

the Conduit

(This is a combined newsletter of Root Cause, Reader's Digester and the Conduit newsletters)

Fall 2007

Ferrous Metallurgy 101

By Ronald E. Munson, P.E.

Steel is by far the most common and important material for the construction of power plants. Steels are made of elements that are both intentionally and unintentionally added to iron. The properties of the steels are governed partly by the combination of the elements, but more importantly by the microstructure of the steel. The microstructure is established by the heat treatment of the steel with a particular alloy content. The combinations of microstructure and alloy provide a range of available properties- thus the versatility of the steels.

Steels are crystalline solids. The crystals at their smallest unit level are stacks of atoms held together by molecular forces. How these atoms are stacked determines the crystal that is formed and the resultant property of the bulk material. Considering all possible combinations of atomic stacking there are fourteen different unique combinations. Thus metallic materials can exist in fourteen different crystal structures. Steel can exist in three of those crystal structures. Steel can exist as *ferrite* (body-centered cubic). Steel can exist as *austenite* (face-centered cubic). Steel can exist as *martensite* (body-centered-tetragonal).

The normal or stable structure for any steel depends on its alloy content and the heat treatment. Most common steels (mild structural steels) are ferrite. Steels with higher alloy contents can be heat treated to form martensite. Some stainless steels are austenite. All steels have an austenitic structure above a certain temperature called the critical temperature. This critical temperature varies by alloy but is generally between 1335°F and 1450°F. During heat treatment (called austenitization) steels are

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heated above this critical temperature, and then given a controlled cooling to form either a ferritic (slow cooling) or

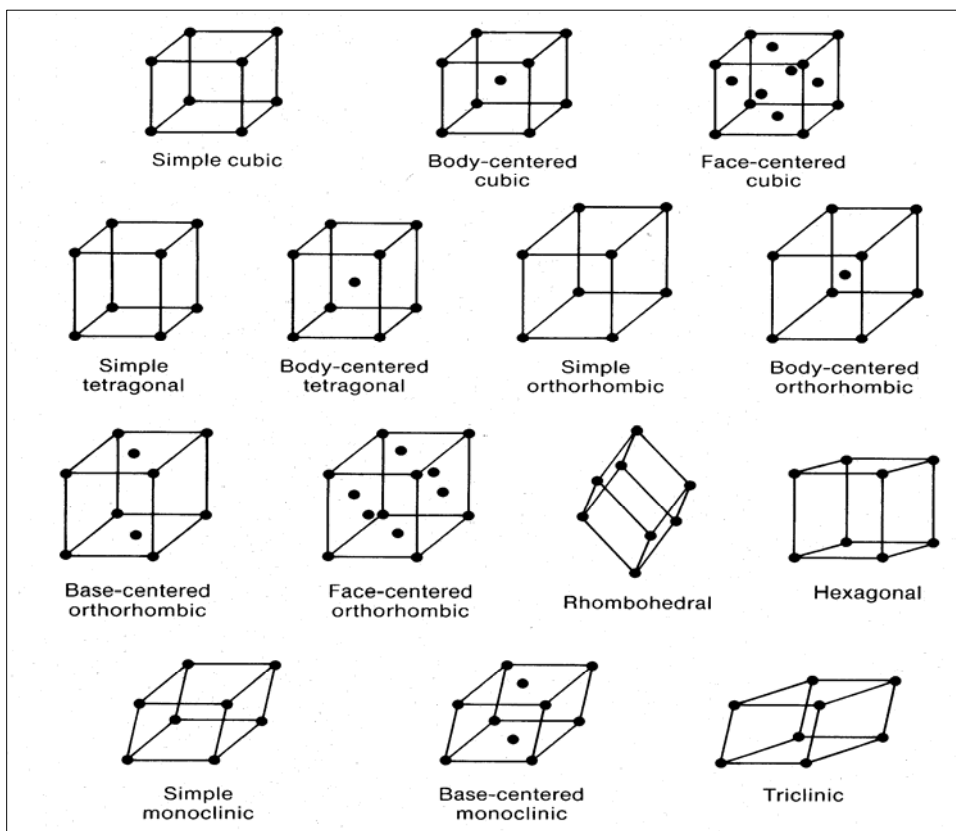


Figure 1. The fourteen possible stacking sequences for metallic substances.

