Metallurgical Comparisons between Operating Conditions, Inoculant Types and Fade Effects in Gray Iron

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ABSTRACT

Inoculant testing has been conducted in two operating foundries with different melting systems (electric vs. cupola). A series of gray iron (GI) ladles were inoculated with various generic inoculants and at different addition rates. The ladles were held for up to 22 minutes and samples were extracted approximately every 2 minutes. Samples were examined for thermal analysis properties and microstructure evolution. The investigation has shown that inoculants fade differently and that the various inoculants behave differently in the two melting systems.

INTRODUCTION

The primary objective of gray iron (GI) inoculation is to produce a shrink-free casting with a microstructure with a maximum of Type A graphite, no carbides and excellent machinability.

It is established that inoculant effectiveness degrades (fades) in GI as the pouring ladle is held over time. Skaland writes, “The principal effects of fading are … to cause greater undercooling to take place during eutectic solidification and to lead to a greater tendency for chilling in grey and ductile irons, particularly in thin sections (and) to reduce the number of eutectic cells growing in flake graphite irons resulting in less uniform size and distribution of graphite in the castings and a reduction in mechanical properties” (Skaland, 1992). Olsen believes the fading of inoculant to the “coarsening and growth of micro-inclusions, also called the Ostwald Ripening Effect. The driving force for this coarsening is a reduction in the specific surface area of the inclusions, thus reducing the total energy of the system” (Olsen, 2004).

Fading of inoculant has been demonstrated in various measurable ways. Inoculant fade was demonstrated in tensile strength by Datta, who states, “Prolonged holding of iron after inoculation is detrimental to tensile strength of iron … (and) the drop in tensile strength is primarily due to progressive increase in Type D graphite and ferrite in the structure with increase in holding time.” Datta also observes, “Besides formation of undercooled graphite and ferrite, prolonged holding of iron also promotes formation of carbide” as measured by casting hardness (Datta, 1977). Fuller measured drops in cell count over time, among other parameters. However, Fuller goes on to write, “There is not a common relationship between eutectic cell number and chill for all inoculating materials (Fuller, 1979). Skaland agrees with this assessment, “An inoculant which gives a high eutectic cell number is not necessarily the most effective in reducing chill” (Skaland, 1992).

Inoculation effectiveness depends on many operating conditions, including chemistry. Skaland writes, “The effects of inoculants may vary according to the composition of the iron, particularly if it has a low sulfur content” (Skaland, 1992). Also, Chisamera writes, “Eutectic Undercooling and Recalescence degrees as main solidification parameters were connected to aluminum level”(Chisamera, 2004). Based on those remarks, one should also expect different fading characteristics of the same inoculant under different operating conditions, such as iron chemistry.

It is firmly established that inoculation mechanisms vary widely between inoculants. Comparing nuclei (complex inclusions of the type MnS) of irons inoculated with Sr- and Ca-FeSi, Riposan writes, “Important elements such as Ca and Sr was (sic) found to distribute differently in the inclusion volume” (Riposan, 2001). Because the active ingredients in inoculants vary in behavior so widely, it is logical to expect different fading characteristics in the same iron for different inoculants; these inclusions are the same ones referred to by Olsen (Olsen, 2004).

Other studies have compared the fading of different inoculants. Skaland writes, "The barium containing inoculant … produces a high initial number of nucleation sites. Compared to other inoculants, it maintains a high number of nucleation sites throughout the holding period" (Skaland, 1992). Fuller concurs in a different study, "With the exception of barium containing inoculants the fading rate decreased with holding time for the first ten minutes. Thereafter fading almost ceased." However, Fuller also adds that "Irons inoculated with strontium containing ferrosilicon which always had the lowest cell number also had the lowest chilling tendency" and acknowledged that cerium (Ce) provided better chill reduction than did barium (Fuller, 1979).

Ultimately, the effectiveness of an inoculant is dependent on the desires of the foundry. While one foundry might desire chill prevention first and foremost, another foundry might never have a chill problem and therefore they seek to maximize tensile strength with inoculation. The relevance of inoculant fade is likewise unique to the foundry.

