Chill by Thermal Analysis
This topic can be difficult to understand so I am presenting a short summary for those who do not want to go into the metallurgy or mathematics of chill measurement.

Summary:
There are several measurements of chill that are practical to use in thermal analysis. They are things that either promote graphite or promotes carbides (chill) and are related to chemistry and/or inoculation. These measurements can be translated into mathematical equations for real-time prediction of chill. The math will tell us how much each factor affects chill, the degree of accuracy of the prediction, and the amount of confidence we can have in the answer. MeltLab started predicting chill in 1995, and we published a paper in the AFS Transactions on the subject in 1996. Today, with nearly 20 years more experience, our techniques have been improved, and chill has been added to the growing list of chemistry and microstructure predictions MeltLab can make for iron based alloys.

Definition
Chill is the tendency of iron, when cooling rapidly to form martensite, and D and E flake. This is often the problem with castings having thin sections and sharp corners. Thicker sections have more heat to lose and thus cool slower allowing the contained carbon to form the more desired types of graphite. The normal way to combat chill is to provide better nucleation of the graphite by increasing the inoculation.

What actually happens (metallurgically speaking) is that the rapid cooling lowers the temperature to the point where various forms of carbide can precipitate. The dissolved carbon, which is still at high levels in the iron, comes out as D and E-Flake—forms of graphite embedded in carbide. This precipitation temperature is a function of the carbide promoting elements of chromium, vanadium, and manganese, which all raise the temperature at which carbides can form. On the other side of the equation—silicon, nickel, copper, and phosphorus lower the temperature at which carbides can form giving more time for the carbon to transform into graphite.

The Chill Wedge
The traditional method of measuring chill has been a chill wedge. These wedges come in different sizes and can range from 1 inch high to 8 inches high to try to model the thickness of the casting. The chill wedge test is subject to some variation in results due to the procedures used. Variations include some of the following:

- Temperature: Sampling hotter iron will produce less “chill” than sampling colder iron if other properties are kept the same. This is because the mold extracts heat from the iron. The less heat there is to extract, the quicker it cools.

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• The size of the meniscus on top of the chill mold can slightly vary the chill results while under-filling the mold will greatly increase chill.

• Breaking the chill closer to the round end will produce less chill, while breaking it toward the far end will produce more chill. Of course, there should be a mark on the chill wedge midway to show where the break should be for consistency.

• Finally there is the problem with some sand or dirt being in the point of the mold and blunting the end of the chill wedge. If you measure from the point to the height of the chill, then you will get a false reading with a blunted point. **It is far better and more consistent to measure the chill width instead of the chill height.** I know that this not common practice, but the measurement we are looking for is what thickness of metal will chill; not what depth of a wedge will chill.

The misused term “Intelligent System”

I thought it might be useful to add some of the science of correlation for our readers to understand the uses and misuses of correlations. As is often the case in marketing, a name is applied to a system that is oxymoronic. The term “intelligent system” is one such term as you will see often. A true intelligent system starts with the knowledge base of the existing science and builds rules from there. A system that starts from scratch without the existing scientific data base is not an intelligent system. The difference can be seen with the time it takes to customize the system. MeltLab typically takes one to two days to configure with 10 to 20 tests providing solid equations, good correlations, and low standard errors. Other systems take weeks and hundreds of tests to “rediscover” what is already known.

Statistics, correlations and other difficult subjects

Correlation analysis is as it says the analysis of the possible correlation between 2 or more measurements. One measurement is called the “Effect” while the other measurements are possible or suspected “Causes”. The “goodness” or efficiency of the correlation is measured by the degree of correlation, by the variance or standard error, and by how well the data does in something called the k-factor test.

In simpler terms, how much of the variation in the “Effect” can be explained by the variation in the individual causes, and the combined causes. If your correlation is 38%, then you are saying that you can explain 38% of the variation in the effect, but you can’t account for the other 62% variation. When you have multiple causes, you might say that **Cause A** explains 73% of the variation, and **Cause B** explains 24% of the variation, leaving 3% of the variation unexplained (similar to the equation for C.E. from Carbon and Silicon).

In actuality, when you do a multiple correlation, you calculate the partial correlations of each cause, and then look at those with the highest correlations. This is how we arrived at the factors we used in the Chill calculation. The main factors were:
1. The driving force or pressure to form graphite based on the chemistry of the sample—mostly carbon and silicon, but with some negative effects due to chrome, manganese and other carbide formers.

2. The degree of inoculation or number of nucleation sites in the metal. This varies greatly from gray to ductile iron. The magnesium in ductile iron is one of the factors retarding the formation of graphite, but once the graphite seed crystals form, the growth can proceed rapidly. In gray iron, there is no delay in the graphite formation.

