The "Sabotage Model" or how to find the cause to difficult and mysterious problems: The case of Recovery Boiler compound tube corrosion.

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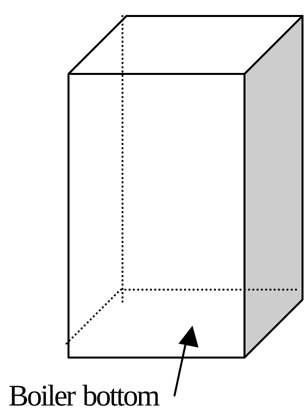
Background

The recovery boiler is a part of chemical pulping process where chemicals are recovered and the calorific value of waste, the black liquor, is used to produce steam for the process.

The pulping process starts in woodhandling where e.g. pine is debarked and chopped up for the fiberline process where chips are cooked with chemicals, NaOH, Na_2S, Na_2CO_3. Typically pine contains some 64% celluloses and 28% lignitic substances. The latter are not wanted but waste and washed later together with the chemicals for regenerating. The chemical pulp goes further in the process for bleaching. The waste, black liquor, goes through evaporation to recovery boiler where the lignine, or carbonaceous substances are burned. The output are steam and valuable chemicals, green liquor, mainly Na_2S and Na_2CO_3, which go for the recausticizing and renewed use as white liquor, NaOH and Na_2S, in fiberline cycle.

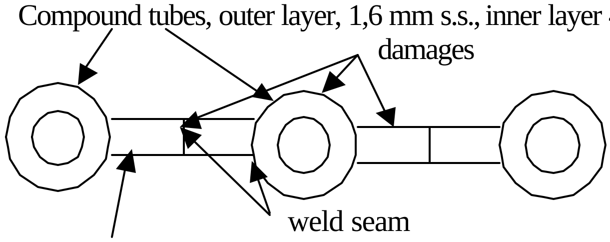
The recovery boiler is a huge boiler of some 70 m height and 125 m^2 of bottom area. The temperature of the burning gases reaches some 900^o C.

The boiler house:



In the mid of 1970's it became customary to build the boiler house of compound tubes connected to each other by fins to form a tight boiler housing. However, later on serious corrosion problems were reported around the world, in the USA, Canada and Scandinavia. This was not related to any particular boiler manufacturer or geographic area but a common feature surprising anybody involved. The damages were in the bottom of the boiler as well as in the air inlet and smelt outlet gutter. Cracks were in the stainless steel part of the compound tube and in the fins between tubes. The weld seams were also damaged.

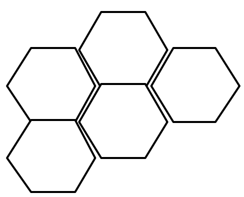
Compound tubes, outer layer, 1,6 mm s.s., inner layer 4,5 mm c.s



The s.s.fins to build tight walls and bottom in the boiler house together with tubing

Several studies have been made concerning these cracks in the countries mentioned. The time period required for the crack to occur varies from a few months to several years, typically four years. The existence of cracks is due to the geometric form of the bottom. In the so-called decanter form, the damages are all over the bottom at random, in the skewed bottom cracks are only near the outlet tube of the smelt.

The cracks have some typical features. They are located in the top and the side of the tube, in the fin and butted welded seams. The cracks may be either longitudinal or perpendicular. In many cases they form netlike figures on the surface of the tube.



Net-like crack figures on top of tubing, magnified

There have been reported cases where the stainless steel part of the tube has completely come off uncovering the carbon steel. The maximum reported size of such cases has been 50x50 mm.

The cracks are typically born in the surface part of the stainless steel. Afterwards they tend to proceed perpendicularly throughout the s.s. part. They might even spread in all directions, but stopped when reaching the carbon steel. More often the crack continues in the s.s. part having reached the boundary region. The crack goes mainly through the crystal. They are also isolated and relatively less spread. The cracks have also found to follow the crystallographic structures of the steel.

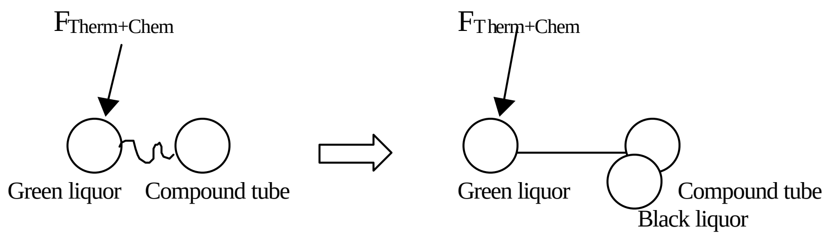
In only a few cases the crack have proceeded to the c.s. In most cases the corrosion is relatively small compared with the s.s. part of the compound.

