Application of Modified NiCrMo Alloy Systems for Boiler Tube Surface Protection in Waste-to-Energy Environments

Iain Hall, Kwang Han and Triratna Shrestha

1. Background 237

2. Weld overlay 238

3. Thermal spray coatings in waste-to-energy units 239

3.1. Historical experience 239

3.2. Coating development 240

4. Conclusion 245

5. References 246

Internationally, Waste to Energy and Incineration markets continue to grow in capacity as fossil fueled facilities decline and nuclear generation is curtailed. With this comes a greater need to burn more corrosive materials combust at higher temperatures and extract more energy. The reliability burden that this places on operators of plants is re-opening opportunities for thermal spray solutions as a cost effective solution for boiler tube protection. Where maintenance costs, opportunity costs and access restrictions may preclude alternative in-situ technologies, thermal spray technology may fill a gap in providing new reliable and flexible process and materials technologies for both mid- and long-term protection of water wall and superheater tubes. While historically thermal spray coating solutions have had a spotty record in waste to energy environments, advances in both process and materials technology specifically for WTE environments is such that coating performance now approaches the performance of high alloy wrought materials. This is verified through accurate laboratory modeling and scale tests and trials conducted by OEM's and plants.

1. Background

The need for incineration capacity for waste materials, whether from municipal solid waste or from industrial waste requirements has increased as a result of zero landfill and progressive recycling policies. For many European and Japanese markets waste incineration is the only viable alternative to previous methods of waste disposal. The European Union Landfill Directive (1999/31/EC) specifically precludes certain materials such as hospital waste, tires, and certain reactive and flammable materials from land filling, [4].

The European directive required over 50 percent diversion of all municipal waste from landfill by 2013. Further revisions proposed in 2014 have extended this to completely phasing out landfill of recyclables and hazardous waste by 2025. Today, more than 2,200 WtE plants are active worldwide with a disposal capacity of around 280 million tons of waste per year. More than 250 thermal treatment plants with a capacity of nearly 60 million annual tons were constructed between 2010 and 2014. Almost 550 new plants with a capacity of about 150 million annual tons are estimated to be constructed by 2024. Existing plants need to be modified and made more efficient [5].

The presence of highly corrosive elements in these waste fuels such as Cl, S, Na, Zn, Pb, Al when taken in combination with free H_2O and oxidizing conditions can lead to rapid corrosion of boiler tube waterwalls and superheater tubes. In order to minimize the extent of this wastage, and in doing so increase plant reliability, plant operators will conservatively maintain maximum steam conditions at 400 °C (752 °F) and 40bar(580psi.). Increased demands for energy efficiency and emission regulations [3] requiring a 2 second maintained temperature of 850 °C, or 1100 °C in the case of halogenated organic substances, further exacerbate tube wastage conditions.

One of the primary methods of increasing reliability and the operational window of waste to energy (WTE) plants is application of corrosion resistant surface engineering technologies. Principle techniques employed are refractory lining, replacement of tubes with Ni alloys, weld overlay and thermal spray coatings.

2. Weld overlay

The use of refractory lining reduces the effectiveness of heat transfer surfaces and as such, has limited scope. Weld overlay technologies have been applied extensively with Alloy 625 being the most commonly specified material. Exhaustive testing of this material under high temperature gaseous and ash covered corrosion conditions has yielded positive results for the wrought alloy [1].

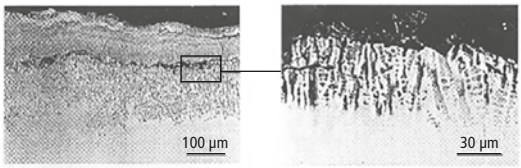

Figure 1:

Corrosive attack of dendrites by oxygen and metal chlorides

Source: Spiegel, M.: Korrosionsarten und Korrosionsmechanismen in Müllverbrennungsanlagen. Max Planck Institute: Improving Waste Incineration Performance Conference, Stuttgart, 1999

Field applications, although largely successful, have not always been as reliable because of high iron dilution with slow weld pool cooling. This results in the formation of dendritic structures that extend into this iron rich region. This, in combination with carbon absorption from the carbon steel tube material, forms corrosion sensitive carbides, which render the material sensitive to localized corrosion (Figure 1) under the influence of salt melts [2, 6, 11]. Further limitations for the weld overlay process are

the relatively slow and expensive deposition rate as well as the difficulty of automation on ceilings and in corners. It is also not well suited for in-situ application on single superheater tubes.