Some folks might consider the C.E. the best measure of number one above. We found that the difference or separation between the gray eutectic and the white eutectic to be much better as it took into account other elements like manganese and chrome as well. Our DualCup© system uses two cups, one with tellurium and the other without to compare the inoculated iron with a fully carbidic iron. So our factor was $T_{E_{\text{gray}}} - T_{E_{\text{white}}}$ or the temperature of the gray eutectic as measured by a plain thermal analysis cup minus the lower temperature of the white eutectic. The gray eutectic will normally show undercooling so the proper eutectic is taken as the TER or TEG (temperature of eutectic recalescence or temperature of eutectic growth)—both are the same and are the best estimate of the true eutectic temperature for the iron sample. If a foundry is pouring a narrow range of iron, the process can be simplified by looking just at the C.E. and the recalescence in a plain cup and equations fine-tuned to that iron, or if need be to a few different irons. This reduces the sample costs by half. Our paper was demonstrating that the process worked over a large range of chemistry which is generally not needed in a production foundry.

**Comparing multiple causes**

When we look at multiple causes and their partial correlations, the sum of the correlations will occasionally be greater than 100% (unity). So you might find that the sum of the partial correlations for chill might be 75% + 28% = 103%. This is called autocorrelation. Factor A and B both moved in unison, so the math could not tell which one or how much of each was causing the effect. A method called “trivariate regression” takes this autocorrelation into account and factors it back out giving us again a total correlation slightly less than 100% and a useable standard error. Beyond that you can use multivariate stepwise regression or linear regression techniques to add in more variables. These techniques are generally beyond most people’s math abilities, so we resort to computers.

**How good is the answer?**

In common speak: what is the “plus or minus” of the answer? If we say that the Chill is +/- 3 and our target is 3, then the answer is no better than what a dart board will give. But if the answer is +/- 0.3, that is generally better than a technician will do. The math of correlation gives a value called the estimated standard error or variance. In most cases, one needs to ask the question—can I live with the standard error of the proposed correlation or do I need to seek a better explanation of the cause and effect?

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2 The measured eutectic temperature can vary with rapid cooling rates. The “Growth Temperature” as used by Bäckerud acknowledges this. With a properly filled cup, we believe that we do achieve a correct eutectic temperature for the sample.
Finally, statisticians use a test called the k-factor to estimate how confident they are that their answer is within the standard error. This test depends on the degree of correlation and the number of measurements made. In this test, you should, at a minimum, be above 90% confidence, and preferably in the 95% confidence range.

**Correlation applied to Chill**

So let’s call the effect “Chill”. What are some possible causes of chill that can be related to thermal analysis?

1. The Liquidus possibly has some effect. The liquidus temperature (TL) is proportional to C + Si/3 + P/2 + Mn/5 – Cr/9 plus some other minor elements $^3$.
2. The Eutectic also probably has some effect, but there are two primary eutectics to consider: the gray eutectic and the white eutectic. The gray (stable) eutectic (TSE or $T_{E_{gray}}$) is the temperature that the bulk of gray iron forms at, while the white (meta-stable) eutectic (TME or $T_{E_{white}}$) is the temperature that the carbide iron forms at. The temperature of the eutectic is determined by the total chemistry including manganese, chrome and other elements. The closer these two eutectics are, the easier it will be to form carbides.
3. Undercooling: the eutectic commonly is subject to undercooling—e.g. the temperature dips down below the eutectic, then heats back up (recalescence) as the formation of graphite releases energy. While this reheating may redissolve some of the carbides formed, in practice the actual amount is negligible. It takes time to redissolve carbides. The temperature dip is called undercooling, and the maximum undercooling is called TEU or temperature of eutectic undercooling. The cause of the undercooling is the energy needed to start the graphite formation. This energy is lowered by catalysts; as inoculation is increased, the separation of TER and TEU and therefore the recalescence is reduced.

So, one could investigate a relationship or correlation between chill and the above measurements as Chill is a function of Liquidus, Gray Eutectic, White Eutectic, Gray-White Eutectic, and Recalescence or

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Chill = (k_1 \times TL) + (k_2 \times TSE) + (k_3 \times T_{E_{white}}) + (k_4 \times (T_{E_{gray}} - T_{E_{white}})) + (k_5 \times (TER - TEU))
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and possibly some more items.

In my paper of 1996, we investigated the factors of TL and $T_{E_{gray}} - T_{E_{white}}$ and found strong correlations across wide ranges of chemistry. Others have copied our 1996 method, and some have come up with some less complete methods using only the recalescence. This of course is simply looking at inoculation and not chemistry. If your chemistry doesn’t vary, you might be okay with this solution. But if the chemistry changes significantly then the equation will need to be adjusted.

