CLEANING AND PREVENTION OF INORGANIC DEPOSITS IN PLATE HEAT EXCHANGERS USING PULSATING CURRENT

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ABSTRACT

Fouling of heat exchangers is a major problem in many industrial processes. The higher temperature of the heat exchange surface compared with the liquid containing precipitable compounds causes the formation of inorganic deposits. Removing the deposits on plate heat exchangers is most often carried out by high-pressure cleaning. This is a laborious task and often increases the corrosion rate of the plates by increasing the roughness of the cleaned surface.

This study presents an electrochemical method to clean heat exchange surfaces fouled by deposits and to prevent formation of deposits. This method utilizes pulsating current to polarize heat exchange surfaces with periodic anodic and cathodic DC current. The shape of the pulse and the current density are adjusted to maximize the deposit removal rate, thus minimizing plate corrosion. The optimal pulsating current depends on the material of the heat exchange surface, as well as the composition of the deposits and the solution. For cleaning, the current densities and the frequency of the current pulse are typically higher than those used for preventing deposition.

Pulsating current can effectively remove deposits with low solubility, such as TiO_2 on titanium heat exchange plates or dense gypsum deposits on stainless steel plates. For cleaning titanium, the cathodic pulse and formation of hydrogen is more essential than in the cleaning of stainless steels. However, the risk of corrosion limits the use of high current densities. Experiments have until now been carried out mainly in the laboratory, though industrial pilot cleaning equipment has also been constructed. An application has already been submitted to patent the method.

INTRODUCTION

Inorganic fouling of liquid filled heat exchangers has been investigated in a larger project funded by the Finnish Funding Agency for Technology and Innovation (Riihimäki et al. 2004). Systematic study of fouling has been based on synergy between process analysis, modeling and experimental methods. This paper deals with electrochemical cleaning and prevention of inorganic fouling using electrochemistry. This work evaluates the suitability of electrochemical methods for various new applications. New equipment and methods have been developed for studying the cleaning of fouled surfaces and prevention of fouling.

Clean surfaces are now sometimes impossible to achieve. Typically, the cleaning of SiO_2 containing TiO_2 deposits on titanium plates is a multistage process. Plates are first washed with a high-pressure water jet at about 500 bar. Most often the result is inadequate, and it is important that the plates are immersed in 40 w-% NaOH (T = 40 °C) for about one week, followed again by pressure cleaning. Often, the cleaning process is followed by heat treatment at a temperature of 120 °C, and then again pressure cleaning. Occasionally, the amount of remaining deposits is still too high and the plates must therefore be scrapped.

An earlier study has presented an electrochemical cleaning method for fouled surfaces and another method to prevent inorganic fouling (Pehkonen et al. 2004). Both methods are based on the utilization of pulse current. However, the number of publications concerning electrochemical cleaning is very limited (Chen 2004, Neville 1995).

The risk of corrosion in electrochemical cleaning limits the use of high current densities. Fouling can be prevented at clearly lower current densities, and the duration of a pulse may be longer.

The main aspect limiting the utilization of electrochemical methods for cleaning and prevention of fouling is the corrosion of the heat exchanger surfaces. Only minor corrosion is allowed. Thus, the corrosion behavior of plate materials needs to be examined in depth before applying pulsating current.

EXPERIMENTAL

Electrochemical cleaning and prevention of fouling were investigated using process equipment and process solutions for two plants producing titanium dioxide pigment and ground calcium carbonate plant. Experiments were carried out on a laboratory scale. The materials investigated were Ti grade 2 in a titanium dioxide process and austenitic stainless steel AISI 316L in a calcium carbonate process. At the plant producing ground calcium carbonate, deposits consist mostly of $CaCO_3$, while the deposits at the titanium dioxide production facility are composed of TiO_2 with some SiO_2. In both cases, SiO_2 forms a tight, thin layer on the metal surface.

Both the electrochemical cleaning and prevention of fouling employ pulsating current with both anodic and cathodic current. However, the corrosion behavior of the

materials needs to be examined before the cleaning in order to prevent excessive corrosion. The corrosion behavior of materials also needs to be known for defining the optimal potential and current to be used in the cleaning and prevention of fouling.

