REVIEW OF 4 YEARS OF OPERATION WITH AN INCINERATOR-BOILER
OF THE SECOND GENERATION

by

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Introduction

At the ASME National Incinerator Conference of 1972 in New York, a lecture was contributed dealing with the solution of corrosion problems in incinerator plants.

A new unit, the fifth of the Düsseldorf-plant, was presented, which showed promising improvements concerning the existing problems by a change of the furnace configuration from a counter-flow- into a parallel-flow furnace.

This boiler is now in service for 4 years, and the operation experiences of this period are communicated here.

1. Presentation of the unit

The incinerator-boiler discussed, is a 4-pass, high-pressure, superheated steam generator, equipped with a roller grate stoker "System Düsseldorf", with the following parameter:

- steam pressure at superheater outlet - 80 bar (1160 psi)
- steam temperature - 500°C (930°F)
- steam output - 30 metric tons/h (33 U.S. tons/h)
- refuse throughput - 12.5 metric tons/h (13.7 U.S. tons/h)
- calorific value - 8800 kJ/ kg (3800 BTU/lbm)

2. Construction principles

The dominating number of corrosion damages in incinerator plants between 1966 and 1970, affected the boiler parts directly behind the furnace.

On the basis of a number of investigations of these cases, it could be admitted with certainty, that an unfavorable combustion control was one of the main causes for these incidents.

The reason for the nonuniformity of the combustion is given, as everybody knows, by the heterogeneity of the fuel. Hereby incomplete burnt flue gases are produced, and a delayed combustion takes place in the first pass behind the furnace. Under combustion conditions of that kind, the tubes, located in that...
area, are affected by severe corrosions under the influence of HCl, which is formed by the incineration of PVC-waste. Moreover it was proved, that by an extension of the furnace, resp. flue, a satisfactory burn-out of the gases can be achieved. The effect of those measures is indisputable after 10 years of operation. No further corrosions occurred at the tubes following the endangered areas.

In realization of these facts, the former usual counterflow furnace was further developed into a parallel-flow furnace, with the aim of achieving a more intensive and uniform combustion within the combustion chamber, and to give the flue gases adequate long time for the burn-out, before they reach the heat transfer-surfaces.

As escorting measures for this change in design, the refuse feeder was improved, and the manual control of the combustion was changed into an automatic controlled one.

To avoid damages on the convection heating surfaces by the combination of erosion and corrosion, the boiler was partially enlarged to obtain sufficient space between the tubing. With the low gas velocities now achieved, the erosion problems generally are under control.

3. Operation Experiences

a. Furnace facilities

The expectations set into the furnace are fulfilled satisfactory referring to the gas burn-out. Although the tubes of the first gas pass have been not at all protected by ceramic lining, after more than one year of operation not any corrosion attack of the former kind was detected.

Referring to the furnace capacity and the residue burn-out the anticipations came true too. By the type of construction, which forms in the front part of the furnace a true combustion chamber, excellent results could be obtained. It is evident that in the combustion chamber higher temperatures are generated as in the elder units, so that the danger of slagg-ing in the furnace had to be taken into account. Partly this problem was encountered in that way, that the furnace roof and the following fire guiding wall was designed as steam generating water-walls, to carry off, already from the furnace, certain amounts of heat.

For the sidewalls the choice between water-walls and uncooled refractory lining was discussed. Water-walls would have solved the problem of slagging. But these tube surfaces need special care and maintenance. To protect them against
corrosion and erosion they must be concealed with ramming lining, of which the condition must be check in short intervals, and if necessary mended.