EXPLANATION OF THERMAL ANALYSIS TERMS

Thermal analysis of iron samples was done in this study with the ATAS® (Adaptive Thermal Analysis System) method. In thermal analysis, a sample of iron is poured into a sand cup containing a thermocouple. The metal cools and begins to solidify. There is a thermal arrest when the first austenite nucleates (Fig. 1, [Sillen, 2003]). This is the liquidus temperature (TL). The sample continues cooling, austenite continues nucleating and the liquid iron grows richer in carbon content until the sample begins eutectic freezing. This is followed by another arrest, the eutectic temperature or TElow. Graphite forms, releasing the latent heat of solidification, and the temperature rises to a peak. This peak temperature is called TEhigh. The difference between them is called the recalescence (R). The sample continues cooling until it is solid. The last temperature of liquid iron is called the solidus (TS). Further analysis of the curve provides Graphite Factor 1 (GRF1), which is an indication of overall eutectic graphite precipitation during eutectic freezing after TEhigh. The angle of the first derivative of the cooling curve at the end of freezing represents Graphite Factor 2 (GRF2).

This technology can be useful in predicting defects such as carbides and shrinkage; for example, if TElow or TS fall below the white eutectic temperature, then carbides will, by definition, form. Sillen explains further, "A low (TElow) temperature indicates that the nucleation is less effective …(and) also means increased risk for chill and macro-shrinkage … If TS is too low it can (identify a risk for) inverse chill … Recalescence is a measure of the initial crystallisation rate of eutectic … the precipitation of eutectic … causes the temperature to increase … high recalescence (may indicate excessive) precipitation rate. The consequence is an expansion ... (that) can cause mould wall movement and also contribute to penetration problems. A good inoculant should reduce recalescence" (Sillen, 2003). A high GRF1, indicating more eutectic graphite value, means the iron is more shrinkage resistant. A lower value of GRF2 indicates more precipitation of graphite at the very end of freezing, leading to an iron that is more resistant to microshrinkage.

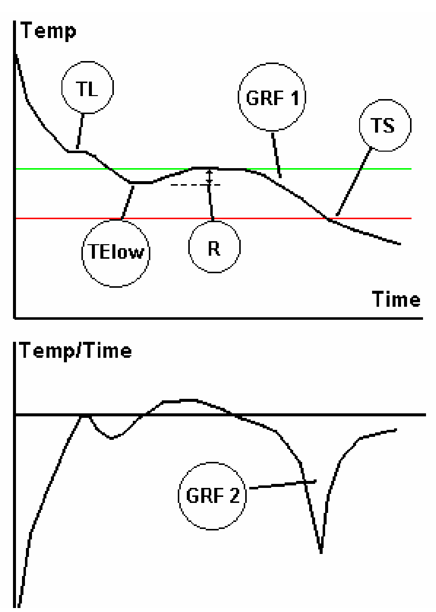

Fig. 1. Example of a cooling curve in hypoeutectic iron is illustrated. (From R. Sillen, ATAS® Manual, 2003).

EXPERIMENTAL PROCEDURE

Table 1 lists the inoculants used in this study.

Table 1. Specifications for Inoculants Used in This Study

Inoculant A
Strontium-Bearing 75% FeSi
Inoculant B
Calcium-Bearing inoculant (note: inoculant based on 50% FeSi at Dalton and 75%FeSi at John Deere)
Inoculant C
(Strontium, Zirconium)-Bearing 75% FeSi
Inoculant D
(Manganese, Zirconium, Calcium, Barium)-Bearing Inoculant
Inoculant E
(Barium, Calcium)-Bearing, 75% FeSi

At Dalton-Kendallville (Dalton)(from now on referred to as Foundry 1), GI was melted in a cupola and held in a 40-ton channel induction holding furnace. It was then tapped into a 2000-lb ladle and inoculated during tapping with an addition of 4.1 lbs of Inoculant A per 2000 lbs (0.205wt%) of iron. Immediately after inoculation, the ladle was sampled with chill wedges, test bars (type B), and thermal analysis cups. The ladle was then covered and set aside. Thermal analysis samples were then taken every two minutes for approximately 22 minutes. Additional chill wedges and test bars were poured as well, though only at (approximately) 12 and 22 minutes after inoculation. This was repeated with Inoculants B-E. The actual solidified thermal analysis samples themselves were then examined for cell counts and flake size.