Thermal spray coatings are increasingly employed in WTE units as they overcome some of these problems. The technology is well suited to in-situ out of position application, with faster coverage rates reducing both material and opportunity costs. [5] As thermal spray is a metallurgically cold process, with little heating of the substrate, no dilution of the base metal occurs and little to no distortion takes place.

3. Thermal spray coatings in waste-to-energy units

3.1. Historical experience

Thermal spray as a technology in highly corrosive applications, such as WTE, has had a checkered history. The reasons for this are as a result of a.) material and process, and b.) application technique. Problems arising from the latter are common to both overlay and thermal spray, e.g. inadequate surface preparation. Analysis of early failures has shown the primary cause to be substrate corrosion and subsequent spalling.

Figure 2, below, is illustrative in gaining an understanding of the mechanisms driving corrosive attack in this application [9].

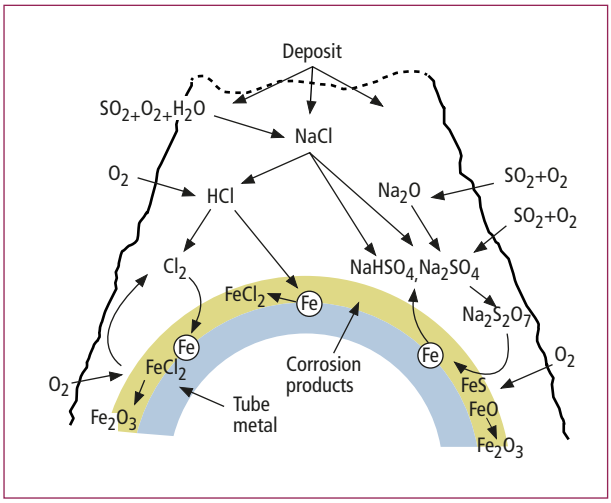

Figure 2:

Corrosion mechanisms at work in salt/ash deposit on boiler tube

It can be seen that the primary corrosion mechanisms are the Chlorination/Oxidation or Sulfidation of Fe with Cl or S provided by salts in the ash. Although this tube may be operating at 400 °C, it is possible, given the thermal gradient through the deposit, for the surface temperatures to be testing of this material under high temperature gaseous and significantly higher. This enables the formation of any number ash covered corrosion conditions has yielded positive results of salt smelt eutectics, having low melting points, in the for the wrought alloy [1]. deposit. Some of these are listed in Table 1.

Table 1: Salt eutectics melting temperature

Eutectic Weight %	Melting Point °C
$ZnCl_2$	318
$PbCl_2$	498
48 $ZnCl_2$ – 52 KCl	250
82 $ZnCl_2$ – 18 KCl	262
84 $ZnCl_2$ – 16 KCl	262
73 $ZnCl_2$ – 27 $PbCl_2$	300
31 NaCl – 69 $PbCl_2$	410
21 KCl – 79 $PbCl_2$	411
17 NaCl – 83 $PbCl_2$	415
39 $ZnCl_2$ – 50 KCl – 11 $PbCl_2$	275
35 $ZnCl_2$ – 48 NaCl – 17 $PbCl_2$	350
16 NaCl – 40 KCl – 44 $PbCl_2$	400
K_2SO_4 – Na_2SO_4 – $ZnSO_4$	384
KCl – $ZnCl_2$ – K_2SO_4 – $ZnSO_4$	292
K_2SO_4 – Na_2SO_4 – $CaSO_4$	776

Although some of the eutectic Chlorine salts can melt at low temperature allowing hot corrosion to take place, Chlorine can accelerate oxidation rates even when present in the vapor phase. Cl_2 gas, HCl gas or NaCl vapor.[8]

In high sulfur environments Sulfur permeation with substrate Iron Sulfidation can be seen to occur, however it is generally found that both mechanisms are mutually exclusive.