Although the problem is a serious one and has been studied comprehensively there has not been a clear and definite determination of the mechanism and reason for the phenomenon. The cause has been diagnosed to be stress corrosion and that of thermal fatigue. The stress corrosion is most likely due to the difference between the thermal expansion coefficient of s.s. and c.s. The tube is working with water around 300^{o} C, hence the s.s. is due to compressive tension 2 to 3 times the allowed design stress.

Some parts of the outer surface might have even higher temperatures due to the touch of green liquor smelt which on the other hand shields the tubing.
What can be done?

The unsuccessful "TRIZ" - solution

The problem is serious and even those who know TRIZ have been engaged. In Substance - field drawing we have the chemical and the thermal field, the instrument and the object which have unwanted relation. The solution might be simple and understandable: add a substance which in the best case is a variant of the component in question:



However in this case in the trial made the end result was a catastrophe: when black liquor was sprayed on the bottom before the actual burning process was started to "protect" the compound tubing the corrosion was if possible much faster. So the "TRIZ"-solution was not at all a success. How come?

The other way round

The normal way in studying these kind of problems would of course be to simulate the real conditions. Build a pilot scale boiler or simulate by other means the situation, apply the conditions in question and make careful observations on what happens. Altshuller uses "Methods, Effects and Tricks" and the 40 Principles. The principle number 13 is the "Do it in reverse". How can we apply this?
Altshuller and his alumni have also mentioned the so called "Sabotage Model". This means that instead of trying to solve or speculate the reason for some obviously mysterious cause, we try to deliberately spoil or damage the object in question.

The Object

The object is a compound tube, the core, load bearing material being St 45.8/III with 0.21%C (max), Si 0.35%(max) and Mn 0.65%. The outer surface is AISI 304 L with 0.03 C%(max), 18.5% Cr, 10.5% Ni. The letter L signifies low carbon content to prevent Fe, Cr and Ni carbides to appear in e.g. the welding. This is important because carbides form electrochemical pairs with the stainless steel base material and thus causes grain boundary corrosion, especially if the temperature in some circumstances is between 450 and 900^{o} C . Low carbon means additional costs in the steel making process. Chromium and nickel make steel "stainless". The necessary formula to assure austenitic crystal structure is Cr %+Ni %> 23 % which in the case is fulfilled.

The Achilles heel of the AISI 304L is the carbon content. How could we spoil that?

Spoiling the object

The answer is simple: in the steel melting process we simply apply additional carbon and the steel is no more stainless. But this gives an association to one's mind. Carbon is also a useful component in steel. It is the cheapest and most often used component to strengthen the steel. However there is a limitation of the use of carbon mainly due to the welding properties of the steel. Normally 0.25% C is the maximum for structural steels.

The very well known procedure of hardening of mechanical parts, shafts etc. is to put the element into a carbon bath, raise the temperature well over 723^o C, the eutectoid temperature, preferably up to 900- 930^o C, hold the temperature and the result is carburized machine element ready for hardening. The carburizing may happen in pack, gas or liquid form. The temperature is required to change the ferritic structure of c.s. to an austenitic one because the diffusion of carbon is much greater in the austenitic crystal.

In the liquid carburizing process cyanites, especially NaCN are used. In addition other substances are used, typically Na_2CO_3, NaCl and $BaCl_2$. The carbon content of the surface might raise up to well over the normal solubility in cases where chromium exists.

What is the chromium sensitive of? The answer was already above: the carbon content. Chromium forms carbides, poison for stainless properties.

What about nickel? The same as chromium, carbon content. Nickel is very useful in forming stainless steels like cutlery steel. But it is additionally very sensitive in even small amounts of sulphur gases especially when the conditions last long. The compound is NiS, which has a melting point of 645^o C. The compound moves to the grain boundaries and this results hot-shortness.

Substance-Field-Resources and the instrument

What do we have in the boiler house during the operation? We already know what exist in the object. The result of the recovery process falls down on the bottom of the boiler house. It forms a stack and flows out of the boiler further in the process. The temperature of the smelt might be several hundreds of degrees. Hence the temperature field is dangerous.

The smelt analysis may vary but mainly there are some 30 % Na_2S and about 70 % Na_2CO_3. In these temperatures these components hardly are solid but rather radicals, e.g. $^+$Na, $^{--}$S, $^{--}CO_3$. These are the instrument substances and dangerous ones as we pointed out in the "spoiling part" where e.g. Na_2CO_3 was used in carburizing steel. Further the conditions are reductive, dangerous for stainless steel.