This study was repeated at John Deere (from now on referred to as Foundry 2). The actual tests were largely the same, with only a few notable differences:

- The metal was melted in a coreless induction melting furnace and the holding furnace is an 80-ton channel furnace.
- Pouring ladles were 6000 lbs.
- Inoculant was added at a rate of 19.8 lbs per 6000 (0.330wt%).
- Chill wedges and test bars were poured at different intervals (immediately after inoculation, 4 minutes after inoculation, and 12 minutes after inoculation).
- The length of fade was shorter due to loss of pouring temperature.
- Inoculant B was based on 75% ferrosilicon instead of 50% ferrosilicon.
- Iron chemistry was different as shown in Table 2.

Table 2. Chemical Analysis of Dalton (Foundry 1) Iron Compared to John Deere (Foundry 2) Iron

	Foundry 1	Foundry 2
C	3.50	3.45
Si	2.05	2.01
Mn	0.47	0.58
S	0.116	0.065
P	0.078	0.015

The actual chill samples taken at each foundry also differed slightly. They are depicted in Fig. 2 (not to scale). In an effort to reconcile the two tests, the area of chilled iron was calculated for each sample.

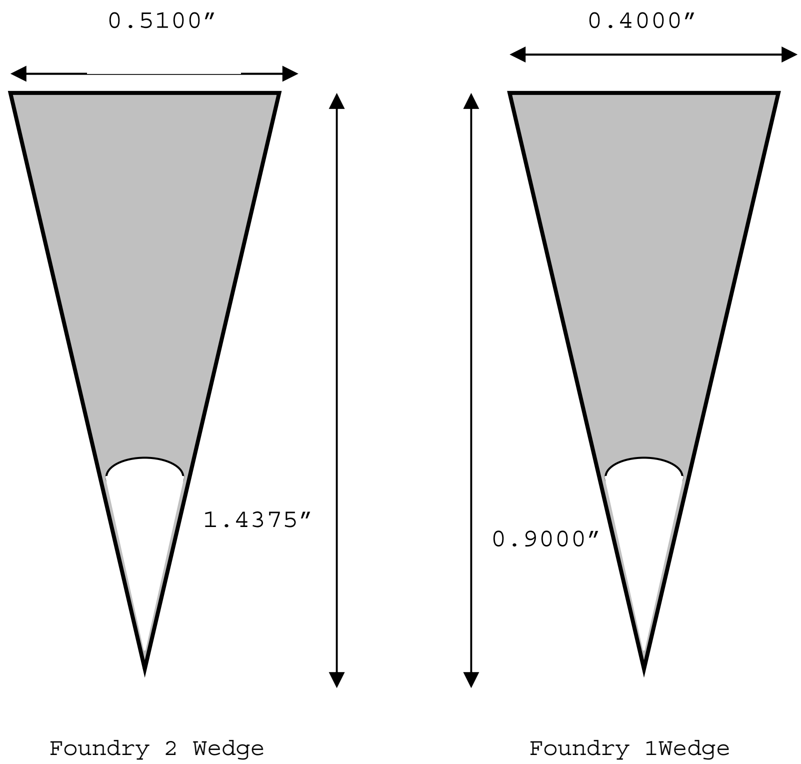

Fig. 2. The comparison of chill wedge geometry, used in study, is illustrated.

RESULTS FROM FOUNDRY TESTING

Due to technical difficulties, this study was unable to draw significant thermal analysis data from the second half of many cooling curves at Foundry 2. As such, determining trends in TS, GRF2 and other such parameters is impossible.

Figure 3 shows the drop in pouring temperature over time for both trials. This data represents the very first temperature registered by the thermal analysis cup. The trends show mostly linear drops in pouring temperature. Foundry 1 experiences more heat loss than does Foundry 2. This is likely the result of a smaller pouring ladle at Foundry 1 that could necessitate higher starting temperatures.

Figure 4 shows the change in tensile strength over time for all inoculants in both foundries. The ultimate tensile strength (UTS) mostly drops over time at both foundries. This confirms the results found by Datta (Datta, 1977).

Inoculant fade appears to be linear with Inoculant A at both foundries. Inoculant E displays a more gradual decline in UTS than Inoculant A with no rise in the middle of the ladle at both foundries.

However, Inoculants B, C and D mostly display an improvement in UTS between the first and second samples, followed by deterioration in UTS. This could be a function of inoculant dissolution and distribution within the metal. Alternatively, it could be the result of a loss in pouring temperature causing the tensile bar to approximate a thinner section after a few minutes of hold time, but inoculant fade seems to overwhelm this effect in the long run, resulting in a final drop in UTS. The end result is that Inoculants C and D display the least deterioration in both foundries, though this does not mean their initial or average strengths were the highest.