An uncooled lining of the sidewalls was chosen too, under consideration that the ignition of refuse with low heating values must be supported. The refractory material, which is most suited on account of its slag repellent property, is SiC. It is on the other hand known, that the use of SiC-materials in furnaces is problematic, when temperatures of 900 - 1010°C (1650°F - 1850°F) are existing, and the flue gas contains a considerable O_2-excess and H_2O. Experiences of American operators communicated to the manufactures of the refractory materials, have been taken into account unsatisfactory only. So, inevitable after 6000 operating hours it came to a total damage of the lining of the front part of the furnace. The furnace was reconstructed with plastic ramming mass on A_2O_3-base. Now the slagging problem came forward again, and during the following operation period several times heavy slag formation occured at the side walls, which made it necessary to shut the boiler down and remove the slag. In order to achieve a further undisturbed operation, the combustion was shifted to the end of the grate. Instead of air, recycled flue gas was injected under the first roll of the grate. Due to the oxygen reduction in the forward combustion chamber, the main combustion zone moved 1 roll downward the grate. Consequently, the burn-out time for the flue gas was shortened, and after an operation time of about one year, the first corrosion on the tube surfaces of the front wall of the first pass occurred. Because of the unsolved problems with the furnace, the endangered area, about 2 m in height, was studded and lined with ramming mass. Later no further corrosion was found in the zone.

In 1974, a new composed SiC-material was offered by "CARBORUNDUM", a manufacturer of refractory, which was supposed to withstand the aforementioned attacks. Two test areas of this material were built in at the zone with the highest heat load. After 11,000 hours of operation, it could be said, that this material promised to give sufficient life and to have satisfactory slag repellence capacity. No permanent extensions of any kind, the cause for the total damage of the first furnace lining, occurred. Only a minor attack and waste of the brick surface was observed. Resting upon this experience, the lower halves of the side-walls were rebuilt with the mentioned SiC-bricks. Moreover, this part of the lining is air cooled by the use of hollow bricks. The secondary air is employed as cooling medium and finally injected into the furnace through 3 horizontal groups of nozzles. Similar designs are know of American plants too.

With this reconstruction, the original combustion guidance could be resumed, with an unobjectionable burn-out within the combustion chamber.
b. Experiences with superheater-corrosions

Contrary to the anticipated effect of a reduced susceptibility for corrosions, considerable difficulties arose with this new unit too. There occurred corrosion phenomena of kinds not known before.

Although the corrossions of the tubes of the first pass are under control, a totally different picture is presented in the superheater area. As well the final stage superheater as the convection superheater were affected by numerous damages. The tube failures of the superheaters have been as follows:

22 failures of convection superheater tubes,
13 failures of final superheater tubes.

An accumulation of that kind of tube failures caused by corrosions has not been observed in former years. Also, a minor corrosion of the presuperheater area of the other boilers could be registered too, here the use of protective shields upon the first resp. uppermost row of tubes, has given satisfactory protection. Already more than 30,000 h of operation are obtained. Only a few failures, caused by erosion, occurred during the past years.

In the time from 1970 to 1972, fireside corrosions of a considerable rate appeared on the final stage platen superheaters, which are installed at the upper end of the first flue. The tube side, being directed against the gas flow, showed a rapid material wastage at a rate up to $4.5 \times 10^{-6}$m/h. At first, this corrosion was interpreted as chlorine corrosion under lack of oxygen. Gas analyses, however, showed that in these parts of the boiler, sufficient oxygen is present at any time. Only extensive analyses of the deposits of the tubes have shown a chlorine-corrosion released by transformation of alkali chlorides into sulphates within the deposits.

Because these corrosions occurred only after some years of operation, the search for the possible cause was concentrated upon changes of operating conditions, which took place within this period. Some remarkable results were found hereby:

Parallel to the accumulation of the damage events, the following points can be stated as changes in the operating conditions of the first years:

a. the increase of the calorific value of the refuse up to 7.120 kJ/kg (3100 BTU/lb);

b. a decrease of $SO_2$-concentration in the flue gases.
Both symptoms can be traced back with certainty, to the increase of wrapping materials (as there are paper, cardboard, wood-wool) and wood in the refuse. The calorific value of paper is about 3 times higher than the one of domestic refuse. On the other hand, the sulphur content in these materials is of no account, so that the $SO_2$ concentration must decrease.