martensitic structure (rapid cooling). If the steel has certain elements present at high concentrations such as manganese or nickel, it will remain as austenite. The martensite is actually a transitional structure between the austenite and ferrite that was not given the time to completely alter its crystal structure from austenite (high temperature) to ferrite (room temperature). Alloy content and cooling rate determine the normal microstructure for a steel grade.

Steel properties are also strongly influenced by carbon that is added to the steel. Carbon resides within the crystal lattice as an interstitial or actually reacts with the iron to form iron carbide (Fe_3C) called cementite. How this cementite exists in the ferritic steel will also determine its property. If the iron carbide forms in an ordered alternating stack with the ferrite (much like a deck of cards) the resultant structure is called *pearlite*. If the carbide forms as individual particles aligned systematically in the grains this structure is called *bainite*. The alloy content and heat treatment determine which carbide “arrangement” is typical. The properties of the ferritic steel are determined by the whether pearlite or bainite forms.

This is just a quick introduction on steels. If you want to know more, contact Ron Munson at Mechanical & Materials Engineering.

Seminars and Workshops Attended

Three M&M Engineers attended the Technical Association of the Paper and Pulp Industry (TAPPI) Engineering conference recently in Jacksonville, Florida. The conference included technical committee meetings focused on Corrosion and Material in the Pulp and Paper industry. Our engineers have worked on the Metals, Nonmetals and Equipment Reliability and Inspection subcommittees to help put together TIPs (technical information papers) for use as guidelines in inspection, repair and failure analysis of papermaking and pulping equipment. Also, applied research and case history papers were presented from around the industry. Paper topics this year included: *Kraft Liquor Corrosion; Reports for the Frontlines, Lower Boiler Furnace Corrosion Seminar and Recovery Boiler Research and Development.*

The BLRBAC Fall Meeting was held at the Crowne Plaza Hotel/Atlanta Airport, October 1-3, 2007. One M&M Engineering Scientist attended the meeting, with more than two hundred members and guests participating in the three days of committee meetings, presentations and discussions covering virtually all aspects of safe firing of black liquor recovery boilers. The usual high level of interest by the attendees was reflected in the plentiful supply of questions and concerns offered for group discussion during the operating problems sessions. A quiz entitled, "Do You Know Your Boiler?" served to effectively separate the “newbies” from the old-timers. The quiz results were graded on a rather generous, unstated curve, and all received an "A" for their participation. The next BLRBAC meeting will be held April 7-9, 2008 at the Crowne Plaza Hotel, Atlanta, Georgia.

Ron Munson, Principal Engineer at Mechanical & Materials Engineering, was invited to present two sessions at the recent AEGIS Boiler Machinery Seminar held in Charlotte, North Carolina, in early October. Ron's presentations were *The Use of Advanced Ferritic Alloys in Steam Generation and Management of Retaining Ring Risk*. Ron Munson also presented at the AES/AGIC and GRC Training Session at the Red Oak Power Plant in Sayreville, New Jersey in mid-September. His presentation was titled *The Creep Show 2* and focused on high energy piping and inspection techniques. For more information on presentations by Ron Munson, please contact Ron at ron_munson@mmengineering.com.



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Chloride Pitting and Stress Corrosion Cracking of Stainless Steel Alloys

By Gary Loretitsch

Chloride stress corrosion cracking of stainless steels (SS) is a rather well-known and documented phenomenon. In general, stress corrosion cracks propagate from initial pits. Once cracking has begun, the process is self-perpetuating. The condition can normally be arrested only by removing the pits, the cracks and the affected metal adjacent to the cracks.