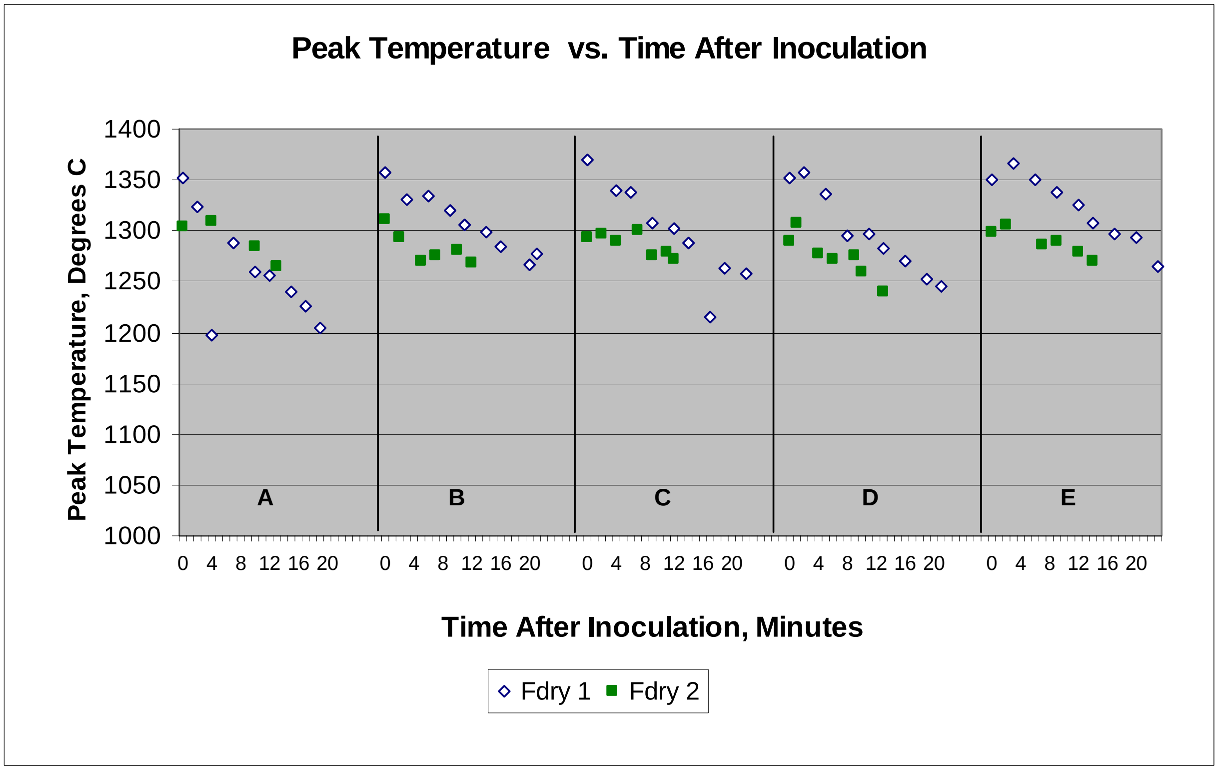

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Fig. 3. Peak temperature over time is graphed.