Coating chips were analyzed from several European WTE units, Linkoping Power Plant, Mullverbrennungsanlage der Stadt Solingen, WTE Stadwerke Dusseldorf and Berliner Stadtreinigung Berlin, [12, 13, 14, 15]. This analysis showed that in the presence of both Sulfur and Chlorine containing environments, Chlorine is the most pervasive, penetrating through interlinked porosity in the coating and accumulating at the coating/substrate interface in the form of $FeCl_2$. This was determined through Energy Dispersive Spectroscopy (EDS) mapping of tube/coating sections. This reaction and subsequent oxidation at the coating substrate interface causes coating separation.

No coating failure has been determined from wastage of the coating material itself, inevitably porous coating materials have been susceptible to permeation and substrate attack.

3.2. Coating development

Initial coating applications in the US were largely unsuccessful as early arc–spray coatings failed rapidly through substrate attack and coating spalls. Having determined that the primary mode of failure experienced in prior WTE coating applications resulted from permeation, attention was directed to the development of process and materials used in a thermal spray system. Alloy 625 is known to present sufficient corrosion resistance to the process and as such has been selected as the bench mark material for optimization. Two systems are most widely used for in-situ thermal spray applications:

1. The **Wire Arc-Spray** process, whereby metal wire, typically 0.063 mils in diameter, wound on two spools, is fed from two spools by a wire drive system into a gun. A DC Voltage potential is created across these two wires and as they intersect, an arc is struck between them, which melts the wire tips. A stream of air directed across this intersection point strips molten metal droplets from the wire tips, these fly towards the substrate, impact, form a splat and freeze. The Arc Spray processes are further differentiated into High Velocity arc (HVAS) processes and conventional, standard, twin wire or Low Velocity arc processes (TWAS). See Figures 3 and 4 for micrographs of Alloy 625 coatings sprayed with different systems.

2. The **HVOF** process whereby metal powder feedstock is fed into a High Velocity Oxy-Fuel gun. Internal combustion of the gases generates high temperature combustion products. Powder is continuously injected into this area from the rear of the gun and is heated to a plastic condition. The combustion product gas stream exits the nozzle and propels the powder particles out of the gun. On impact with the substrate, the particles form flat *splats* and freeze instantaneously. Subsequent particles are deposited similarly and the coating thickness is built up until it meets a specified thickness.

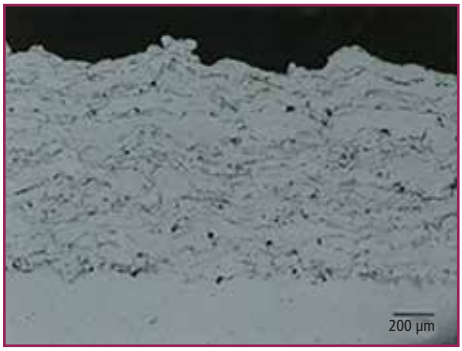

Figure 3: Micrograph of conventional *Twin Wire Arc Spray* (TWAS) process

Figure 4: Micrograph of *High Velocity Arc Spray* (HVAS) process

Process refinement – Wire Spray Technology

By changing the design and process characteristics of the thermal spray torch the splat morphology can be characterized at any point between these two positions, by changing the stripping angle and power density of the air stream at the point where the wires intersect. Figure 5 below shows this effect.