There are several ways to avoid the combination of conditions that make possible the initial chloride ion induced pitting. Since chloride ion concentration is a prime factor, limiting the chloride ion concentration in the liquid that contacts the walls of the vessel or lines is one method. Temperature is a key factor (Figure 1) so limiting the temperature of the liquid is another step to be considered. It is known that chloride ion induced pits require some uneven or other inconsistency in the surface of the stainless steel to allow the pits to get established. For this reason, stainless steel reaction vessels, other types of pressure vessels and

associated piping and equipment are often prepared with highly polished internal surfaces and resurfaced whenever necessary to the original condition in order to eliminate rough surfaces as a factor in chloride ion pitting. Dissolved oxygen is another key factor in the establishment and development of chloride induced pits. In some cases oxygen can be minimized or even eliminated as a factor. However, in many cases the only practical means to prevent chloride pitting is to alloy the vessels with >50%Ni SS alloys or 6% moly SS alloy or better, metals which are virtually impervious to chloride attack and not susceptible to the resulting stress corrosion cracking (Figure 2) when surfaces are prepared properly and kept clean and free of deposits.

Stress corrosion cracking can cause irreparable damage to equipment and in some cases can lead to catastrophic failures of pressure vessels. The following is one example of a rather unusual incidence of chloride stress corrosion cracking at a US refinery complex.

The refinery operates several hydrogen plants of nearly identical design. These plants employ stainless steel deaerators because of the high concentrations of carbon dioxide in the condensate from the reactors. The carbon dioxide makes both the steam condensate and the feedwater (the blend of condensate and demineralized water) a highly corrosive solution of carbonic acid. In most other respects the condensate and the feedwater is of suitable quality for reuse.

During routine pressure vessel inspections of the deaerators significant pitting attack was identified. Further examination showed that the pitting had contributed to rather extensive cracking of the stainless steel shell of the deaerating section of the heater.

The cracking was unacceptable, so alternative metallurgy was considered. The only alternatives to 316 SS seemed to be either carbon steel or one of several superior SS alloys. Carbon steel is relatively inexpensive and it is not affected by chloride stress corrosion cracking, but it is highly susceptible to corrosion from carbonic acid. More expensive SS alloys that are not susceptible to stress cracking could likely solve the pitting/cracking

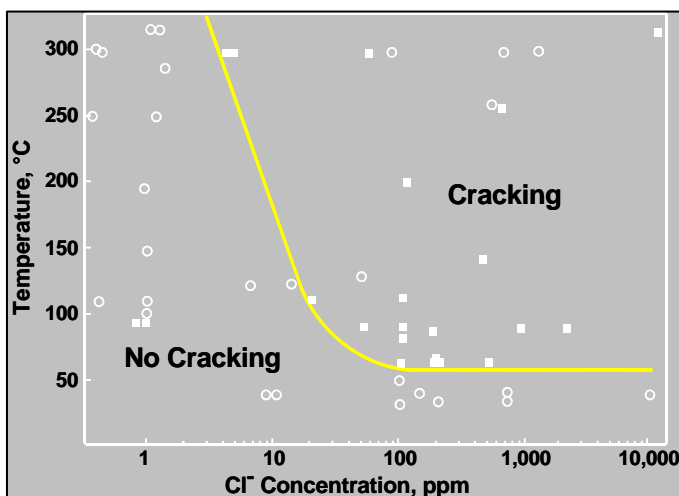


Figure 1. Temperature and Cracking.