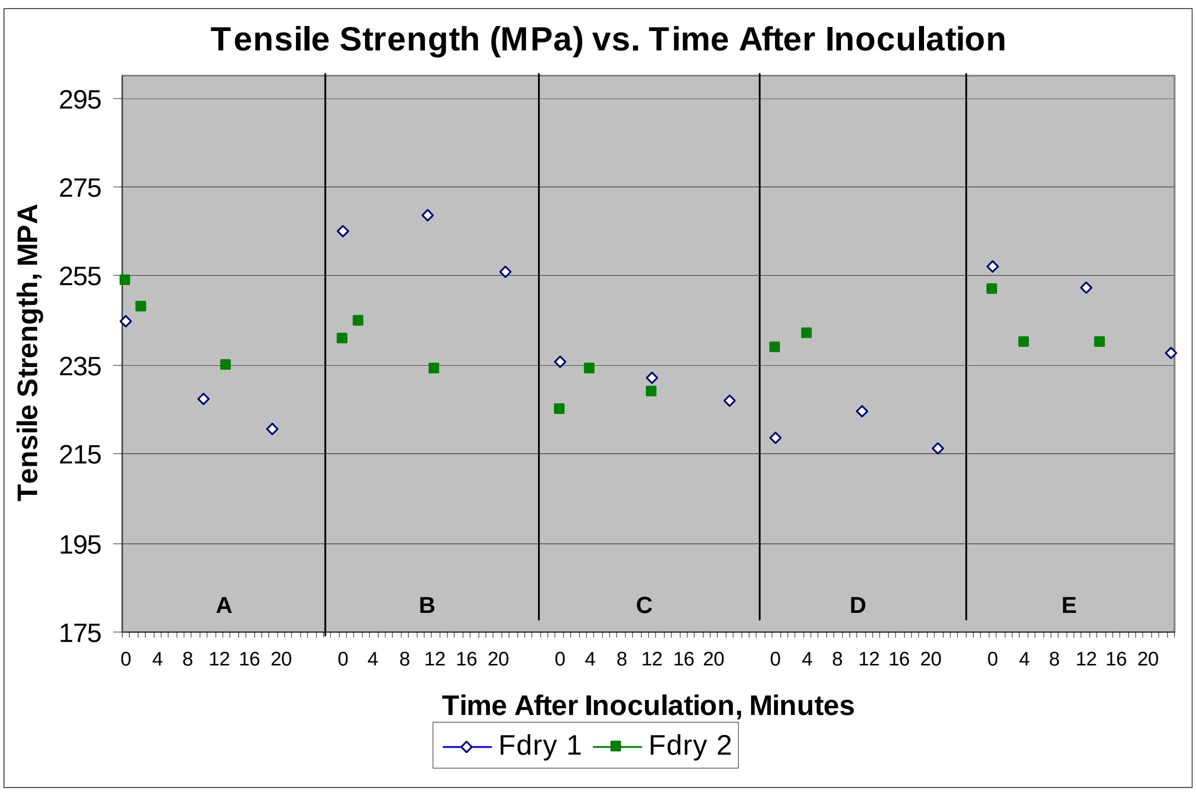

Fig. 4. Tensile strength over time is graphed.

Figure 5 shows the changes in TL as well as tensile strength over time with each of the six inoculants tested in both foundries. TL and UTS at Foundry 1 appear to reflect that Inoculant B provides less graphitization at Foundry 1, resulting in an artificially low carbon equivalent (CE) condition. It is logical to believe that this would be revealed in GRF1 and this is indeed the case (Fig. 6). The "T" statistic, based on a 95% confidence level, shows that GRF1 is significantly lower with Inoculant B compared to Inoculant A. These results are further supported by the difference in ACEL (Active Carbon Equivalent) between these two ladles (Fig. 7). The difference in ACEL is only partially the result of the fact that Inoculant B was based on 50% FeSi instead of the more common 75% FeSi; the balance of the difference in ACEL can only be the result of a difference in graphitization between inoculants. Overall, there appears to be a clearer correlation between TL and UTS between inoculants at Foundry 1, with little to no such correlation at Foundry 2 (Fig. 5). Figure 6 shows that GRF1 seems to have no relationship with time after inoculation. Figure 7 shows clearly that inoculant choice impacted ACEL significantly at Foundry 1, with little to no impact at Foundry 2. It also shows that ACEL clearly varies more with inoculant choice at Foundry 1 that at Foundry 2.

Maximum flake size was studied because of the impact of this parameter on tensile strength. As stated by Bates, "strength was found to be a function of the reciprocal of the square root of the flake length" (Bates, 1991). However, this study showed no clear correlation between maximum flake size and tensile strength (Fig. 8). Inoculants A, D and E only displayed flakes size getting smaller with hold time at Foundry 1. This is likely the result of colder pouring temperatures and this result is not reflected in UTS. Furthermore, there was no evidence of systematic changes in maximum flake size between inoculants or over time.

Figure 9 shows the changes in eutectic cell count over time. It suggests that the Foundry 1 iron dropped in cell count over time while the Foundry 2 iron remained mostly unchanged. Both of these observations are independent of inoculant choice. The correlation between cell count and properties (such as chill) is problematic already, and this study does not suggest any relationship between cell count and any other characteristic.