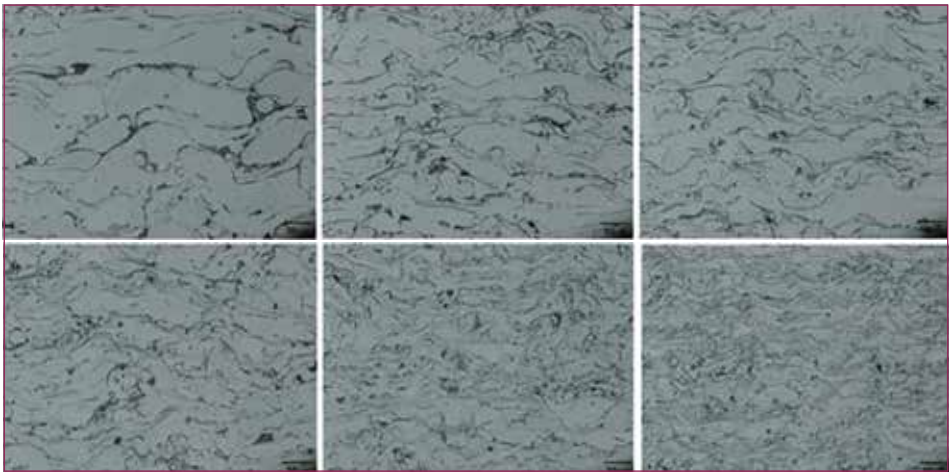

Figure 5: Coating quality change with process modification (micrographs at same magnification)

As has been shown, within a given system having a single material feedstock, there may be great variability in the structure of a coating. In order to determine the effectiveness of a given coating against a permeable corrosive species, electro-chemical testing was undertaken as a way of quantifying the corrosion rate of one material relative to another. To calibrate the test equipment for these experiments the potentiostat was tested using the standard reference test method designated in the ASTM G5 standard.

Tafel analysis was used for determining corrosion rate measurements from the potentiodynamic test set. This technique was used to obtain a corrosion rate value for the various coatings in an aqueous NaCl solution of 0.1N HCl. The cell current was measured during a slow sweep of the potential from -200mV to +200mV relative to EOC (open circuit potential). The scan rate used was 1mV/sec with a sample period of 2 seconds. A fit of the data to a standard model obtained an estimate of ICORR (corrosion current density) which was used to calculate a corrosion rate. All of the calculations used a density of 7.87 g/cm^3 and an equivalent weight of 27.92. The test cell measures the activity of the substrate material through the coating. As all materials evaluated in this test sequence were Alloy 625 type materials, a representative sample of Alloy 625 plate was also evaluated to determine the degree of activity of the material itself. It is important to note that the corrosion rate values are sensitive, and comparable with each other, but do not represent the actual corrosion rates expected in a boiler, due to differing electrolyte concentration and temperature.

The TWAS arc and HVAS arc coatings were evaluated for varying thicknesses. Wire spray systems generally form coatings with thin interlaminar bands of oxide material. This interlaminar oxide forms as a result of inflight oxidation of the particle. As the particles need to be fully molten in order to separate from the wire and are heated in the arc on separation, they have a high oxidation potential. Measurement of the oxide film composition by EDS shows them to be predominantly Chromium Oxide. These oxide bands are occasionally spongy and fractured and as such represent a potential conduit for corrosive media. This also leaves Chromium depleted, Nickel rich, areas

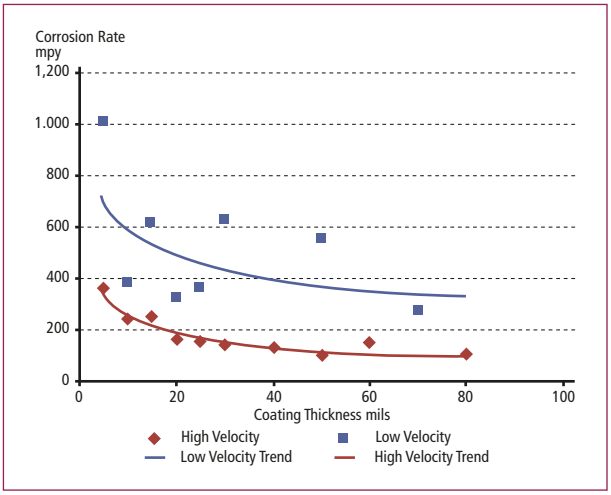

Figure 6:

Corrosion rate versus coating thickness for high and low velocity systems

adjacent to the oxide films, which are susceptible to corrosion. Figure 6 shows the corrosion rate dependence on coating thickness for the high and low velocity end of the range. The scatter apparent for the low velocity readings is likely due to the large splat size and statistical likelihood of interconnected porosity through to substrate, as well as thicker oxide structures which are more conducive to ion transport. It is apparent, from the high corrosion rates in these service conditions that little to no protection is offered for the conventional process. The high velocity system is better behaved as the finer splat size and greater number of particles between the coating surface and substrate significantly reduce the degree of interconnected porosity.

