

DEPOSIT FORMATION IN THE EVAPORATOR OF A SULPHURIC ACID RECOVERY PLANT FOR TiO₂ PIGMENT PRODUCTION

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ABSTRACT

To produce high quality white pigment, concentrated sulphuric acid is used to separate TiO₂ from the raw material, which is usually an ore, or a slag produced from titanium rich iron ore. After dilution of the sulphuric acid in the crystallizer, it is re-concentrated in a multiple-effect evaporator set to a concentration of about 95%. The large variety of dissolved components in the process acid leads to the formation of very hard and resistant deposits on the surfaces of the high temperature heat exchangers. Typical cleaning intervals of these heat exchangers, which are made from tantalum to resist corrosion, are 5-7 days. The present paper reports the results of an extensive investigation into the mechanisms and mitigation of scale formation in an industrial TiO₂ plant. Numerous side-stream measurements have been performed to study the effects of operating conditions on the deposition rates and to investigate the potential of various mitigation techniques such as turbulence promoters, fluidized beds and magnetic fields.

INTRODUCTION

Titanium dioxide is commonly produced by the sulphate process, which is illustrated in Fig. 1.

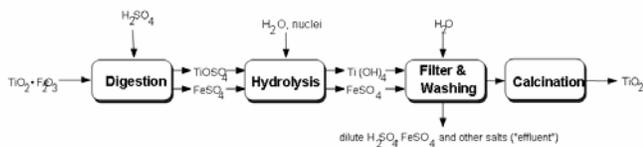


Fig. 1 TiO₂ production process overview

Slag originating from the steel industry is used as raw material, from which the titanium is digested with concentrated sulphuric acid. In subsequent hydrolysis and washing steps, the titanium is separated in form of hydroxide, which is later calcined to titanium dioxide. One effluent of this process is dilute sulphuric acid, which is loaded with different dissolved metal ions such as magnesium, aluminium, calcium and iron. In the past, most of the dilute sulphuric acid has been discharged into the sea. For economic and environmental reasons, the acid is now generally re-concentrated and recycled.

In the TIOXIDE TiO₂ plant in Calais, acid is concentrated from about 20% sulphuric acid concentration to about 95% sulphuric acid concentration in a multiple-

effect evaporator unit. Fig. 2 shows the TIOXIDE acid recovery plant in Calais.



Fig. 2 TIOXIDE sulphuric acid recovery plant

During the concentration process, substantial amounts of dissolved salts precipitate due to supersaturation with respect to the different dissolved materials. Filtration units are installed before the high concentration stages, to remove precipitated solids. Nevertheless, severe deposits still form on the heat transfer surfaces of the heat exchanger of the high concentration stage, which lead to reduced heat transfer and acid flow rates. Typical plant operating data are shown in Fig. 3.

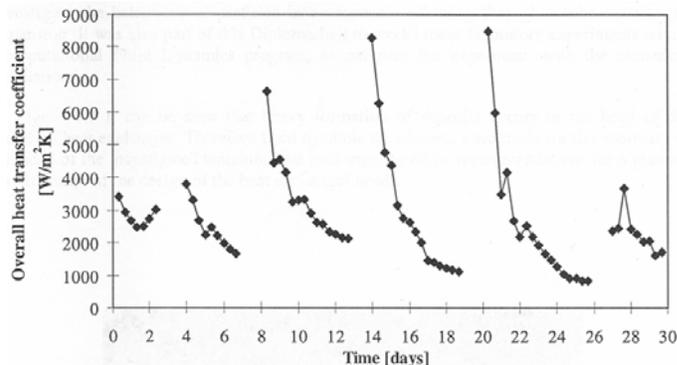


Fig. 3 Heat transfer coefficients in the high concentration sulphuric acid evaporation plant

Two different kinds of fouling layers have been observed: the first fouling layer on the surface of the tantalum wall consisted of fine, regular crystals and was very hard and dense. This deposit is caused by crystallisation fouling. A second fouling layer was discovered on top of the first fouling layer, consisting of large, irregular crystals. This fouling layer was a soft deposit and occurred mostly after runs with a low acid velocity or even during shut-down. Analysis of the deposits showed that the main component of the hard crystalline deposit is magnesium sulphate. Analysis of the particulate deposit indicated ferrous sulphate and aluminium sulphate as the main components of the soft layer.

In order to maintain proper operation, these heat exchangers, which are manufactured from tantalum, needed to be taken out of operation for cleaning every 3 -10 days. Cleaning occurs by washing with water and with clean acid, or by high pressure water jetting. Due to limitations in the plant buffer capacity, these shut-downs have a detrimental effect on plant productivity.