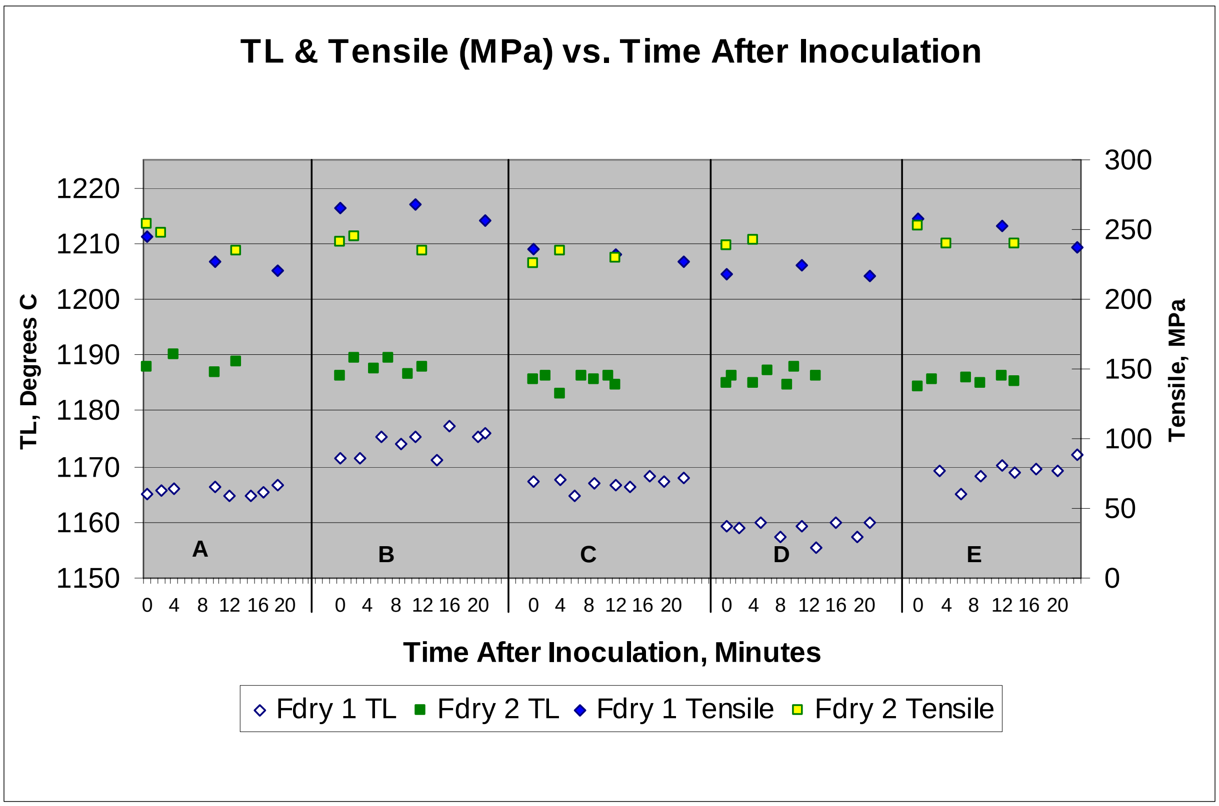

Fig. 5. TL (liquidus) and tensile strength over time is graphed.