Corrosion tests

Corrosion experiments were carried out in an Avesta-cell, which was heated in a water bath (Fig. 1). Reference electrode consisted of a saturated calomel electrode (SCE). Platinum was used as a counter electrode.

The corrosion behavior of Ti grade 2 was investigated using open circuit potential and potentiodynamic methods. The process solution consisted of H_2SO_4 at about 430 kg/m^3, and soluble Ti at about 230 kg/m^3, Fe (II) at about 115 kg/m^3, together with other impurities. Potentiodynamic polarization measurements were performed after stabilizing the sample in the cell for about 30 min. The test solutions were maintained at 80, 90 and 110 °C. Polarization was started at a potential of -700 mV vs. SCE and scanned in the anodic direction at a sweep rate of 10 mV/min.

Although corrosion is not a problem in the calcium carbonate process, the corrosion behavior of austenitic stainless steel AISI 316L needed to be investigated in order to find the proper parameters for electrochemical cleaning.
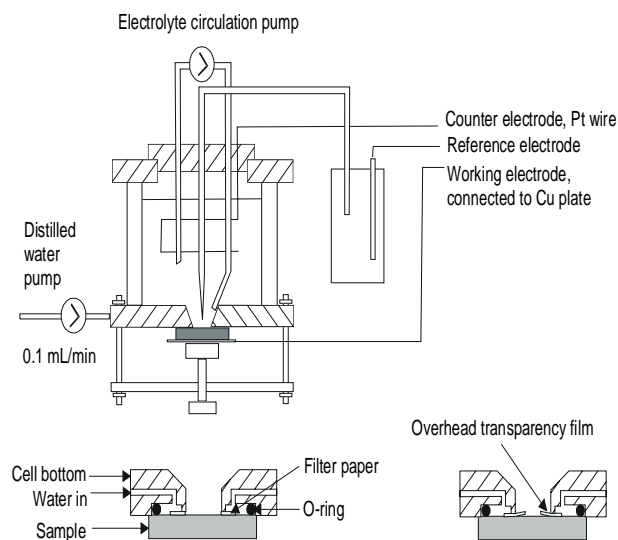

Fig. 1 Schematic diagram of Avesta-cell.

Experiments were conducted with a process solution (70 w-% $CaCO_3$ in water with some impurities, e.g. SiO_2) and another process solution diluted to concentrations of 20, 40, 50 and 60 w-%). In addition, we also used a synthetic 40 w-% $CaCO_3$ solution. The test solutions were maintained at 80 and 95 °C.

Electrochemical tests were performed as described above for titanium, except that polarization was started at the corrosion potential in both the anodic and cathodic direction.

Cleaning tests

Cleaning of fouled heat exchanger plates was investigated using an electrochemical method. Samples for the experiments were gathered from scrapped units. Test plates obtained from the titanium dioxide process had been intensively cleaned before the laboratory experiments with a high-pressure water wash, immersed in NaOH solution (seven days) with heat treatment (150 °C) and pressure cleaning. Plates were not clean enough for reuse, and were therefore scrapped. Samples from the calcium carbonate process were taken after high-pressure water wash.

Removing the deposits on Ti and AISI 316L surfaces was studied using galvanostatic, potentiostatic and pulse current. Cleaning experiments for Ti were carried out using a process solution, 10 w-% sulphuric acid and 10 w-% sulphuric acid with 1000 ppm citric acid. The cleaning solution was maintained at 60 °C. Cleaning of AISI 316L was investigated using sulfuric and phosphoric acid solutions with citric acid additions. Some tests were also conducted in a NaOH solution.
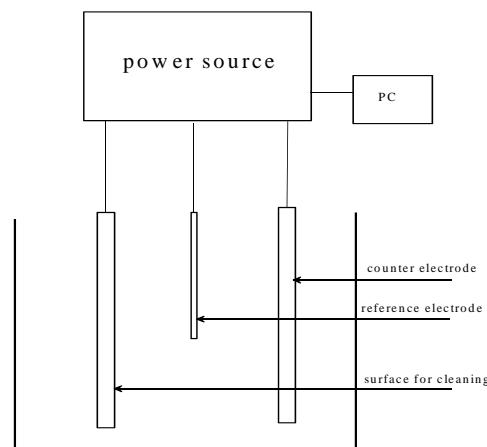

Fig.2 Cell for electrochemical cleaning.