EXPERIMENTAL SET-UP

To improve the understanding of the effects of operating conditions on fouling rates and to investigate potential avenues for fouling mitigation, a test facility was designed in cooperation between TIOXIDE and the University of Surrey. Following construction and instrumentation in the University of Surrey, this test rig has been installed in a side-stream of the TIOXIDE sulphuric acid plant in Calais, where it has been operated for a period of 2 years. Fig. 4 shows a picture of the test rig, which consisted of three separate and individually controlled test sections. Each test section consisted of an electrically heated tantalum pipe with the inside diameter of 32 mm and a length of 700 mm. Tantalum is a heavy ($\rho \approx 16600 \text{ kg/m}^3$) and very hard metal with a stable oxide layer, which makes it nearly inert to chemical attack. All other piping is made of PTFE-lined steel tubes to resist up to 90% sulphuric acid.

For the experiments with the fluidised bed, one of the test sections was modified with a siphon and a collector made of two standard 40x80 reducing pieces. The siphon contained the fluidised bed particles if there was no flow in the test section. The collector was installed as a precaution in case that some particles were carried out of the fluidised bed.

Process acid was pumped through the test tubes and then returned to the plant acid stream. Operating conditions were up to 230°C wall temperature and 4 bar acid pressure. For safety reasons, no personnel are allowed in the production area during operation; hence all control instrumentation and data acquisition for the test facility were installed in a container outside the production unit, and additionally linked to the plant control room. All

thermocouples, pressure sensors and flow meters have been calibrated before start-up and checked several times during the subsequent 2 years of operation.



Fig 4 Installed test rig

EFFECT OF OPERATING CONDITIONS

All experiments as well as the analysis of plant operating data showed a more or less linearly increasing fouling resistance with time, as depicted in Fig. 5.

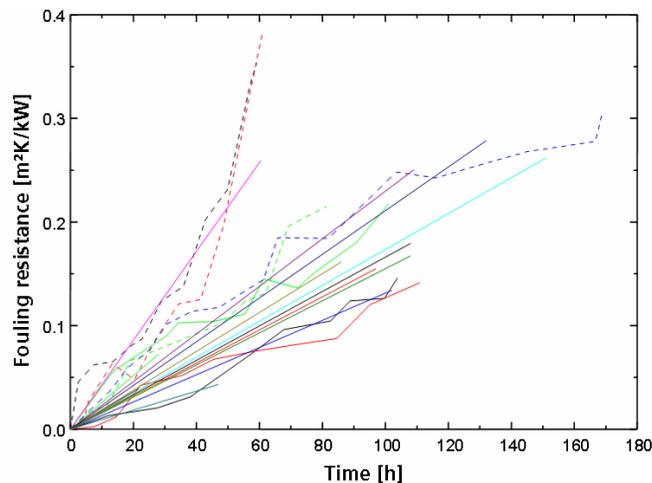


Fig. 5 Fouling resistances vs. time for different flow velocities and surface temperatures

Based on previous experience with numerous other fouling problems [1,2], first attempts have focused on reducing the fouling rates and/or fouling resistances by increase

the flow velocity. However, no significant effects have been found for flow velocities between 0.5 m/s and 5 m/s.

In most fouling processes, the deposition rate increases with increasing surface temperature for constant flow velocity and bulk temperature. It was, therefore, most surprising to find for the present system a decrease in fouling rate with increasing surface temperature, as depicted in Fig. 6. This finding must be due to the complex solubility behaviour with temperature for the multi-component solution present during plant operating conditions.

Since the test facility was installed in a side-stream of the actual processing plant, no variation of acid composition and acid bulk temperature has been possible.

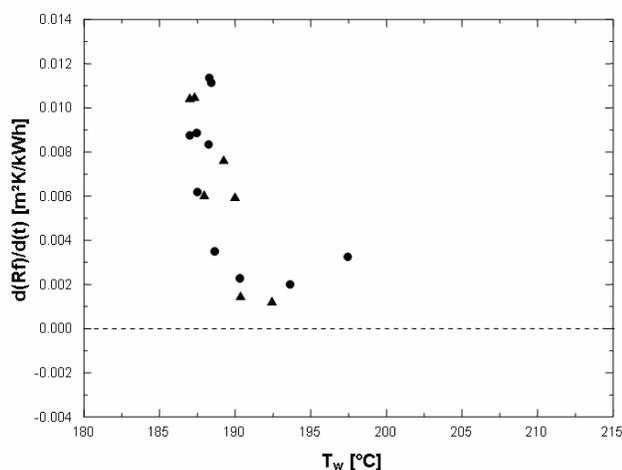


Fig. 6 Fouling rate as a function of wall temperature, from two periods of investigation in different years

ON-LINE FOULING MITIGATION METHODS

Due to the complex mixture of dissolved salts, the high concentration of sulphuric acid and the high temperature level, it was obvious that chemical additives would not be an option for fouling mitigation. Furthermore, the composition of the acid was quite variable, depending on the raw metal of the process. Therefore, on-line fouling mitigation methods based on mechanical or physical effects have been seen as the most promising option.