The process mechanism driving splat refinement can be seen in Figure 7, where the total air power (not velocity) available to strip molten material from the wire tip is seen to reduce the corrosion rate.

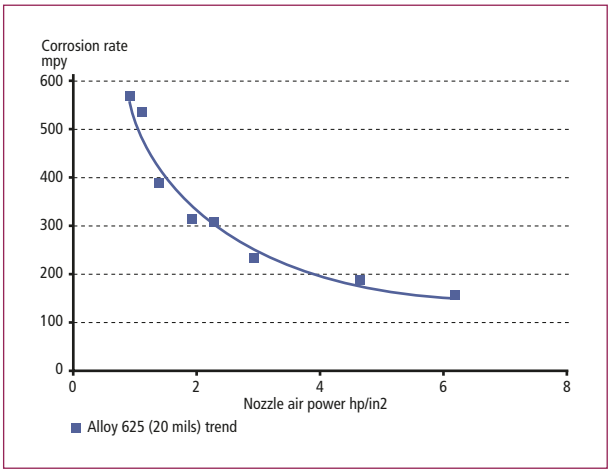

Figure 7:

Corrosion rate versus nozzle air power

Improvements in air flow control through wire spray units have given rise to an approximately four-fold decrease in permeability. Of greater significance is the fact that the behavior of the coating in a corrosive environment is more predictable, and less susceptible to the anomalies present in traditional arc systems. This improvement is corroborated by the good performance of this material in less corrosive areas of WTE units.

Process and material refinement – powder feedstock technology

Optimization of HVOF systems is conducted routinely by adjusting and calibrating new gas flow parameters to ensure optimum deposit efficiency. This is broadly indicative of good coating quality. However, the biggest advances in corrosion performance with these materials has come about as a result of the flexibility that exists with powders for tweaking the composition of standard alloys to define better microstructure, bond strength, and in some cases, erosion properties as well. This development can happen at a faster pace due to the shorter lead times and batch sizes required in the supply of new powder materials.

Figure 8 represents the corrosion data from two Alloy 625 coatings. These have been modified by a few percentage points in terms of nominal composition, but as can be seen for the IGS 2025 material, a modified NiCrMoNbXX system, the difference in performance is remarkable. At a thickness of 12 to 15 mils this material yields a corrosion rate of 1.5 mpy, which is almost negligible when compared to the corrosion rate in excess of 600 mpy for conventionally applied arc spray materials. An earlier NiCrMoNb material, IGS 2100CB is a material that has already seen substantial service in tyre burning and electronics copper recycling incinerators.

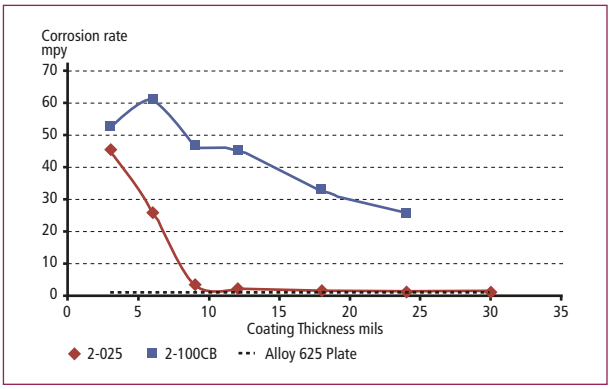

Figure 8:

Corrosion resistance of HVOF alloy 625 type materials

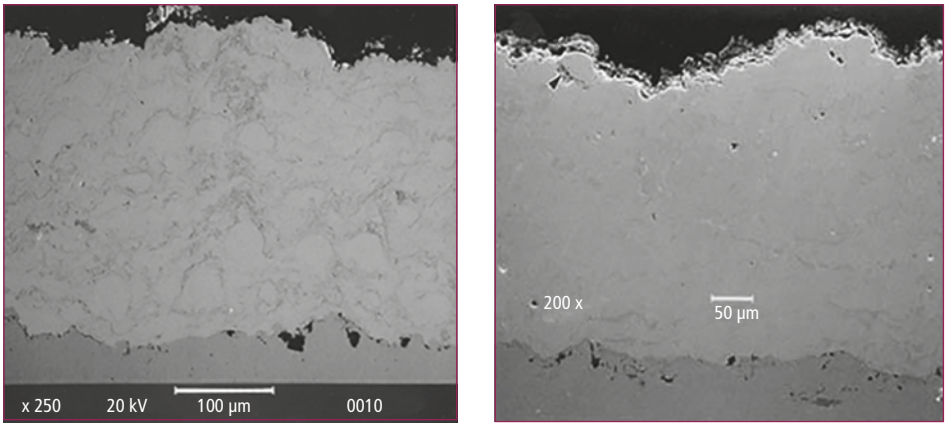

Figure 9: Alloy 625 as sprayed and modified alloy 625 HVOF coating in post exposure condition

To simulate high temperature corrosive conditions, several sections of coating were inserted into an autoclave with NaCl, KCl and ash mixed into a wet paste and applied to the coupon. After a period at elevated temperature (550 °C), the coupons were allowed to cool before being sectioned for microscopic evaluation. Figure 9 shows coatings in pre- and post-test condition.

Corrosion tests were also conducted by Babcock Hitachi KK. An autoclave was used with metered SO_2. HCl, CO_2, N_2 and H_20 gas flows. $NaSO_3$, K_2SO_4, NaCl, KCl and ash

at 550 °C were used to test the modified NiCrMoNb and NiCrMoXX materials against Alloy 625 and 2.25Cr1Mo alloy in the autoclave. The results are presented below [7].

Table 2: Data from simulated waste-to-energy high temperature corrosion tests

Material	Corrosion Loss um
IGS 2025	16
IGS 1027	60
Alloy 625	27
2.25Cr1Mo	586

Although exceptional performance can be achieved with this powder based process, one limitation of HVOF coatings is that parameteric control and surface finish requirements need to be exacting to obtain the desired result. Additionally, HVOF coatings have a higher internal stress state. This condition poses two limitations for field application. Firstly, thickness controls of the coating require a fairly tight band between the minimum coating thickness required to obtain corrosion mitigation, and the maximum tolerable thickness before internal coating stress states overcome the bond strength, and risk coating fracture. This has an impact on reparability and tie ins between adjacent coating areas.

Material refinement – HVAS wire feed systems

The last evolution in attaining high performance high alloy metal coating of surfaces for aggressive service conditions was obtained by combining the microstructural improvements associated with the high velocity wire feedstock (HVAS) coating and the lessons learned in material modification with powder based HVOF.

A number of high performance NiCrMoXX alloys exist, with demonstrated wrought alloy corrosion resistance. The challenge in obtaining the same performance out the sprayed coating from the material pertains to the weaknesses introduced due to the spraying process. A novel technology has been developed for alloy modification of the wire feedstock to desensitize the spray droplets to material degradation and to reduce coating stress. A further benefit is the introduction of hard phases when required to provide ancillary erosion resistance. The structural considerations of the feedstock are tuned for the HVAS process to ensure a fine homogenous distribution of coating chemistry. It is known, that broadly speaking, the corrosion resistance of an alloy correlates with a PREN number that is calculated as PREN = 1 x %Cr + 3.3 (%Mo + 0.5 x %W) + 16 x %N. Inconel alloy 625 and Hastelloy alloy C-276 alloys both have high PREN numbers in the range of 46.4 – 56.0 and 64.0 – 73.8 respectively. The modified wire thermal spray material, IGS 5470, coupled with the HVAS process technology produces a dense, low stress coating with a PREN of 80. In a recent 400C, controlled environment with H_2O and KCl/ZnCl salt cake, no coating or substrate degradation was determined.

4. Conclusion

As increasing demand for waste incineration capacity and higher emission control legislation comes into play in US, European and Japanese markets, there is an escalating need for a medium term, low opportunity cost solution to improve plant reliability.