Cleaning experiments were performed in a glass cell (Fig. 2) with heating in a water bath. Counter electrode was platinum, and a saturated calomel electrode was used as the reference electrode.

Prevention of fouling

Prevention of fouling was studied in the cell system shown in Fig 3 and 4, where the temperature of the sample could be higher (up to 120 °C) than that of test solution in

order to simulate environments in the plant heat exchangers, in which the solution is heated by steam. This was accomplished from outside using an electric resistance. Synthetic deposits using this cell were also formed from process solutions containing TiO_2/SiO_2.

Some experiments were also carried out using a laboratory-scale tube heat exchanger, with one tube for formation of synthetic calcium carbonate deposits. The properties of these deposits were, however, very different than those formed in industrial environments. Thus, prevention of fouling in calcium carbonate solution was not studied further.
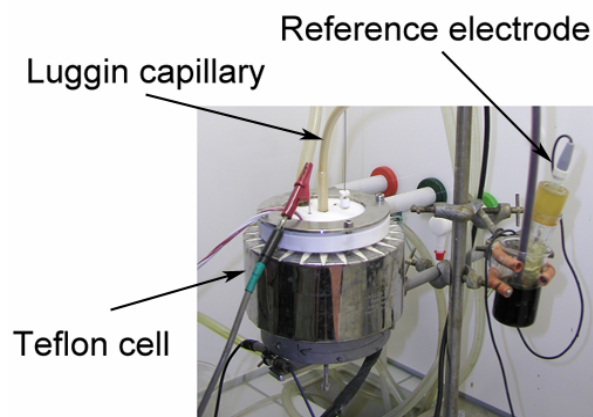

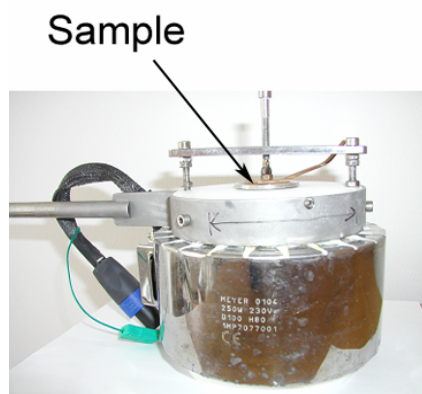Fig. 3 Cell for prevention of fouling.

Fig. 4 Cell upside down with a specimen.

RESULTS
Corrosion behavior of Ti

The corrosion potential of Ti initially increases slowly at a constant rate. After about 40 – 60 hours of immersion, the corrosion potential increases more rapidly from +50 – +100 mV vs. SCE to +200 – +300 mV, with the potential increasing more rapidly at higher temperatures than at lower temperatures. However, the potential did not attain a completely steady state even after 100 hours immersion.

Increasing the potential thus depends on the passivation of titanium, which is partly due to the formation of deposits on the surface. Deposition formed during the immersion was easily removed by water before drying the surface.

