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15 Years of Operating Experiences with Thick Nickel Plating
Electrolytic Nickel Coated Tubes in Waste Incineration Plants
– Protection against Corrosion –

Jörg Eckardt

Depending on the mode of operation of the plant, some parts of the waste incineration plants faces corrosion problems resulting in wear rates of more than one millimetre a year on the flue gas side. The reasons for this vary considerably. Whereas below a temperature of around 370 °C the corrosion is mainly due to melted chlorides, above approximately 400 °C corrosion is due to HCl (*active corrosion*) and melted sulphates (500 to 600 °C) comes into operation. Depending on the process steam temperature, the corrosion rates apparently tend to increase at higher temperatures.

It is not only in recent years that there is high-temperature corrosion. Whereas in the early years of waste incineration the corrosion rates were relatively acceptable, currently the increasingly aggressive incineration products such as HCl have led to very much greater damage. This damage gives rise to repair costs which, together with the cleaning costs, account for millions within the operation budget of waste to energy plant:

- replacement of material,
- down time,
- cleaning costs,
- cost of fulfilling contracts.

In recent years several firms have attempted, with varying degrees of success, to bring the corrosion problem under control by means of cladding, flame spraying and sintering methods. Originally, predicted ideas of an improvement in service life to around 40,000 hours have not always been materialised.

The use of these methods also showed that they were subject to limitations, not only with regard to the plant-specific operating temperatures. Cladding, and also flame spraying, are processes that display their peculiarities because of the process-induced heating. The cladding process, for example, gives rise to mixtures with the base material. This results in incorporation of iron in the welded material, which may in subsequent operation sustain a chemical process with all its consequent phenomena. Furthermore, both processes are subject to limitations owing to the relatively complicated shapes of the steam generator components.

The general fact, that applying protective coatings offers advantages is not under question any more. The principal factor in this phenomenon, as can be seen from Figure 1, appears to be the nickel [2, 3].

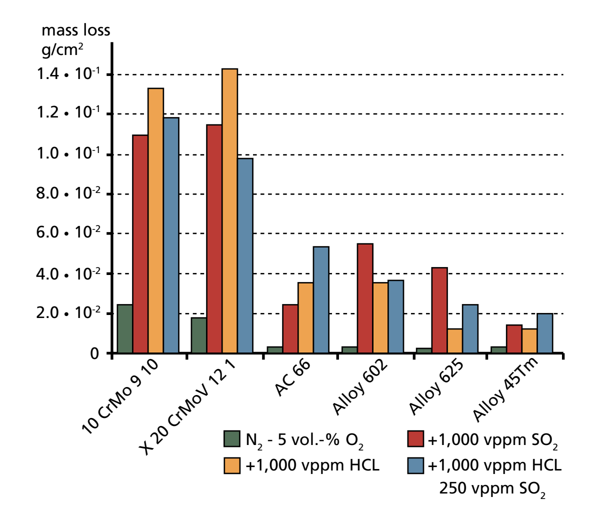

Figure 1:

Comparison of weight loss of steels and nickel base materials in different gas atmospheres under a molten $CaSO_4$-K_2SO_4-Na_2SO_4-$PbSO_4$-$ZnSO_4$ mixture at 600 °C after 360 hours exposure

Source: Spiegel, M.: Materials and Corrosion, 2000

1. Historical development [2, 3]

In the light of this consideration, the various manufacturing processes have been reviewed with regards to economic aspects and the possible influence of the corrosion mechanisms acting especially in waste to energy plants.

Special attention was devoted to the following criteria:

- anticorrosive properties,
- preventing access of chloride to the base material by applying pure non-porous layers without mixing,
- relatively tension-free application,

- good adhesion,
- possibility of applying thick coatings,
- application of coatings that also withstand abrasive wear,
- use for complicated shapes.

In the year 2000 tests have been started within the Rugenberger Damm waste to energy plant. At first, we built in eight tubes in an area which had in the past proved to be particularly prone to corrosion.

- four tubes with pure nickel plating,
- four tubes with a Ni-Co-Si-carbide coating which had exhibited good properties elsewhere with regard to abrasion resistance at high temperatures.

After some three months' of operation, the superheater areas was inspected for the first time and it was found that the tubes were clean and free from crest formation. No tube wall thickness reduction could be detected.

After eight months' of operation, the experimental area was examined again. The nickel-plated tubes still stood out clearly from the neighbouring steel tubes because they were so clean, but the nickel-plating in the region of the incident airstream had been almost entirely worn away. Tubes with NiCoSi plating showed in some places breaks within the coating. Crests were formed following the failure of the coating, in evidence of the influence of iron on the formation of ash deposits on the tubes.