As a measure of remedy, the endangered tube parts were provided with protective shields in form of flat-steel. This proved to be sufficient, but as these steel bars are cooled insufficiently, an inspection and eventually a partly renewal has to be made at every shut-down of the boiler.

To cut down the maintenance costs, it was looked for another tube material of better resistance against these corrosions. In a series of laboratory tests, a high alloy austenitic steel was chosen out of a number of samples, which promised to give better results. This steel has the German standard specification:

$$X8CrNi Nb 1613,$$

its composition is:

<table>
<thead>
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<th>Element</th>
<th>Min.</th>
<th>Max.</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>0%</td>
<td>0,08%</td>
</tr>
<tr>
<td>Si</td>
<td>0,25%</td>
<td>0,55%</td>
</tr>
<tr>
<td>Mn</td>
<td>1,10%</td>
<td>1,4%</td>
</tr>
<tr>
<td>Cr</td>
<td>15%</td>
<td>17%</td>
</tr>
<tr>
<td>Ni</td>
<td>12%</td>
<td>14%</td>
</tr>
<tr>
<td>Nb</td>
<td>10 times C.</td>
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</tbody>
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1,972 tubes of this material were built in. On occasion of a boiler inspection, after 16,000h, no substantial material wastage could be found. But lately, the first failure of these tubes happened. The loss of material is strictly limited to the outside surface of the 90° bend of the U-shaped tube. The horizontal and vertical parts of the tubes are completely unharmed. By the appearance of this damage, it can perhaps be concluded that by bending the tubes, not only a reduction of the thickness of the outer wall occurs, but a structural change of the material too, which makes it sensitive for corrosion. Tests about this matter are running, but not yet concluded, so that final statements cannot be made. In relation of the corrosion rate of 1970, these tubes have been a significant improvement, although no protective shields have been used on these tubes.
Returning to the boiler which is in service since 1972, it must be said, that similar good experiences with this unit could not be achieved.

The final superheater which is of nearly the same design and arrangement as the others, had to be renewed in two steps in the years 1973 and 1974. Determinant for this measure was a fault in the design. The 14 tubes of each platen superheater had been welded together instead of being clamped. Hereby, the tubes were hindered in their extension, so that after a short operation period, they were completely twisted and did no longer hang vertical in the gas stream. Because the corrosion takes place at the leading edge of the tubes, not only the outward tubes were endangered, but the superheater plates presented larger surfaces to the corrosion attack. With the renewal of the first half of this superheater, the first four outward tubes of each plate were made of the same austenitic steel mentioned earlier. But after about 6,000 hours of operation, it came to a failure of one of these tubes, and the others too showed considerable attack. Investigations made in order to trace the cause of the deficient life, in opposition to the same tubes in the other boilers, showed a new phenomenon not known up to that date.

On the presuperheater too, being located at the upper end of the second gas pass as a convection tube bundle, corrosions occurred to an extent, not known from the other boilers. Not only the tube bends are affected, but the middle-section of the tube bundle too. But while at the tube bends the material was carried away at the top side, the material loss at the middle-sections occurred at both sides of the tubes at an angle of about 30° to the vertical axis as a long-faced erosion. In addition, not only the first or second row of the tubes is affected, but the damages continue throughout the whole upper tube bundle.

4. Causes of the corrosion

By search for the possible reasons of these intensified corrosion, it was found that likewise about 1 year after the boilers start up operation, a new situation had come up referring to the method of operation.

In May 1973, a shredder-installation for bulky refuse (wood of any kind, furniture, boxes, crates etc.) was started. Due to space arrangements between shredder and boiler, most of the shredded material is fed into this unit. The tests carried out thereupon, showed that this fact is of important influence upon the products of combustion and the corrosions. Comparative tests between the fly-ash of boiler 5, which is fed with shredded refuse, and the fly-ash of boilers 1 - 4,
which burn preponderant municipal refuse, showed significantly higher contents of potassium (21.9 mg/g) and chloride (40.2 mg/g) for boiler 5 opposite to potassium (14.2 mg/g) and chloride (16.3 mg/g) of boilers 1 - 4. In parallel to the fly-ash tests, comparative flue-gas analyses were made and tested for the HCl, HF and SO₂ contents. The results of these tests can be summarized as follows:

During the incineration of normal domestic- and commercial-refuse, the concentrations of sodium (Na), potassium (K) and chloride (Cl) in the fly-ash, are of similar values in all units. During the additional incineration of shredded refuse in boiler 5, however, all values, especially those for potassium (K) and chloride (Cl) are increased, the latter by about 100%. But, as expected, the concentrations of HCl and HF are in opposed ratio to that. This means, that a partial dry scrubbing process has taken place. Upon the SO₂-concentration, the shredded refuse has had no measurable influence. The contents of sulphates in the fly-ash showed values of 60 - 85 mg/g with different fuels, but had no definite tendency.

5. Corrosion-mechanism

The appearance of material wastage showed on the boilers 1 - 4 the following picture:

a. the highest rate of tube wall reduction was always found at the horizontal-sections at the side facing the gas stream;

b. the tube wall weakening proceeded below deposits of normal thickness, which contained mainly compounds of sulphate; (partial chlorine containing in contact with the layer near the tube surface);

c. below these layers there was found a hard scale, loose adherent at the tube wall, which could easily be removed with the deposits;

d. between the steel surface and the scale, there was found a thin layer of light brown color, porous composed, hygroscopical reacting, with chlorine contents between 10 - 15% (weight).

In opposition to point (c) and (d) of the aforementioned appearance of the corrosions, on the platen superheater of boiler 5, on the tubes of the corroded areas, there is a mostly white, dry remaining layer in contact with the steel surface. These whitish batches of the deposits can be determined as frozen fusions (spiky crystallization). X-ray
structure analyses of these layers showed the presence of alkalisulphates (K₂SO₄; K₃Na(SO₄)₂) besides minor quantities of alkaliferrosulphate (K₃Na₃(Fe,AL)(SO₄)₃ and compounds of alkali-calcium-zinc-lead-sulphate. In the layer with direct contact to the steel, the main consistence is alkalyferro-sulphate besides metaloxides. Chemical analyses of the deposits on different tube sections showed the following picture:

a. In non-corroded areas, the deposits contained alkali compounds in amounts which have been found never before, (about 20% weight K₂O + Na₂O). The contents of chlorides is low.

b. In corroded areas, the high contents of chlorides is missing, especially at the boundary to steel. The sulphate contents is high.

These results demand another explanation of the corrosion mechanism as hitherto. The progress of the observed chlorine-corrosions until now was as follows:

Upon the tube surfaces, especially those facing the gas stream, a deposition of alkali-chlorides took place. The sublimation of volatile chlorides at the boundary to the steel seems to have played the main part. These chlorides were sulphatized (accelerated by the increase of the SO₃-partial pressure as the result of a catalytic SO₃-formation by ferroxides) whereby chlorine in "stato nascendi" was set free and the tube material attacked:

1. \(2 \text{KCl} + \text{SO}_3 + \frac{1}{2} \text{O}_2 \rightarrow \text{K}_2\text{SO}_4 + 2 \text{Cl}\)
2. \(\text{Fe} + 2 \text{Cl} \rightarrow \text{FeCl}_2\)

The corrosion rate depends on:

a. the amount of the sublimated chlorides;

b. the rate of retension of the released chlorine by the oxides of the depositories, as follows:

\(\text{SiO}_2 + 4 \text{Cl} \rightarrow \text{SiCl}_4 + \text{O}_2\)
\(\text{Al}_2\text{O}_3 + 6 \text{Cl} \rightarrow 2\text{AlCl}_6 + 1,5 \text{O}_2\)
\(\text{Fe}_2\text{O}_3 + 6 \text{Cl} \rightarrow 2\text{FeCl}_3 + 1,5 \text{O}_2\)

c. the choice of the steel quality for the tubes; the austenitic steel mentioned showed much less wastage than low alloy chromium-molybdenum steels.
In the case of the superheater corrosions of boiler 5, chloride is not the case, resp. the rate of chloride corrosions is of no account. The absence of significant amounts of metal-chlorides at the boundary steel/deposit; the high alkali contents in the deposits, the appearance of partial fusion and the formation of alkali-ferrosulphate down to the steel surface, permit the following conclusion. The causes for these corrosions are:

a. By the formation of partial fusions of sulphates (and little amounts of chlorides) next to the tube surface, corrosions by fused salts take place.