Potentiodynamic polarization measurements at temperatures of 80, 90 and 110 °C show that titanium has a corrosion potential of about -120 mV vs. SCE at temperature of 80 °C and about 0 mV at 90 °C. At a higher temperature of 110 °C, the corrosion potential is about -500 mV, the point at which the cathodic current changes to anodic, though the current momentarily remains cathodic at a potential of about 0 mV (Fig. 5). This indicates that the free corrosion potential of Ti lies within an area of the passive/active border. At lower temperatures, Ti remains passive. However, the current density increases in the passive region with increasing temperature. In the transpassive region, current densities are about one decade higher at temperatures of 90 and 110 °C than at 80 °C. Current densities of cathodic polarization curves are high at all temperatures, indicating that the corrosion rate of Ti caused by hydrogen formation rapidly increases as the potential is changed into the cathodic direction.
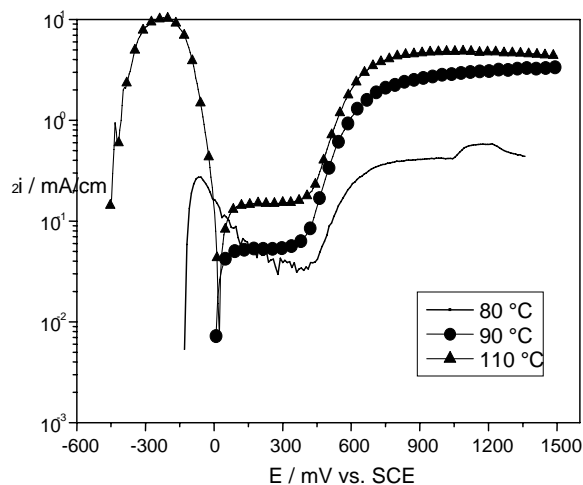

Fig. 5 Polarization behavior of Ti grade 2 in process solution, T = 80, 90 and 110 °C.

Electrochemical cleaning of Ti

In these experiments, both the anode and cathode were titanium fouled with TiO_2. Samples cut from scrapped industrial heat exchanger plates could not be cleaned at a temperature of 60 °C using only anodic potentiostatic current even at high potential (10 V vs. SCE). Although the fouled samples could be cleaned using cathodic current and potential below -0.6 V vs. SCE, the risk of corrosion is too

high. Thus, these samples would also be impossible to clean using only cathodic current.

The cleaning efficiency of these plates could be notably improved by pulsating current. In these potentiostatic experiments, the polarity of the current was changed every 10 - 30 s at a current density of 5 - 12 A/dm^2. In pure 10 w-% sulfuric acid, cleaning of the surfaces could be obtained within 10 – 15 min at a temperature of 60 °C. Addition of Citric acid at 1000 ppm increased the efficiency of the cleaning and decreased the cleaning time to 2 – 4 min. Process solution required only 20 – 25 min to clean the surface. Fig. 6 shows the result of cleaning in H$_2$SO$_4$ with 1000 ppm citric acid.

Fig. 6 Sample scraped due to excess fouling before and after cleaning using pulse current, 10 w-% H$_2$SO$_4$ + 1000 ppm citric acid, T= 60 °C, pulse current 5 min.
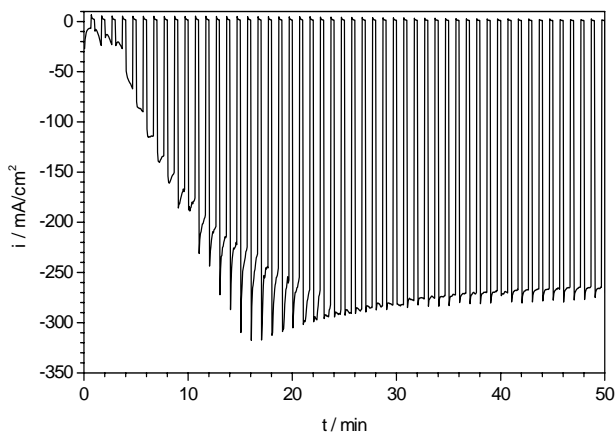

Fig. 7 Electrochemical cleaning of Ti in 10 w-% H$_2$SO$_4$. Potentials: anodic +3 V vs. SCE 30 s, cathodic -0.8 V vs. SCE 30 s, T = 60 °C.

The anodic potential was +3 V vs. SCE for 30 s, and the cathodic potential -0.8 V vs. SCE for 30 s. The surface is found to be clean when the cathodic current reaches the maximum or soon thereafter.

The cleaning time required for the process solution was longer than that for the pure acid solutions. However, it remained below 10 min, even when the cathodic potential fell below -0.8 V vs. SCE. Fig. 7 shows the effect of time on the current density during electrochemical cleaning in 10 w-% sulfuric acid.