2. Assessment of ash analyses [2, 3]

Samples of the ash deposits from the

- crests,
- direct from the adjacent steel tube of the superheater,
- direct from the pure nickel layer and
- direct from the surface of the dispersion-coated NiCoSi tube

were analysed with a scanning electron microscope. The results were extremely interesting.

From the crest

The deposits at a distance from the surface of the tube contain mainly heavy metals in combination with sulphur, as other studies have also shown. In this region, the proportion of chloride compounds is relatively low.

Direct from steel tube

In the products measured directly at the steel tube, the iron and chloride components are predominant in the cumulative analysis.

Direct from the electrolytic coating

The products on the nickel-coated surfaces are similar. Here, the entire spectrum of elements in this boundary layer region is determined (except for oxygen, which is not covered by the analysis). K, Ca, Pb, Zn in conjunction with S and Cl, plus Ni and Co in the case of the NiCoSi-coated tube. It is striking to note that Cl is present, and probably exists in the form of metallic chlorides. Elsewhere ($T_{Gas} \approx 460$ °C $T_{Medium} \approx 310$ °C) no Cl was detected; instead the dominant compound was NiS, probably as millerite.

Assessment

The chemical corrosion processes that take place on the steel tubes during operation are relatively complex, and their details are certainly even not yet clarified entirely. However, the reaction processes of chloride-induced corrosion due to HCl gas can be explained in simplified form as follows:

During operation an oxide coating forms on the tubes. Chloride diffuses through this and forms a ferrous chloride layer as a reaction compound of the gas atmosphere with the iron. It is certain, that the melting point of $FeCl_2$ is around 676 °C. In conjunction with alkali chlorides and heavy metal chlorides it is conceivable that a eutectic mixture forms at temperatures below 400 °C. It was assumed, that at certain temperatures the compound forms a dough-like eutectic paste surrounding the tubes, thereby providing the particulate components in the gas atmosphere with a point of attack that allows them to adhere firmly. In the case of nickel, the thermodynamics for the formation of $NiCl_2$ are rather less favourable than for iron, which may mean that no $NiCl_2$ is formed and hence no molten salt. The formation of molten salts of alkali metals and heavy metals will undoubtedly remain possible, but here there is probably a different bonding mechanism at work, which given a marked gas current in the steam generator results in the suppression or reduction of ash deposits.

At the same time, depending on the temperature, either a molten salt mixture of chlorides and sulphates is formed which permits continuous exchange between the surrounding gas atmosphere and the species contained in it (O_2, NH_3, HCl SO_2 etc.), or there is an exchange between the adhering particles and the layers. Here, iron has a very marked affinity with chloride. At temperatures above 400°C this combination gives rise to the familiar chloride corrosion. The intensity of this mechanism depends very strongly on the temperature and partial oxygen pressure.

It could be determined that the proportion of Cl displays a marked drop here, especially in the case of pure nickel. Subsequent studies revealed that Cl could no longer be detected at all.

One cannot rule out the possibility that a protective nickel oxide layer forms below the emerging sulphate layer ($T_{Gas} \approx 560$ °C, $T_{Medium} \approx 390$ °C). Since the usual surrounding substance transport is interrupted, there is no formation of a pasty eutectic mixture to provide the adhesion mechanism for particulate material. It has been found elsewhere that millerite, a nickel sulphide, is probably formed directly at the coating in a certain temperature field ($T_{Gas} \approx 460$ °C, $T_{Medium} \approx 310$ °C). The lack of Cl in these boundary layer areas also points to the interruption of substance transport, especially since one cannot expect any evaporation of $NiCl_2$ at the medium temperature in question.

It was interesting to note that the particles on the steel tubes were adhering very firmly and were file hard and displayed pozzolanic bonding, whereas the products on the nickel tubes were easy to remove and had to be treated with great care when preparing samples, as these crumbled easily.

3. Result analyses [2, 3]

The results from of the first tests in the years 2000 up to 2002 were promising and abrasion were found on nickel-plated tubes resulting mainly from sootblowers but not from corrosion. Therefore, we decided to continue our tests with pure nickel plated tubes only and left all other possibilities a side since the pure nickel coated tubes appeared to perform best.