$^3$ ASM Handbook, Vol 15, Castings, 1992 version *Thermodynamic Properties of Iron-Based Alloys*, D.M Stephenescu, pgs 68, 69 and conversation with author to correct some typos in publication (Mn factor is 0.27 not the 0.027 published).
What can (will) go wrong?
Let’s look at what is wrong with this method of looking for any and all correlations and then just using a bivariate model. The first problem is called happenstance. If you run a tight series of tests with all the same values, you are not going to be prepared for what happens when the conditions move out of this comfort zone. Say all of your tests are taken from a single holding furnace and you vary the inoculation. The carbon and silicon and other main elements remain the same, and the relationship or equation you come up with will only be valid for an iron of that chemistry. Vary the chemistry and your equation fails. Here is some data from the 1996 paper for chill ranges from 1 to 7 mm:

<table>
<thead>
<tr>
<th>Liquidus</th>
<th>TEU - TME</th>
<th>Chill in mm</th>
<th>Calc. Chill</th>
<th>Error</th>
</tr>
</thead>
<tbody>
<tr>
<td>2267</td>
<td>95.4</td>
<td>1</td>
<td>0.945</td>
<td>-0.055</td>
</tr>
<tr>
<td>2269</td>
<td>72.3</td>
<td>3</td>
<td>2.806</td>
<td>-0.194</td>
</tr>
<tr>
<td>2267</td>
<td>81.5</td>
<td>2</td>
<td>2.056</td>
<td>0.055</td>
</tr>
<tr>
<td>2286</td>
<td>23.0</td>
<td>7</td>
<td>6.874</td>
<td>-0.126</td>
</tr>
<tr>
<td>2275</td>
<td>67.4</td>
<td>3</td>
<td>3.243</td>
<td>0.246</td>
</tr>
<tr>
<td>2131</td>
<td>57.8</td>
<td>3</td>
<td>2.927</td>
<td>-0.073</td>
</tr>
<tr>
<td>2207</td>
<td>37.1</td>
<td>5</td>
<td>5.151</td>
<td>0.151</td>
</tr>
</tbody>
</table>

This was a sample from a normal small parts foundry that ran about a 3 mm chill. As the separation between the gray iron curves undercooling (TEU) came closer to the white eutectic (TME) our chill increases. We varied the inoculation and the sources of the iron (base and final) to get a spread in results. First let me say that this is a very small sample. Second, after 20 years more experience, we have better techniques today than a simple bivariate regression. But let’s look at how good this data really is.

**Sigma = Square Root of ((Sum (X^2) – (Sum(X)^2/Count))/(Count -2))**

Note: because the sample size is small, we use Count-2. For large samples we would use Count-1.

**Sigma = Square Root ((0.148208 - 0.000016/7)/5) = 0.17216603**

So at 6 sigma the results are +/- 0.516498 mm chill—actually pretty good and probably better than the average foundry tech can read a wedge without an electronic caliber and magnifying glass (what we used to reduce operator error).

Methods of Correlation
The very simplest of correlations is a bivariate or least squares regression and solves the equation Y = m*X + B from our high school days. This method is used in MeltLab to solve the AFS silicon calculation. The next level is a trivariate regression that is about 4 times as complex but solves the equation Y = k1*X + k2*Z + k3. This form is used in MeltLab to solve the BCIRI silicon calculation and usually yields a standard error that is 25% smaller than the AFS method.
As more factors are added to the equations, each additional factor will improve the correlation and reduce the standard error. One should be careful to only include the new factor if there is a significant improvement in the correlation. Each new factor will reduce the degrees of freedom in the equation (statistician talk) and therefore always improve the equation. Don’t include the trivial improvements; they are probably just happenstance and not real.

**Stepwise Regression Analysis**
The next step up is stepwise regression analysis. In this form, you take the best correlation variables, calculate the error, and then correlate the error with the unused causes to improve the correlation. This method sometimes has problems with autocorrelation, or when two variables are dependent on each other or both move in the same way during the measurement trial. The math cannot sort this out and you don’t capture the complete effect of those variables.

**Linear Regression**
The final method is linear regression, which is the most complex form and requires the most test data. As they say, it takes a computer and sometimes one is not too sure if it was the garbage in that is causing problems. There will always be some residual error in the calculation because the measurements have what we call gauge error or measurement error caused by people, instruments and procedures. Of course, before trying any correlation, be sure that you minimize your testing error by reviewing procedures, calibrations and training.

The best method for doing correlation analysis is to use all the above tools as needed. Before jumping to the most difficult method, prove that there something there to correlate with a simple bivariate regression. Then once the actual causes have been identified, remove the autocorrelation by moving up the latter to trivariate and even linear regression tools if needed.

If you have further questions or need help analyzing data, please let us know.

David Sparkman, August 2015