Fig. 8 shows the results of the corresponding experiment carried out in 10 w-% H$_2$SO$_4$ + citric acid solution with an anodic potential of +3 V vs. SCE for 30 s and cathodic -0.8 V vs. SCE for 30 s. Citric acid clearly decreases the time needed for the cleaning.

The cleaning time of the process solution at a temperature of 60 °C for the Ti sample (anodic potential +3 V vs. SCE 45 s and cathodic potential -0.8 V vs. SCE 15 s) is higher than that of the sulfuric acid solution containing citric acid (Fig. 9). The time required to clean the surface is difficult to estimate based only on the curve; therefore, the surface also needs to be visually examined.
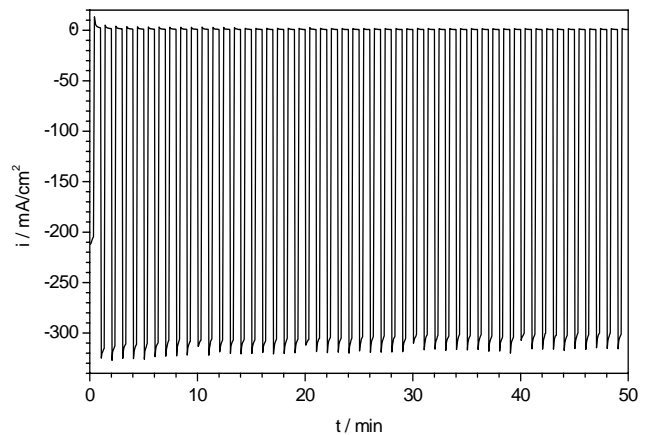

Fig. 8 Electrochemical cleaning for Ti in 10 w-% H$_2$SO$_4$ + 1000 ppm citric acid solution. Potentials: anodic +3 V vs. SCE 30 s, cathodic -0.8 V vs. SCE 30 s, T = 60 °C.

The current densities in the above experiments are rather high with respect to corrosion. To minimize corrosion, galvanostatic electrochemical cleaning was performed in sulphuric acid containing citric acid using a cathodic potential of -600 - -500 mV vs. SCE at a current density of 2 mA/cm^2 and a anodic potential of +4 V vs. SCE. The duration of both pulses was 30 s. Experiments were carried out at room temperature. Despite partial loosening of the deposit on the surface, the surface is still not clean even after 1 h. The galvanostatic cleaning experiments used current densities of ±1 mA/cm^2, and bothpulses were applied for 30 s. The surfaces clearly became cleaner than

those in the potentiostatic experiments, though the surface was not completely clean even after 1 h of the experiment.
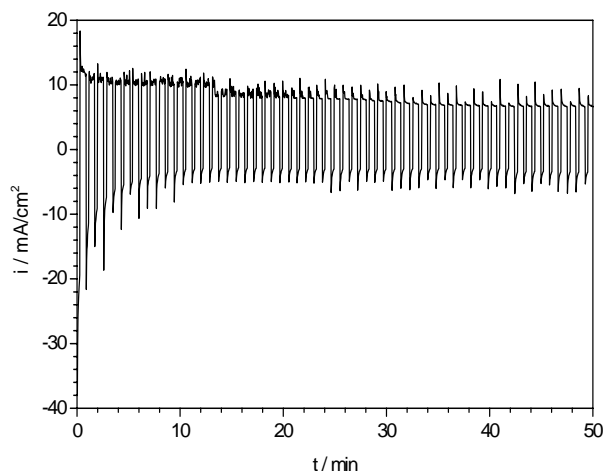

Fig. 9 Electrochemical cleaning for Ti in the process solution. Potentials: anodic +3 V vs. SCE 45 s, cathodic -0.8 V vs. SCE 15 s, T = 60 °C.