Permanent Magnets

Magnetic treatment devices have been marketed by a number of companies for over 40 years for applications ranging from small-scale domestic to large-scale industrial [3-7]. Claims made by the suppliers include the reduction of the amount of scale formed, the formation of soft scale and the removal of existing scale. For this particular case, two products have been selected where the manufacturers claimed previous experience with industrial process liquors.

The first device consisted of several sets of commercial **permanent magnets** which had to be installed around the piping leading to the heated test section in a specified way. The explanation for the claimed beneficial effects were that the magnetic field modifies the nature of the surface charges of the crystal nuclei, leading to different solubility in the solvent or different crystal modifications with weaker adherence. No information about the magnetic field strength has been provided by the supplier.

The magnets have been applied to test section 1, while the parallel test section 3 was operated at the same conditions, but without any modifications. Fig. 7 shows the increase in fouling resistance with time for the two test sections, indicating that there is no notable difference in fouling behaviour. In a second experiment, a lower velocity of 1 m/s was applied for the two test sections. No difference in fouling behaviour was observed for the first 20 hours of operation, after which the test section with the magnets showed a slightly higher fouling resistance.

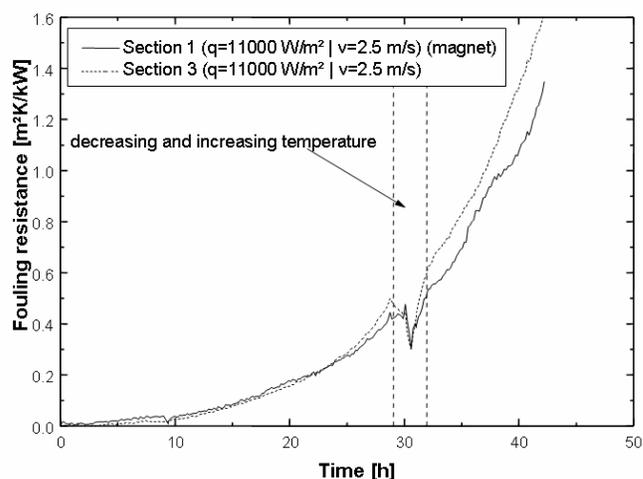


Fig. 7 Fouling resistance as a function of time for Test Section 1 with magnets and Test Section 3 in original condition.

The second physical fouling mitigation device was a so-called **electronic descaling system**. It consisted of an insulated cable wrapped in a certain way around the pipe leading to the heated test section in conjunction with a frequency modulator unit which provides an oscillating square wave to the coil. The oscillating electromagnetic field is said to move the ions in solution in a non-random way, increasing the likelihood and impact of collision of oppositely charged ions in the liquid bulk. For commercial reasons, the supplier did not provide any details such as frequency and electromagnetic fields. Experiments for 1 m/s and 2.5 m/s flow velocity showed no difference in fouling behaviour as compared to the parallel test section without electromagnetic field.

Rod Turbulator Technology

Heat exchangers with rod turbulators, such as the design shown in Fig. 8, have been recommended for some years. The rod turbulator is basically a cylindrical rod of a suitable material which is inserted into each tube and which has a diameter considerably smaller than the tube inside diameter. The resulting oscillating movement of the rod in horizontal and vertical direction is said to lead to an abrasive effect on that heat transfer surfaces and to a higher level of turbulence in the liquid flow, both mitigating against the formation of deposits. For the present experimental conditions, a PTFE rod of 12.5 mm diameter and 700 mm length was selected.