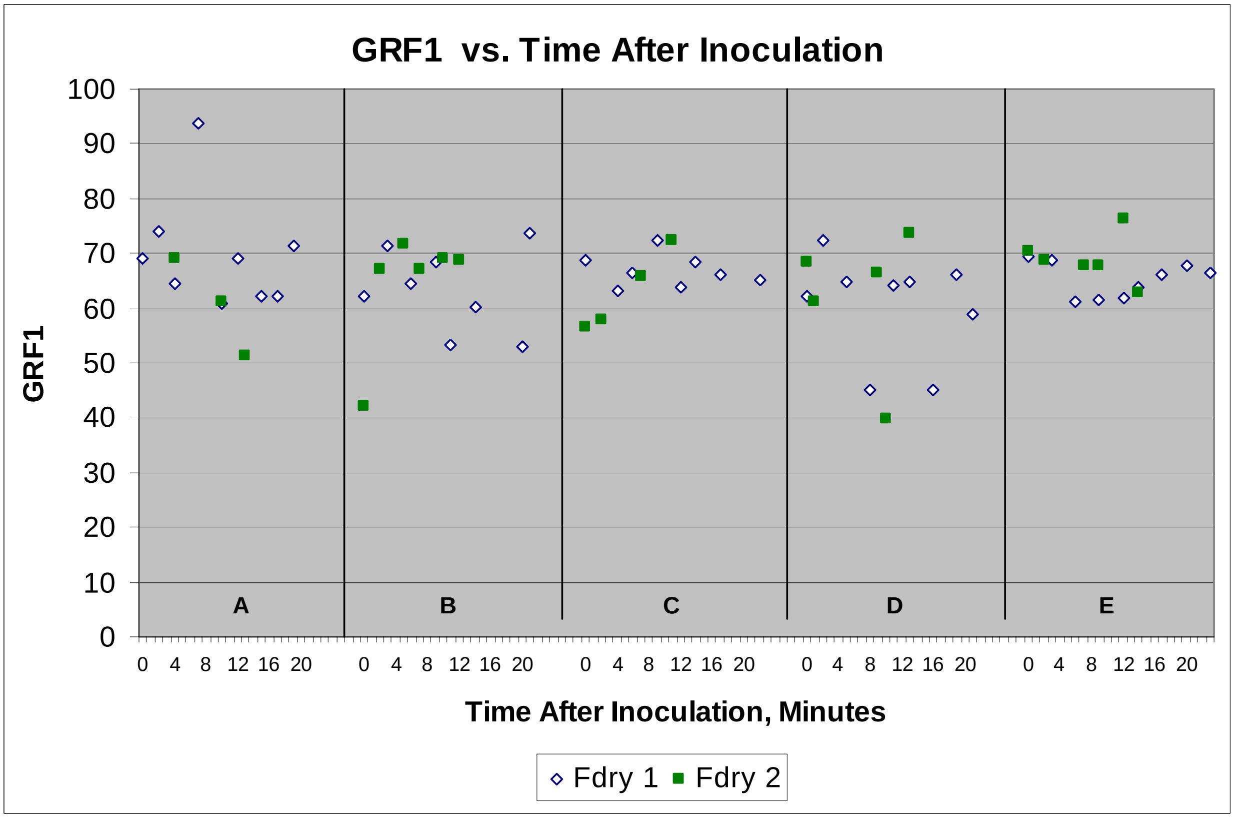

Fig. 6. GRF1 over time is graphed.