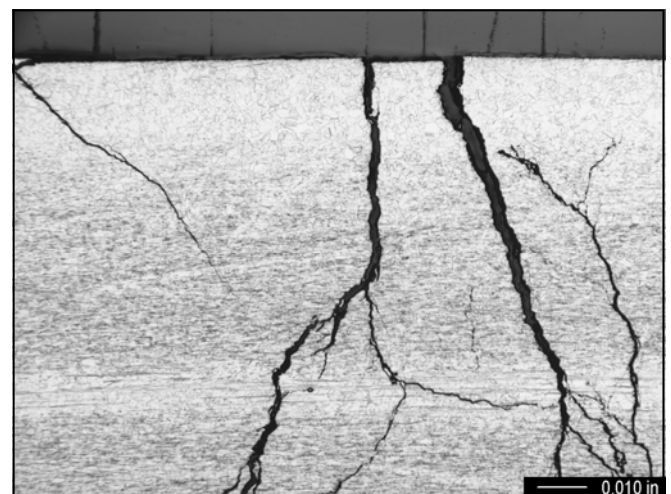


Figure 2. Stress Corrosion Cracking.

problem, but there was no guarantee that that upgrade alone would eliminate the problem and the higher cost would be difficult to justify on that basis.

Here is some of the pertinent information that came out of the root cause investigation:

The affected deaerators were of conventional Cochrane-Crane[®], spray/tray type so the equipment design did not appear to be a factor in the corrosion problem.

The chloride concentration of the feedwater to the deaerator was very low by any standards at <1.0-ppm before dilution by steam. Even the most conservative chloride concentration limits employed by industry are much higher. 10-ppm maximum was the strictest standard for this service that was encountered. In fact, the chloride concentration was so low that some believed that the cracking was not chloride-based at all.

The operating pressure and temperature of the deaerators was normal for the service and not excessive by any standard.

Although it had been years between internal inspections and even longer since the internal surfaces of the deaerating and storage sections of the deaerators had been prepared, the internals were found to be reasonably clean and passive.

Deaerators ordinarily utilize low pressure steam that would otherwise be vented. However, for these hydrogen plant applications the deaerators were supplied with superheated steam. Although more expensive to produce than low pressure saturated steam,

superheated steam appeared to cause no obvious operational problems when used to deaerate and heat feedwater.

The quality of the steam used for deaeration was very good (virtually no chloride at all). The quality of the condensate and the auxiliary make-up source was consistently good (<1.0-ppm chloride) also.

Since the path forward was not yet clear, additional analytical work was done to confirm a chloride mechanism. Subsequent SEM-EDX examinations confirmed that in fact the pitting and the resulting stress cracking was due to chloride ion. The very low chloride ion concentration of the feedwater had pointed to a different pitting mechanism as a possibility, but chloride was definitely present in the pits.

In order to obtain the chloride level required for pit initiation from feedwater with <1.0 ppm chloride and indicated by the SEM-EDX analysis, some concentration mechanism was deemed necessary. Evaporation to dryness of feedwater in the deaerating section of the deaerator vessel by superheated steam was ultimately shown to be that mechanism.

The affected deaerators were replaced with new ones made of chloride resistant SS alloy. The new deaerators also used only saturated steam. The pitting-cracking problem has not occurred in those vessels, however, pitting-cracking failures have occurred in other hydrogen plant deaerators, including at least one catastrophic failure. It would appear that all hydrogen plant deaerators should be

inspected for chloride pits and cracking, especially those made of 304 and/or 316 stainless steel and utilizing superheated steam.

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In the News...

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User groups show owners what to look for and where

2 HRSG User's Group. Discussion forums, formal presentations, expedition provide guidance needed to improve plant performance, availability. Preventing damage to heat transfer surfaces (p. 2), water chemistry considerations (p. 4), steam piping concerns (p. 4), controls (p. 6), valves (p. 6)

10 Western Turbine Users. Expanding asset base, valuable system opens recent attention. Market investigation performance assessment (p. 14), LME2000 (p. 16), LM5000 (p. 20), LM5000 (p. 26), overall technical presentation (p. 28)

33 251 Users Group. RI compressor blade failures dominate discussion at annual meeting