Hypotheses

The prevailing assumption of the cause is the stress corrosion. This might be the main mechanism although the stress should be in the first hand tensile stress not compression. On the other hand on the boiler walls, where the conditions are almost the same, such cracks as on the bottom part have not been reported. What differentiates the bottom from the wall? The answer is obvious: the touch of smelt.

But the stress corrosion is not effective unless there are faults in the crystal structure. These are e.g. segregation all over the crystals due to carburizing conditions and thus precipitation in the grain boundaries are favourable in the temperature in question . We do not speak of some additional hundredths of percentage but rather up to several percentage of carbon content as pointed out by Kopietz under high carburizing conditions and especially when Cr exists.

There are several possibilities in the process. Carbides $(Fe, Cr, Ni)_nC_m$ are born, sulphides exist and all of these are unfavourable and you cant prevent them by additional components like molybdenium or niobium because the disturbing substances are renewable, the compound tube not.

We have very favourable conditions for sabotage. All needed elements exist: the high temperature to boost carburizing conditions to form metal carbides, the sulphur to spoil nickel, the temperature to cause sensitiveness to grain boundary corrosion and perhaps the temperature to add hot-shortness of nickel-sulphide. What else could we need to spoil the tube? Yes, of course, 24h service, long lasting unfavourable conditions for even modest harmful elements. Long periods of normal production conditions are followed by shutdowns for maintenance, when temperature shocks might occur in cooling down the boiler for required maintenance conditions..

What can be done?

Altshuller had 10 Standards to solve Substance-Field problems. None of these seems to apply. We know however that an excessive field is removed by a substance and an excessive material is removed by a field. In a Substance-Field drawing we should introduce in between a new substance to prevent the harmful chemical and thermal field and the elements not to touch each other. This could be an additional lining, like the one of electrolytic copper which is used to prevent carburizing in c.s. where hardening is not required or desired. But this will not perhaps apply as the s.s. part of the tube is already a lining. There would be lining above lining and no knowledge exists whether copper will last in these thermal and chemical conditions. An other possibility is brickwork. The last one is a very obvious solution and also used elsewhere in process industry.

Further we might speculate that the problems is due to the austenitic structure of the compound steel (the diffusion or absorption of carbon is much faster and comprehensive into the austenitic steel than into ferritic). Thus a lot of carbides are segregated to the grain boundaries and form a net around the crystal. Further we ought to avoid nickel, which makes the structure austenitic and which is also sensitive to sulphur.
The danger occurs when the temperature is lowered and the s.s. part of compound is due to tensile stress and the carbide nets will not hold but crack the material. The

carburizing conditions will produce and segregate carbide nets around the crystals and cause the cracks together with the sulphides and the tensile stress.

The recommendation

The recommendation is to give up from 18 % Cr, 10 % Ni low carbon compound tube and to replace the tube by either ferritic low carbon 30 % Cr-lining above c.s. tubing or 30 % Cr-compound tube at the bottom part of the boiler (Cr> 30 %, fire resistant, S-resistant, with Al and Si components or Mo).
The Cr-lining could also be alloyed by small amounts of titanium, molybdenium or wolfram to compensate the harmful effect of chromium to the carbon content in the alloy's ferritic crystal. However the existence of such commercially available compound tubes is not likely. The sheet might be available.

The other possibility is to abandon the compound tubing and apply masonry above c.s. tubing to give thermal and chemical shield.

Discussion

The recommendations made above still leave questions to be answered. There exists even in the 30% Cr alloy possible problems. To mention but a few there are the so called 475^o C and the sigma brittlenesses. The Cr content could be in the range of 14 to 30 %. The lower content requires low carbon content, the latter up allows up to 0.25 % C. But the danger still lurks for carburizing and carbides.

Masonry has also pros and cons. The fire resistance is probably no problem, but the chemical properties of different kinds of mortar are not known to the author. The clear disadvantages are the on the site manufacturing process and the additional weight. Further one's mind is occupied by the fact that there has not been found corrosive or other defects on the boiler walls, especially those related to sulphur gases.

However, the unsuccessful trial with black liquor might prove the "carburizing" defect to be the main cause of the defects, because black liquor contains even more carbon than green liquor.

Authors note

The author is a Management Consultant holding the degree of Master of Engineering. Since my knowledge of structural metallurgy is almost 40 years of age the reader should understand that I am in fact a layman. The metallurgy is a very complicated science and all the resulting recommendation should of course be verified by actual tests before installation.

However, with the "Sabotage Model" applied and the refresh of elementary metal physics in only a few days resulting maybe new ideas, might be enough to prove the power of the TRIZ.

Any comments?
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