Thermal spray solutions have progressed considerably from earlier days when the technology was insufficiently developed to provide a reliable solution. Developments in modern materials and process understanding have led to the development of alloys tailored for thermal spray application that can now produce corrosion resistances matching those of the wrought alloy. This alloy/process development has enabled the delivery of NiCrMoXX coatings with higher native corrosion resistance both in terms of microstructure and chemistry, and as importantly, with application tolerances required for successful field in-situ application, inspection and maintenance. These results have been verified through extensive in-house testing, independent OEM test bed qualification, and good results from recent inspections of installed systems.

5. References

[1] Baker, B.; Farr, N.: Corrosion resistant Features of High nickel Alloys in Relation to Waste Incineration Applications. Special Metals, Improving Waste Incineration Performance Conference, Stuttgart, 1999

[2] Baker, B.; Kiser, S.; Webster; Cooper, C.: Welding Products for Extension of Waterwall and Superheater Tubing Life in Waste-to-Energy Plants. INCO Alloys International, Improving Waste Incineration Performance Conference. Stuttgart, 1999, p. 3

[3] Directive 2000/76/EC of the European Parliament and of the Council of 4 December 2000 on the incineration of waste, p. 11

[4] EU Council Directive (1999/31/EC) on the landfill of waste, Office for Official Publications of the European communities, pp. 1-19

[5] Fordham, R.J.; Baxter, D.; Hunter, C.; Malkow, T.: The impact of increasing demand for efficiency and reliability on the performance of waste-to-energy plants. In: Materials at High Temperatures 20(1), pp. 19-25

[6] Kreuger, J.: Operation experience and future perspectives with degradation at high steam parameters in WTE-plants. Materials at High Temperatures 20(2), 2003, pp. 185-193

[7] Kure Research Laboratory, Babcock Hitachi K.K.: Corrosion Test Results of Coating Samples made by Metalspray United. June 2003

[8] McNallan, M.J.; Liang, W.; Kim, S.H.; Kang, C.T.: Acceleration of High Temperature Oxidation of Metals by Chlorine. High Temperature Corrosion, NACE 6, 1981, pp. 316-321

[9] Miller, P.D.; Krause, H.H.: Corrosion of carbon and stainless steels in flue gases from municipal incinerators. National Incinerator Conference, American Society of Mechanical Engineers, 1972

[10] Shrestha, T.; Hall, I.S.: Corrosion Mitigation Using Thermal Spray Coating. NACE Corrosion 2014, San Antonio, 2014

[11] Spiegel, M.: Korrosionsarten und Korrosionsmechanismen in Mullverbrennungsanlagen. Max Planck Institute: Improving Waste Incineration Performance Conference, Stuttgart, 1999

[12] Wang, B.; Zheng-Rong S.: Analysis of Coating Chips retrieved from a WTE Plant, Berliner Stadtreinigung, Berlin. Metalspray Technical Report, 2003

[13] Wang, B.; Zheng-Rong, S.: Metallographic examination of two 1-015b coated tube samples of wing wall sections from WTE Plant Dusseldorf. 2001

[14] Zheng-Rong, S.; Verstak, A.: Evaluation of coating chips received from a tire-waste firing boiler. Linkoping Plant, Metalspray Technical Report, 1998

[15] Zheng-Rong, S.; Verstak, A.: Evaluation of coating chips received from WTE Boiler Superheater. Müllverbrennungsanlage der Stadt Solingen, Metalspray Technical Report, 1996

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. (Eds.): **Waste Management, Volume 6**
– Waste-to-Energy –

ISBN 978-3-944310-29-9 TK Verlag Karl Thomé-Kozmiensky

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Publisher: TK Verlag Karl Thomé-Kozmiensky • Neuruppin 2016
Editorial office: Professor Dr.-Ing. habil. Dr. h. c. Karl J. Thomé-Kozmiensky, Dr.-Ing. Stephanie Thiel, M. Sc. Elisabeth Thomé-Kozmiensky, Janin Burbott-Seidel und Claudia Naumann-Deppe
Layout: Sandra Peters, Anne Kuhlo, Janin Burbott-Seidel, Claudia Naumann-Deppe, Ginette Teske, Gabi Spiegel und Cordula Müller
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