The explanation of the tube wall abrasion is relatively simple. As already mentioned, a nickel oxide of very hard and brittle consistency is formed on the nickel layer. This property appears to reach its limits under the present conditions, as it does not stand up well to the mechanical strains. In the course of the constant cleaning processes, the emerging layer actually breaks away from the base material and thereby results in a steady reduction in wall thickness.

Amazing results could be seen in the Rugenberger Damm waste incineration plant on tube samples that had been in operation for about 15 months. The influence of the sootblower in the 6 o'clock position was clearly recognisable. Around the circumference of the tube, however, it was not possible to detect any tube wall abrasion. Here the NiCoSi coated tubes did not behave differently from those coated with pure nickel.

A fortunate chance in the subsequent investigations led to the approach to understand the mechanism and action of the corrosion that takes place in the temperature spectrum between 300 and 600 °C.

Results from the Stellinger Moor plant (horizontal operation, $T_{Flue\ gas} \approx 850$ °C, $T_{Medium} \approx 410$ °C) yielded findings that suggest even better performance of nickel-coated tubes if specific parameters are complied with during coating or if alloy components are deposited. No wear could be detected in these tubes. Only in the region of the sootblower was abrasion amounting to a few tenths detected after one year's operation.

4. Principle of galvanic nickel plating process [1]

Electroplating is an electrolysis with the aim to apply a metal layer on metals or other conductive materials. The more noble metal layer protects the less noble metal against oxidation and corrosion.

During the galvanic nickel plating process, electrical current is conducted through an electrolytic bath. At the positive pole (anode) (A) is the metal (nickel) that is to be applied.

At the negative pole (cathode) is the object to be coated (B). The electrical current removes metal ions off the electrode of consumption and deposits them on the material by reduction. This way, the object to be refined is evenly coated with nickel on all sides.

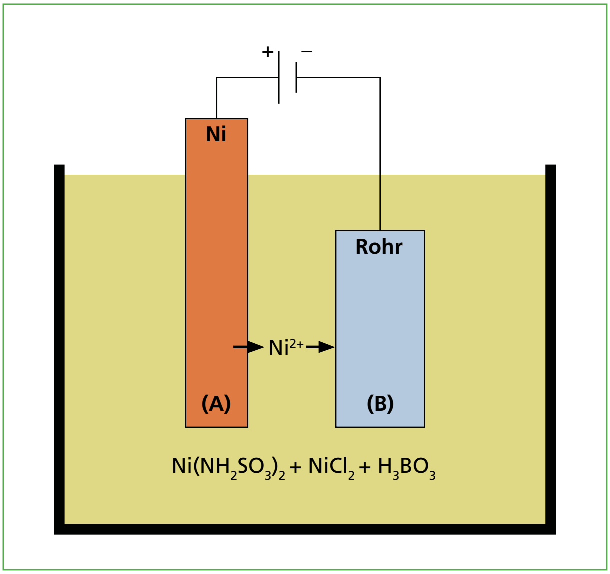

Figure: 2:

Diagram of galvanic nickel plating

5. After 15 years

Due continues efforts and improvements, today thick nickel plate coating is a well know alternative to other corrosion measures and long term experiences exist. It is a proven fact that our assumptions from the early days are correct.

At the Rugenberger Damm plant, more than 120,000 operating hours with nickel-plated tubes are accumulated, still today, we do not detect any reduction in wall thickness.

Figure 3: Latest quality of nickel layer

The process for manufacturing the nickel-plated tube has been advanced continuously and the quality improvement is amazing. Today, we can control thickness of the nickel layer and surface quality to an outstanding high level (Figure 3).

Typical application for our patented thick nickel plating are superheater and evaporator tubes within waste to energy plants.(Figure 4)

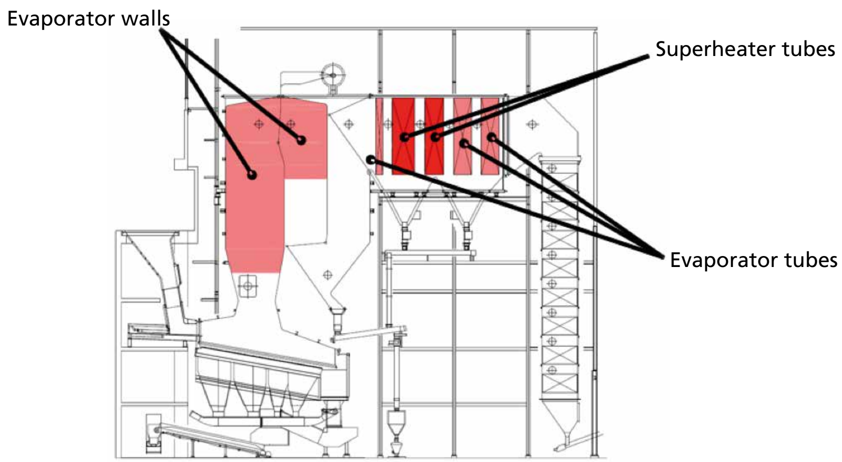

Figure 4: Typical application

6. References

A number of waste to energy plants have been equipped with thick-nickel-plating since the first tests early 2002 has been undertaken.