Prevention of fouling in TiO_2 solution

The ability to prevent fouling in TiO_2 solution was investigated using cathodic, anodic and pulsating current. Although anodic current can delay fouling, some deposits nevertheless formed on the surfaces. Conversely, the risk of corrosion was high when cathodic current is applied. Using a cathodic and anodic current of ±0.1 mA/cm^2 could not prevent the formation of deposits. However, the did remain
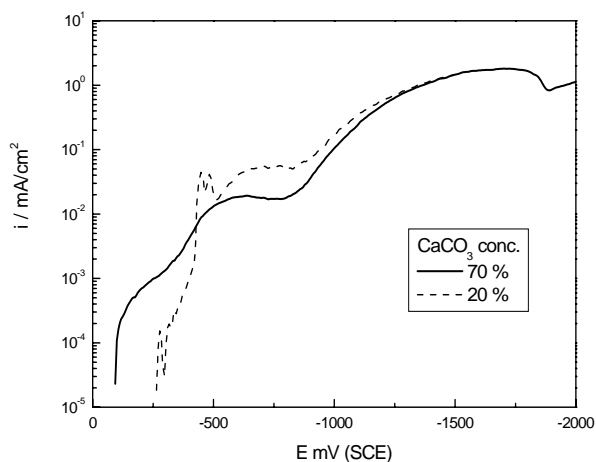

Fig. 10 Cathodic polarization behavior of AISI 316L in 20 and 70 w-% calcium carbonate solutions, T = 95 °C.

clean when a pulsating current was applied using potentiostatic anodic polarization (2 V vs. SCE) for 24 h and a cathodic polarization of -0.7 – -0.8 V vs. SCE for 2 - 3 min. The temperature of the solution was maintained at 90 °C, with the longest experiment lasting 11 d, after which no weight loss or fouling was noticed. However, the risk of corrosion was found to increase with increasing current density of the cathodic polarization.

Corrosion behavior of stainless steel in $CaCO_3$ solution

Figure 10 shows the cathodic polarization behavior of AISI 316L in 20 and 70 w-% carbonate solution at a temperature of 95 °C. Although corrosion potential is lower in 70 w-% carbonate solution, the curves are otherwise relatively similar. The cathodic polarization curves show similar current densities for both solutions and temperatures at potentials below -1000 mV, at which no hydrogen evolution occurs. In contrast, the anodic polarization curve
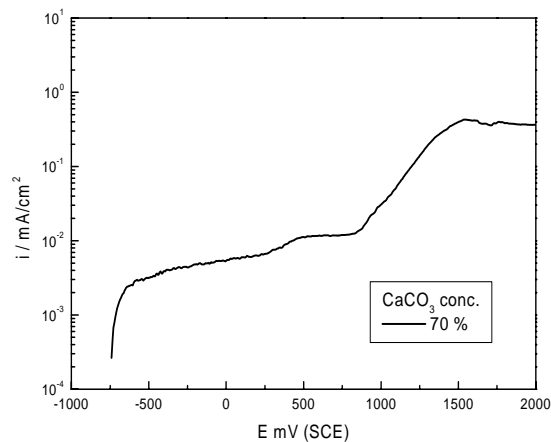

Fig. 11 Anodic polarization behavior of AISI 316L in process solutions (70 w-% calcium carbonate), T = 95 °C.

at a calcium carbonate concentration of 70 w-% (Fig. 11) reveals that the current density remains low until reaching a potential of about +1000mV vs. SCE, the point at which oxygen begins to evolve.

Electrochemical cleaning in $CaCO_3$ solution

In the calcium carbonate process, the deposit consists of a thin SiO_2 layer on the metal surface and a thick $CaCO_3$ layer. Using anodic current alone enabled most of the outer layer to be removed, whereas cathodic polarization alone was unable to clean the surfaces, and pulsating current was able to improve somewhat the cleaning. calsium carbonate deposit mostly dissolves into the cleaning solution, a thin,

dark SiO_2 deposit remained on the surface. Calcium carbonate could be removed from surfaces using solutions of either sulphuric and phosphorous acid or NaOH. However, the effect of NaOH was slightly better than that of the acids.