b. The reaction of the metal-oxides of the tube material with sublimating alkali-sulphates, for example:

\[
\text{Fe}_2\text{O}_3 + 3 \text{K}_2\text{SO}_4 + 3 \text{SO}_3 \rightarrow 2 \text{K}_3\text{Fe} (\text{SO}_4)_3
\]

This reaction wastes the protective oxide layers, and in addition to the fused-salt-corrosion, the new oxidation of the tube material takes place.

Up to now, corrosions of that kind could not be observed, because the small amounts of alkalisulphates, found on the tubes, and those formed by reaction within the deposits could react with other deposited flue gas constituents to undangerous compounds. By the incineration of significant portions of shredded wood, now the formation of alkali-compounds is increased to a point, that corrosive reactions with the tube material can run down.

Obviously, the aforementioned chloride (resp. chlorine) corrosion is present too. But due to the higher resistance of the special steel, this process seems to have been of little importance. Hence, it can be explained why the steel, at other times resistant to some extent, has not proved itself in the case.

6. Summary of the corrosions and protective measures

At the incinerator plant at Düsseldorf, the following corrosions were observed and protective measures were taken:

a. Corrosions on new superheater tubes, free from deposits.

Even under conditions with sufficient presence of oxygen chlorine-corrosions can take place during the formation of the first protective layers upon the tube surface. This process normally comes to a standstill by itself. No special measures of protection have to be taken as long as the process is not disturbed by erosions or similar incidents.
b. Corrosions in atmosphere poor in oxygen.

By this kind of corrosion, mostly the boiler parts behind the furnace have been affected.

To protect the tubes, at first a satisfactory guidance of the combustion is necessary; in the second place, the construction of long flues for a perfect gas burn-out. A final protective measure is the ceramic cover with refractory.

c. Chlorine-corrosions on superheater tubes.
The mechanism of this corrosion was already communicated.

An imaginable measure of defense would be the elimination of either alkali or chlorides. This is mostly impossible because of the composition of the refuse. But a better distribution and mixture with harmless refuse decreases the concentration upon one single unit. This decreases the corrosion rate too, as experiences have shown. The mounting of protective shields and shells is successful but increases the maintenance expenses. The third measure, the use of special steel in this case, has brought remarkable improvement too. Another method of protection, the coating of the tubes with either metallic or ceramic materials, applied by plasma-gun-spraying will be tested next.

d. Corrosion on superheaters by fused salts.

Due to the fact that these corrosions are dependent on the amounts of alkali released in the furnace, wood or wood products, which are alkali carriers, should be fed only in small portions as long as presence of chlorides can be expected to.

For the time being, there is no special steel known which is resistant against fused salt corrosions and chlorine corrosions as well.

So as protective measure, the use of shields and shells is the only one with some success.

If the problematic refuse, as in the Düsseldorf case, is special refuse with characteristics of important differences to the normal municipal refuse, the design and construction of an incinerator for special refuse ought to be taken into account to.
7. Summary

The 1972 new constructed fifth incinerator unit at the plant at Dusseldorf has brought forward a number of new recognitions and experiences during the past four years of operation. Due to the increased incineration capacity, problems with the furnace lining came forward, which could be overcome by use of new refractory materials in combination with air cooling. The former know corrosions of the heat surfaces next to the furnace, are of no importance at this unit. New problems arose, however, with corrosions on the superheaters. The effect is produced by the incineration of larger amounts of shredded refuse according to the knowledge of today.