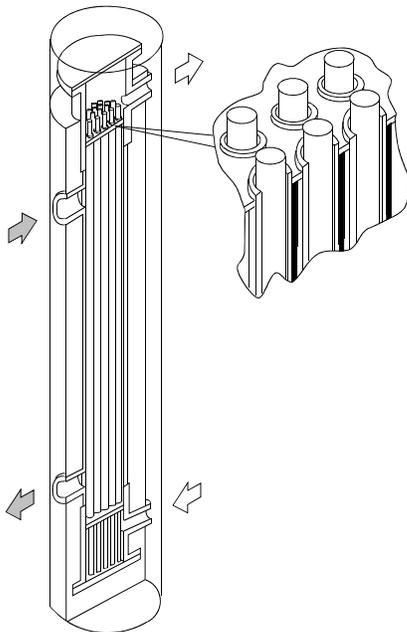


Fig. 8 Sketch of heat exchanger with rod turbulators

In the pilot test rig it was not possible to install a free moving rod turbulator, since it would have interfered with the flow control valve. It was also not possible to do preliminary tests in the laboratory to investigate how flexible the Teflon turbulator would be in 188 °C sulphuric acid. Since the danger that the rod turbulator would be carried out with the acid was too high, the rod was fixed with a tantalum wire into the first test section, a design which still allowed relatively free movement. Preliminary experiments showed, however, that the heat transfer coefficients measured with the rod inserts were even somewhat lower than the values without insert, even if appropriate corrections for annular flow had been taken into account. It was hence concluded that no additional turbulence occurs which might reduce the extremely tenacious deposit. This assumption was confirmed by the fouling experiments, where no significant effect of the

turbulator rods and in some cases even an increase in fouling has been observed, see Figure 9.

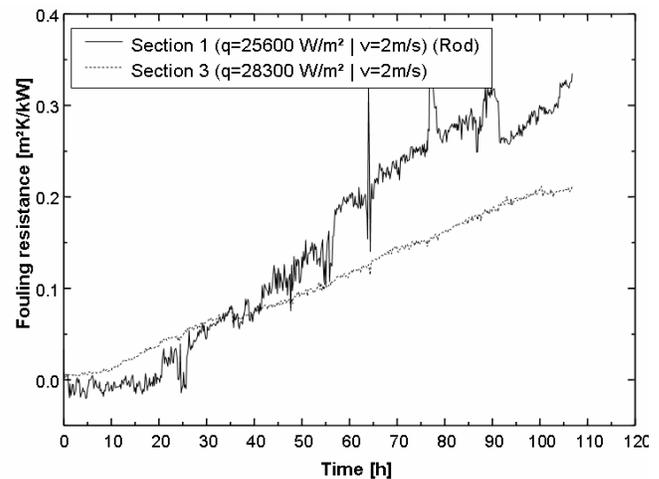


Fig. 9 Fouling resistance over time for the rod turbulator test section and the empty tube

Turbulence promoters

Tube inserts, such as twisted tapes, coils or wire matrix inserts are commonly used in the chemical and petroleum processing industry to enhance heat transfer to viscous liquids in the laminar or transitional flow regime. Through the wall contact of the insert, the viscous sublayer of the fluid is disturbed and mixed with the bulk fluid. This effect has also been found to be beneficial for mitigation of fouling in crude oil preheaters [8-10].

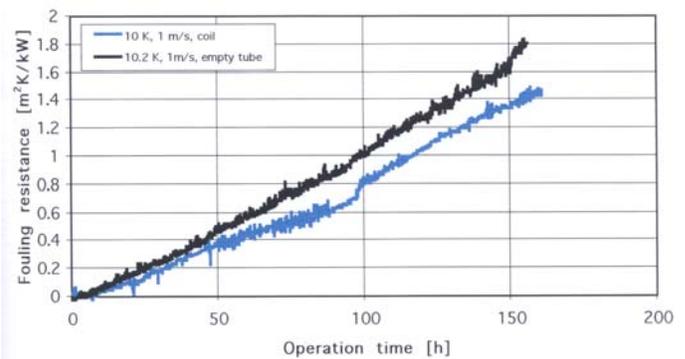


Fig. 10 Effect of tube insert (lower data set) on fouling

Two types of inserts have been custom-made from tantalum for the present investigation, the first being a conventional spiral and the second a commercially optimised design. Both types of inserts have been able to increase the clean heat transfer coefficient at a flow velocity of 1 m/s from about 1200 W/m²K to about 2500 W/m²K. However, fouling occurred with both inserts, even though to a somewhat reduced extent. Since the improvement due to the inserts has not been significant, see Fig. 10 for lower

data set, and because of the increased problems with mechanical cleaning, such tube inserts were not considered as a promising solution to the fouling problem occurring in the sulphuric acid evaporator.