During experiments using only the electrochemical method, which was unable to remove deposits completely, we also studied the effect of heating the test sample before electrochemical cleaning. The fouled samples were heated 5 – 10 min at temperatures of 650 °C and 700 °C in air atmosphere. Heating at 650 °C is shown to have only a minor effect in improving the electrochemical cleaning, even though deposition was loosened by cooling the sample in water. At a higher temperature of 700 °C, deposition was relatively easily removed by electrochemical cleaning. A completely clean surface was obtained by heating the sample for 10 min at 700 °C in air atmosphere, followed by immersion for 5 min in 50 w-% NaOH-solution, and then electrochemical cleaning for 5 min in 25 w-% H_2SO_4 solution with addition of citric acid 1 g/l. Both cathodic and anodic current pulses for cleaning were applied for 10 s to achieve current densities of 3.5–7 A/dm^2. Cleaning was further improved by increasing the temperature of the cleaning solution up to 60 °C. However, the effect of heating on the shape and profile of the heat exchanger plate was not investigated, which may prevent the use of such heating.

Fouled samples cut from process heat exchanger plates can be seen in Fig. 12 before and after electrochemical cleaning. The plates were washed earlier using high-pressure water jet cleaning.

DISCUSSION

It is important to know the chemical composition and structure of the fouled deposits before using the electrochemical cleaning method to clean the deposits forming on heat transfer surfaces as well as before the prevention of fouling, since the deposits forming on surfaces are seldom homogeneous. The composition of deposits on the metal surface may differ from that on the outer layer, thus also requiring analysis of changes appearing in the vertical direction. Differences in the composition may also occur in different parts of the heat exchangers. Thus, for electrochemical cleaning, it is also essential to know whether deposits are amorphous or crystalline.

Choice of the cleaning solution

The cleaning solution needs to be chosen based both on the corrosion behavior of the heat transfer metal as well as the chemical composition of the fouling. Acidic solutions, such as sulfuric of phosphoric acids, are most often suitable. The effect of these acids can be increased by a complexing

agent, e.g. citric acid. The cleaning acids should be suitable for the material to be cleaned in order to

Fig. 12 The effect of heat treatment and electrochemical cleaning on AISI 316L fouled by the calcium carbonate process. From left to right: the fouled sample, sample after heat treatment and electrochemical cleaning, and the sample resulting from electrochemical cleaning only.

reduce the corrosion rate and, in case corrosion does occur, to keep it uniform. Sulphuric and phosporic acids often have these properties at low concentrations (e.g., 5 – 10 w-%) and are thus able to keep the corrosion rate of the most typically used austenitic stainless steel grades low and the corrosion uniform.

Complexing agents, e.g. citric acid, increase the effect of acids by binding the dissolved metals formed during corrosion reactions into compounds.

The choice of the cleaning acid is also affected by the chemical composition of the fouling. Deposits need not necessarily be soluble in the cleaning solution, e.g. the solubility of SiO_2 and TiO_2 is very low in many acids. Another drawback might be that the corrosion rate of metals can become very high if these compounds dissolve, since they are protecting the metal by passivation.

Oxide deposits are more easily removed from heat transfer surfaces in acidic solutions than in alkaline solutions. Conversely, sulphate and carbonate deposits can be more effectively removed in alkaline solutions. The effect of the cleaning solution in electrochemical cleaning can not be estimated using only the stability of the deposit. The structure and porosity of the deposit greatly affects the cleaning. Those compounds, e.g. $CaCO_3$, which in principle have high solubility in many solutions, may be difficult to remove, since they may form thick and very dense deposits.

It thus seems that crystalline deposits are more difficult to remove than those that are amorphous.

Electrochemical measurements

Predicting the electrochemical cleaning of heat transfer surfaces requires further study of the corrosion behavior of metals. To prevent damage during cleaning, the corrosion resistance must be high enough in the cleaning solution. Corrosion resistance in the cleaning solution was studied through corrosion potential measurements and cyclic polarization curves. It is important that these measurements be conducted at the temperature of the cleaning solution.

Potentiodynamic polarization curve measurements are started at a corrosion potential slightly lower than that in the anodic direction. A sweep rate of 5 mV/min was used. Potential was turned back in the cathodic direction at current density of 5 mA/cm^2. If the corrosion resistance of the stainless steel is high in the solution, or the test material is titanium, the turning point will be set at + 3V vs. SCE.

Measurements of potentiodynamic polarization and corrosion potential usually give sufficient information about the corrosion behavior of the material. However, if the material corrodes in the cleaning solution at too high a rate, a less aggressive solution should be chosen.