41 CTDFP. Experience, ideas shared by colleagues benefit all in attendance. GE Roundtable (p. 42), LM5000 Roundtable (p. 43), Legacy, Alston, and PTF Roundtable (p. 47), reactor fuel (p. 48), Generic Roundtable (p. 50), user experience with PFI (p. 52), ZLD/Environmental Roundtable (p. 55), Nonnuc Roundtable (p. 59)

63 501F Users. Design refinements, upgrades help improve fleet performance

90 HRSGA Users. User presentations, discussion dominate OK City program that attracts near record attendance. User presentation (p. 66), clean air filtration (p. 66), Siemens Day (p. 66)

101 V Users Group. Can HEPA filters really eliminate the need to wash components—mine and offset?

109 501F Users Group. If you weren't there, you missed "a really big show" in terms of content, next chance, Orlando, Jan 14-17, 18C Forum (p. 106), recent compressor from FGD/ROD (p. 111), Post-Mal implementation experience (p. 112), failure investigation (p. 114), experience with non-ORIG HRP parts (p. 117), web-based training for plant personnel (p. 117), finding leaks in natural gas lines (p. 117), coping with air-cooled generator issues (p. 118), how to heat GT inlet air (p. 119)

124 Operation/WDPF Users' Group. Benefit by adding this group's meetings to your 2008 calendar

126 Business Partners, etc

HRSGA Users' Group
Human Resources Working Group

INDEPENDENT VOICE OF THE GAS-TURBINE-BASED GENERATION SECTOR

For information on recent presentations given by Mark Tanner and Ron Munson at the 251 Users Group and 501F Users Group meetings, turn to pages 36 and 114 of the **Second Quarter 2007 Edition of the Combined Cycle Journal**.

Also in the same edition, on page 33, is an article regarding another M&M Engineering presentation on RI Blade Root Cause Analysis (RCA).

And on page 126, Dave Daniels gives an expert opinion on the use of hydrazine in an HRSG. This information can also be accessed on the **Combined Cycle Journal** website www.combinedcyclejournal.com

Proper Use of Bromide in a Cooling Water Treatment

By David Daniels

Cooling systems that operate under alkaline conditions often use a combination of commercial bleach and sodium bromide to create hypobromous acid. This acid is much more effective than bleach under alkaline pH conditions. However, the misapplication of these chemicals can cause much of the bromide to be wasted. If the two chemicals are reacted properly and fully utilized, plants could reduce their dosages and/or frequency of treatments, saving chemicals and money. One utility was spending over \$200K per year on bromides.

First, it is important to know something about how bleach is manufactured. Commercial or industrial bleach is commonly purchased in strengths from 10% to 15%. It is manufactured by bubbling chlorine gas through a sodium hydroxide solution. Excess hydroxide is maintained in the final bleach solution to increase the stability of the bleach. Typically, a commercial bleach solution has a pH of 11 to 13. Under these conditions, all the hypochlorite in solution is in the form of hypochlorite ion.



Figure 1. Improper application of biocides can result in biofouling.

pH	% Hypochlorous Acid	% Hypobromous Acid
6.5	95	100
7.0	90	100
7.5	50	94
8.0	24	83
8.5	9	60
9.0	3	33
9.5	0	11

Table 1. Percent of HOCl and HOBr at various pH Levels.

When the concentrated bleach is diluted, it reacts to form hypochlorous acid. The percentage of acid that forms when the bleach is added to the cooling water depends on the pH of the cooling water. The percentage of hypochlorous acid formed at various pHs can be seen in Table 1.

It is only in the acidic form, as hypochlorous acid, that the bleach is a potent biocide. The acidic form penetrates the cell membrane and interferes with a variety of cellular processes, killing the cell. Whereas, the hypochlorite ion, apparently never makes it into the cell where it can do damage.

