give rise to a  $\text{Mg}(\text{OH})_2$  and a  $\text{CaCO}_3$  - coating on the iron cooler. After a short time it could be seen that the thick, spongy rust-red coat on the surface of the cooler was replaced by a thin greyish, chalky coat.

FIGURE 1.

LH/63/6



Cathodic protection of Sulphuric acid coolers.

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This fact is not insignificant for the heat transmission, but it is difficult to give an accurate figure for it as the heat transfer - coefficient during normal working conditions for our acid-coolers depends, first of all, on the speed of the acid in the pipes and secondly, on the interior scaling of these pipes.

With the cathodic protection it should be possible to stop the exterior corrosion of the iron coolers thus giving them a much longer life.

From our experience, the yearly costs for cathodic-protection for a cooler system of 70 sections using zinc anodes amount to approximately £500 i.e. approximately 15% of the present costs.

This comparatively large figure for cathodic protection is connected to the fact that a possible leakage of acid, because of a fault in the casting or a leaky packing, will cause a violent attack on the anodes.

It is therefore probable that use of the cathodic protection by means of lead anodes and applied current will be a cheaper solution and we reckon on going over to this method during the course of this year.

The experiences of the past two years in which we have used the cathodic protection have not given us sufficiently accurate figures about the saving in acid-cooler repairs, but we are convinced that this will be quite considerable.