Starting originally with a waste to energy plant in the city of Hamburg, today, we have a significant distribution all over Germany including also a plant in Belgium and one in the Netherlands.

- MVR Müllverwertung Hamburg (420 °C, 45 bar), Rugenberger Damm
- EBS Kraftwerk Romonta/unit 5 (400 °C, 40 bar), Amsdorf, Chausseestraße
- EEW Energy from Waste/MHKW Pirmasen, (400 °C, 40 bar), Staffelberg
- GfA Gesellschaft für Abfallbeseitigung/MHKW Iserlohn (400 °C, 40 bar), Iserlohn, Giesestraße
- Weener Energie, EBS Kraftwerk (320 °C, 26 bar), Weener – Industriestraße
- Biostoom Oostende (400 °C, 40 bar), Fortsstraat, Belgium
- Gemeinschaftskraftwerk Schweinfurt/unit 11, (435 °C, 65 bar) Schweinfurt – Hafenstraße
- MHKW Frankfurt Nordweststadt/unit 13 (500 °C, 59 bar) Frankfurt – Heddernheimer Landstrasse

- Sleco, Slib en Co verwerkingscentrale NV/unit 2 (400 °C, 41 bar), Beveren – Doel, The Netherlands
- Spreerecycling GmbH & Co.KG (400 °C, 40 bar), Spremberg

7. Conclusion

Pioneering and forward thinking can create outstanding solutions but it needs joint efforts, hand in hand with manufacturer and plant operator, to achieve trust in new technologies. 15 years of operating experiences proves that long service life for corrosion-affected materials can be achieved by nickel coating.

The initially stated theoretical reasons for a galvanic thick nickel plating, like

- corrosion protective quality,
- well-adherent connection,
- smooth surface,
- free of pores coating,
- easy to process (for example bend or weld),
- no thermal stress to the tubes by manufacturing process, could be proved in long-term operation.

It must be admitted, that this nickel-plating is not suitable in the impact area of soot blowers.

Operation experiences ranges from 120,000 operating hours for evaporator tubes (45 bar) to 65,000 operation hours for super heater tubes (400 °C, 40 bar) without significant corrosion wear.

We will not stop here. New areas will be explored were nickel plating can contribute to better plant economics and longer life of the equipment.

We expect a new level of results from the MHKW Frankfurt plant which is operating with 500 °C high pressure steam temperature. We hope, to present some results during the verbal presentation since they are not yet available.

8. Sources

[1] Baumgarte Boilers Systems GmbH, product presentation thick-nickel-plating; 01/2017

[2] Publication Ansey, Dr. Zwahr, VGB Power Tech.; 12/2002

[3] Publication Ansey, VGB Power Tech.; 06/2003

[4] Spiegel, M.: Materials and Corrosion, 2000

Bibliografische Information der Deutschen Nationalbibliothek

Die Deutsche Nationalbibliothek verzeichnet diese Publikation in der Deutschen Nationalbibliografie; detaillierte bibliografische Daten sind im Internet über http://dnb.dnb.de abrufbar

Thomé-Kozmiensky, K. J.; Thiel, S.; Thomé-Kozmiensky, E.;
Winter, F.; Juchelková, D. (Eds.): **Waste Management, Volume 7**
– Waste-to-Energy –

ISBN 978-3-944310-37-4 TK Verlag Karl Thomé-Kozmiensky

Publisher: TK Verlag Karl Thomé-Kozmiensky • Neuruppin 2017
Editorial office: Dr.-Ing. Stephanie Thiel, Elisabeth Thomé-Kozmiensky, M. Sc.
Janin Burbott-Seidel and Claudia Naumann-Deppe
Layout: Sandra Peters, Anne Kuhlo, Ginette Teske, Claudia Naumann-Deppe,
Janin Burbott-Seidel, Gabi Spiegel and Cordula Müller
Printing: Universal Medien GmbH, Munich