Electrochemical cleaning

It is sometimes necessary to produce artificial fouling under laboratory conditions. Such laboratory conditions may provide the only means to form fouled samples with well-defined deposits, as the composition and the structure of the fouling formed in industrial processes can vary greatly. Often, it is also difficult to obtain fouled samples from processes. Furthermore, because fouling is a slow process, the formation of fouling within a reasonable period of time may also pose a problem. This can be resolved using the method described in this paper whereby the temperature of the sample is increased using external heating. Increasing the temperature raises the fouling rate.

The current density and/or potential used for electrochemical cleaning is chosen based on the corrosion behavior of the material in the cleaning solution. When cleaning titanium, the effect of cathodic current is essential, whereas the stainless steels are cleaned mainly with anodic current.

When both electrodes in an electrochemical cleaning cell are titanium with a dense TiO_2/SiO_2 deposition, the cleaning without corrosion should be done in 10 w-% sulphuric acid with 1000 ppm citric acid at 60 °C for 5 min. The most effective method used pulse current with a 30-s anodic and cathodic pulse and anodic potential of +3 V vs. SCE and cathodic -0,8 V vs. SCE.

Cleaning of stainless steel with SiO_2 containing $CaCO_3$ deposit could be carried out more effectively in a NaOH solution than in an acidic solution. However, a completely clean surface was not possible to obtain without heating the sample to about 700 °C before electrochemical cleaning. Heating of the heat exchanger plates may cause plastic deformation, which should be investigated before possibly applying this method to entire plates.

Prevention of fouling using an electrochemical method

The factors affecting the electrochemical fouling prevention method can be estimated using the same methods as those used in planning the cathodic and anodic corrosion protection systems. The most important factors to be considered are the type and structure of the heat exchanger and the solution. The conditions necessary for fouling prevention are that both electrodes should be situated near enough to each other in the same solution of sufficiently high conductivity. The geometry and heat transfer area of the heat exchanger are also essential factors.

The method has been investigated in this research using small (2 x 3 cm) plate samples and a laboratory one tube (20 cm) heat exchanger. However, implementing this method on an industrial scale still requires further investigation.

In TiO_2 solutions containing sulphuric acid, the formation of fouling can be prevented effectively by applying a pulse current with anodic polarization of 2 V vs. SCE for 24 h together with cathodic polarization of - 0.7 - - 0.8V and 2–3 min. Surfaces remained clean for at least 11 days at a temperature of 90 °C. Using only anodic polarization decreases the fouling rate, though some deposit will form, whereas excessive cathodic polarization will increase the corrosion rate of titanium.

It was not possible to prevent fouling in a carbonate solution using a laboratory tube heat exchanger. This was due to the excessively slow flow rate of the solution, which causes fast bulk precipitation of calcium carbonate.

On an industrial scale, utilizing the method for tube heat exchangers would obviously be too expensive, since each tube would require the installation of an electrode.

CONCLUSIONS

1. A electrochemical method has been developed that could be used to clean heat exchangers plates discarded due to excess inorganic fouling.
2. Cleaning could be carried out in a sulphuric acid base process solution, as well as in pure sulphuric acid solution. The cleaning efficiency was increased by adding citric acid.
3. Pulsating current improves the cleaning procedure compared to cleaning using only cathodic current.
4. Cathodic current is essentially important for cleaning titanium. Cleaning is partly based on the formation of hydrogen on the surface. This also limits the

application of the electrochemical cleaning method, as the corrosion rate of titanium increases with decreasing potential. Moreover, the risk of hydrogen embrittlement should be investigated before the method can be taken into use.

5. Formation of fouling could be prevented using pulse current. The current densities needed for prevention are clearly lower than those for electrochemical cleaning.

6. When the fouled heat exchanger plates are cleaned using process solution, the cleaning solution and possibly also the deposits can be returned to the process. This gives a great benefit compared to the conventional acid cleaning.

7. The power source increases the investment costs of the cleaning equipment but the operating costs will be lowered, because the cleaning rate increases.

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