Solid/liquid fluidized bed

Solid/liquid fluidized bed heat exchangers have a proven track record for excellent performance under severe fouling conditions [11-13]. Particles of a suitable material are added to the fouling liquid which flows on the tube-side of the heat exchanger. In industrial application, a flow velocity is adjusted which leads to circulation of the particles. Under the present experimental conditions, a stationary fluidized bed was preferred where the liquid flow velocity equals the particle sinking velocity. While the scouring action of the particles on the heat transfer surfaces is somewhat less for these conditions, the experimental set-up is much simpler. Due to the temperature, density and aggressiveness of the concentrated sulphuric acid, cylindrical tantalum particles with a diameter and a length of 4 mm had to be manufactured. Without fouling, the presence of these fluidized particles increased heat transfer to the hot concentrated sulphuric acid by a factor of 2-3, for the same flow velocity and heat flux, see Figure 11. The fluidisation regime is approximately between 0.4 m/s and 0.8 m/s; for lower and higher flow velocities, the heat transfer coefficients match those for convective single component flow.

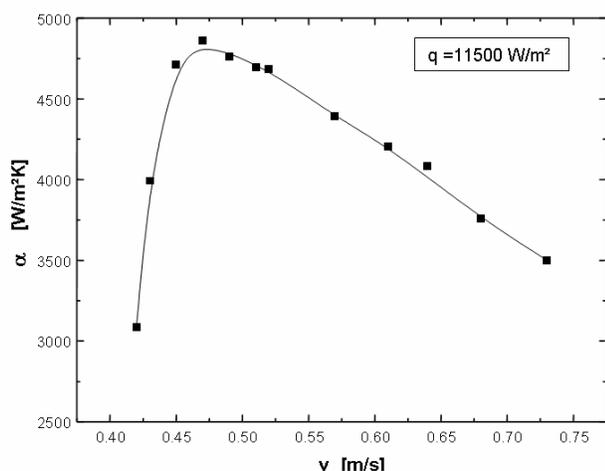


Fig. 11 Heat transfer coefficient over velocity for the fluidised bed in sulphuric acid (bulk temperature 188°C)

Bed voidage and heat transfer coefficient as a function of flow velocity can be calculated with standard correlations, see for example [14].

Several experiments have been performed with parallel test sections with and without particles. Conditions have been adjusted such that the heat transfer coefficients and

hence the wall temperatures in both parallel test sections have been identical at the beginning of the experiments.

Fig. 12 shows that no fouling was observed in the fluidized bed test section during the whole time of operation, while the fouling resistance in the parallel pipe without particles increased rapidly. Identical results have been obtained for other test conditions, as well. While no longer experimental runs were possible due to the dependency on the production plant operating cycle, these results provide a strong indication that significantly longer operating cycles would be possible with fluidized bed heat exchanger technology.

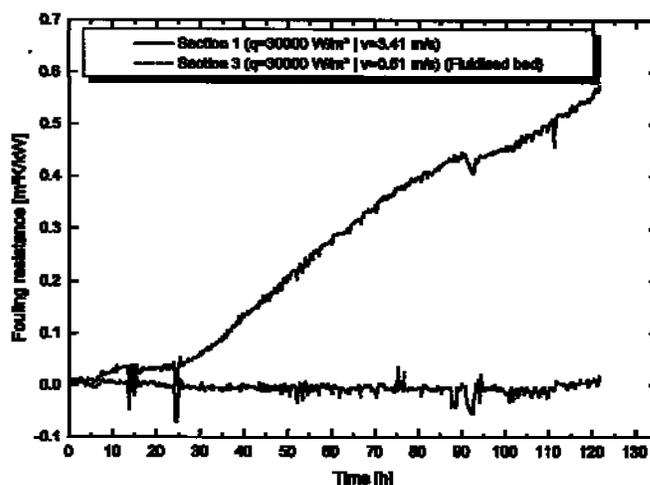


Fig. 12 Effect of solid/liquid fluidized bed on fouling

SUMMARY AND CONCLUSIONS

The effects of operating conditions and the effectiveness of various fouling mitigation techniques have been investigated for scale formation in the heat exchangers of an industrial sulphuric acid evaporator plant. Two promising strategies have been identified, i.e. i) increasing the heat transfer surface temperature by using a combination of reduced flow velocity and increased steam pressure, and ii) modifying the existing vertical multi-pass heat exchanger to a solid/liquid fluidized bed heat exchanger. Due to the additional costs involved in changing the plant hardware, option i) may be preferred in the near future.

SYMBOLS

| | |
|----------|---|
| R_f | fouling resistance, m ² K/W |
| t | time, s |
| T_w | wall temperature, °C |
| u | flow velocity, m/s |
| U | overall heat transfer coefficient, W/m ² K |
| α | film heat transfer coefficient, W/m ² K |

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