However, the hypochlorite can react with any number of other organic and inorganic compounds including metals. If the cooling water contains amines or ammonia, chloramines are formed. These consume hypochlorite and thus increase the amount of bleach required to produce the desired results. Chloramines have been shown to be poor biocides.

Hypobromous Acid to the Rescue

Hypobromous acid, HOBr, is also a very potent biocide, acting in a similar way to hypochlorous acid; however, it is a weaker acid and therefore remains in its acidic form at a higher pH. Thus, HOBr is much more effective as a biocide at the higher pH.

As can be seen in Table 1, hypobromous acid is still in the acidic form between a pH of 8.0 and 9.5 whereas the percentage of hypochlorous acid remaining in the same pH range is very small.

In ammonia and amine-containing waters, hypobromous acid has the added advantage that the bromoamines formed are much better biocides than chloramines.

Hypobromous acid and hypobromite ion is considered less stable than bleach. A potential decomposition product of HOBr is bromate (BrO_3^-). Bromate is a carcinogen and regulated at a rate of 0.01-ppm in drinking water.

While there are forms of stabilized hypobromous acid (Nalco's Stabrex[®] is one) and other hypobromous acid-generating chemicals for sale (i.e., BCDHM), typically hypobromous acid is generated on site and used immediately by combining bleach and sodium bromide.

The formation of hypobromous acid from bleach is not as simple as mixing the two concentrated chemicals together. To rapidly form hypobromous acid from bleach and bromide, you must start with hypochlorous acid.

Hypobromous acid cannot be generated in a reasonable amount of time from the hypochlorite ion; the kinetics are far too slow. The good news is that even slight

decrease in pH, to say 9, is sufficient to increase the reaction kinetics to a range where flow through a static mixer and a few feet of piping should be adequate to complete the reaction.

Furthermore, there is a limit to the amount of sodium bromide that can be activated by bleach.

Research shows that the maximum amount of bromide that can be activated by bleach is approximately 2500-ppm as Cl₂.

The preferred bleach/bromide mixing arrangement for optimum bromide usage is to dilute the

sodium bromide solution with cooling water (ensuring mixing through a static mixer) then add bleach and mix with a second static mixer. The bleach and bromide flow rates should be set to produce a total halogen level of 1000-ppm to 2000-ppm.

A complete set of instructions regarding the proper setup for adding bleach and bromide can be found at www.wateradditives.com. Look under the LiquiBrom[®] chemicals for more detailed instructions or contact M&M Engineering for assistance in properly configuring your biocide treatment program.

Check out our new website at www.mmengineering.com

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- Repair Specifications
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UPCOMING EVENTS

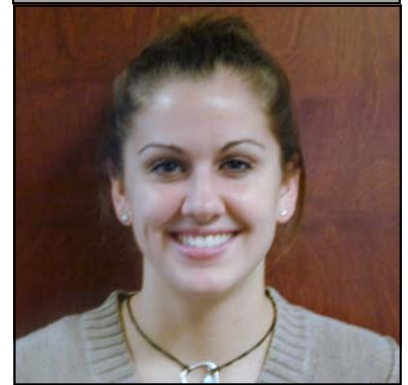
Check back soon for upcoming events...

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Employee News

Andi Cragen Joins M&M Engineering



Andi Cragen joined M&M Engineering this year and is a recent Graduate with a BSME from Baylor University, School of Engineering, Department of Mechanical Engineering.

Ms. Cragen is involved in the failure analysis and condition assessment of a wide range of components, including pressure vessels and piping, boilers and auxiliaries, heat exchangers and rotating equipment submitted to our Materials Science Laboratory.

Failure analysis examinations include development of laboratory testing programs for parts received, supervision of laboratory work, interpretation of laboratory results, and issuance of written and/or oral reports.

Congratulations to Lee Schmerling

Lee Schmerling, Consulting Engineering, celebrated her 10 year anniversary with M&M Engineering this month. Congratulations, Lee !

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