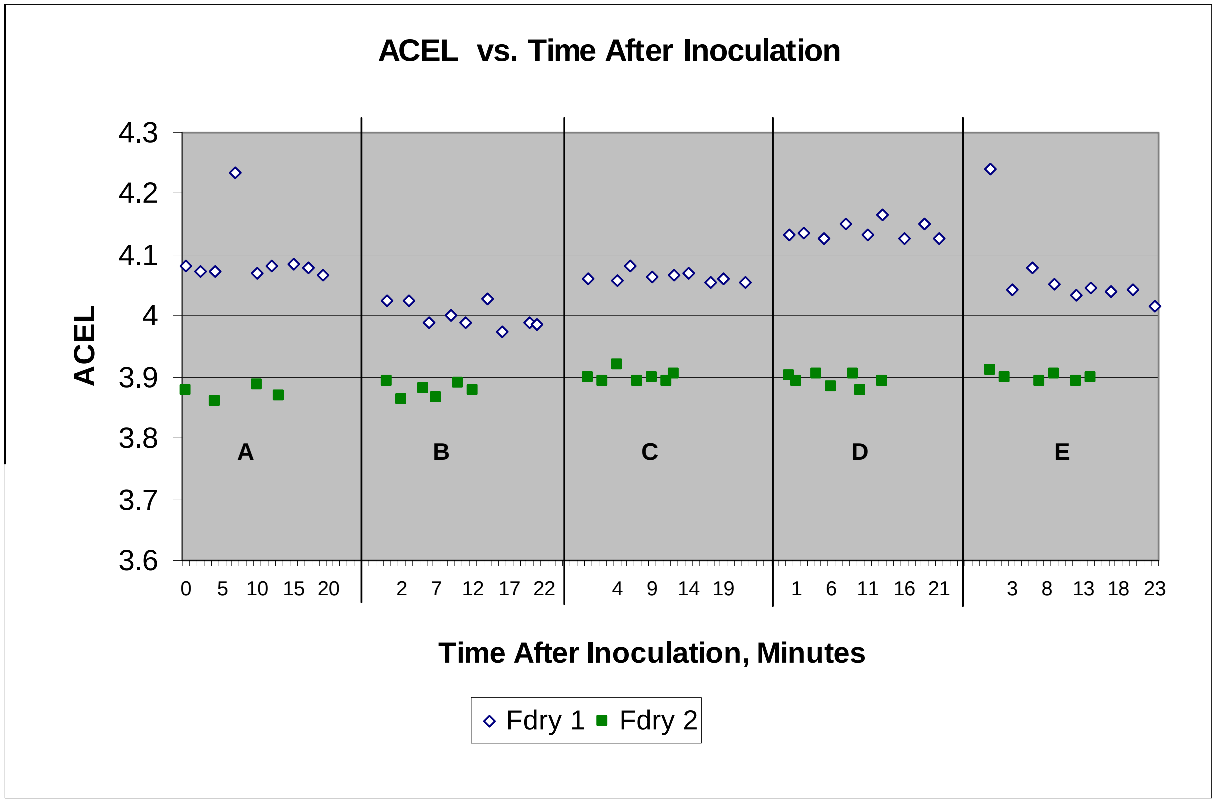

Fig. 7. Active carbon equivalent (ACEL) over time is graphed

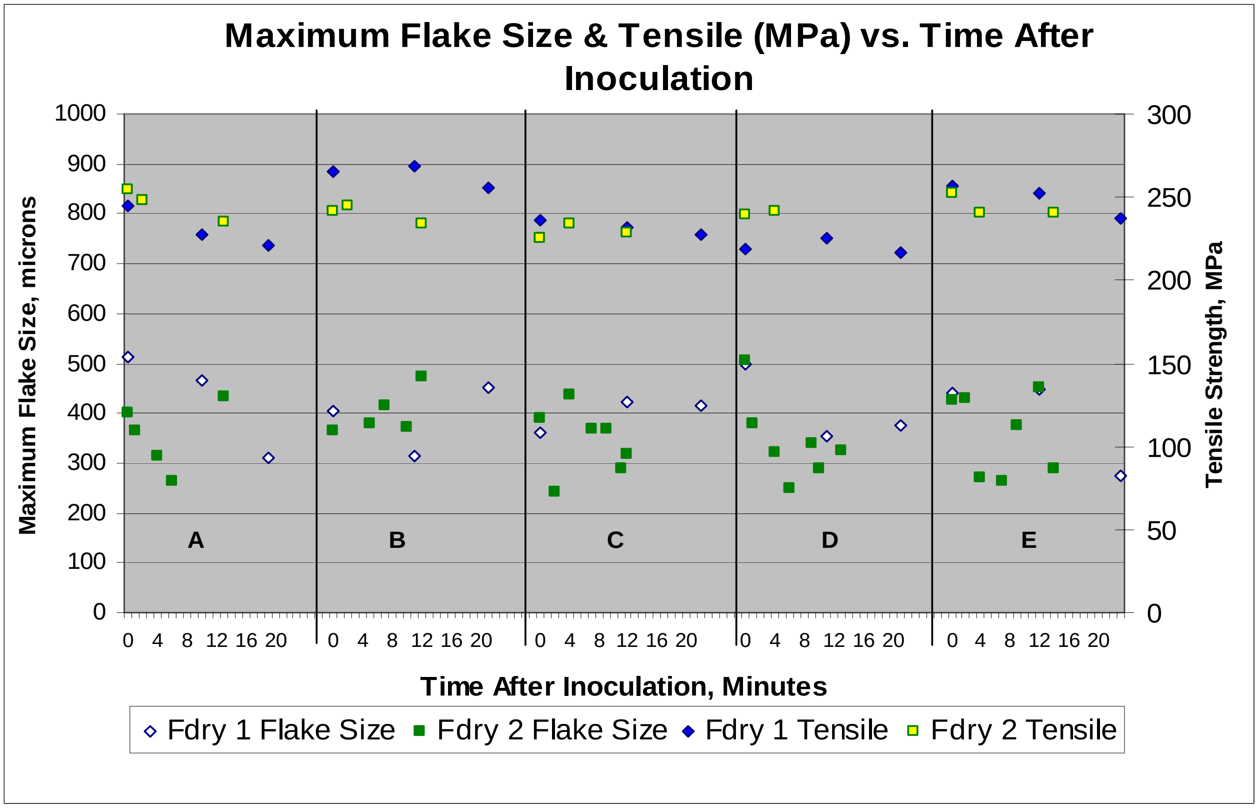

Fig. 8. Maximum flake size and tensile strength over time are graphed.

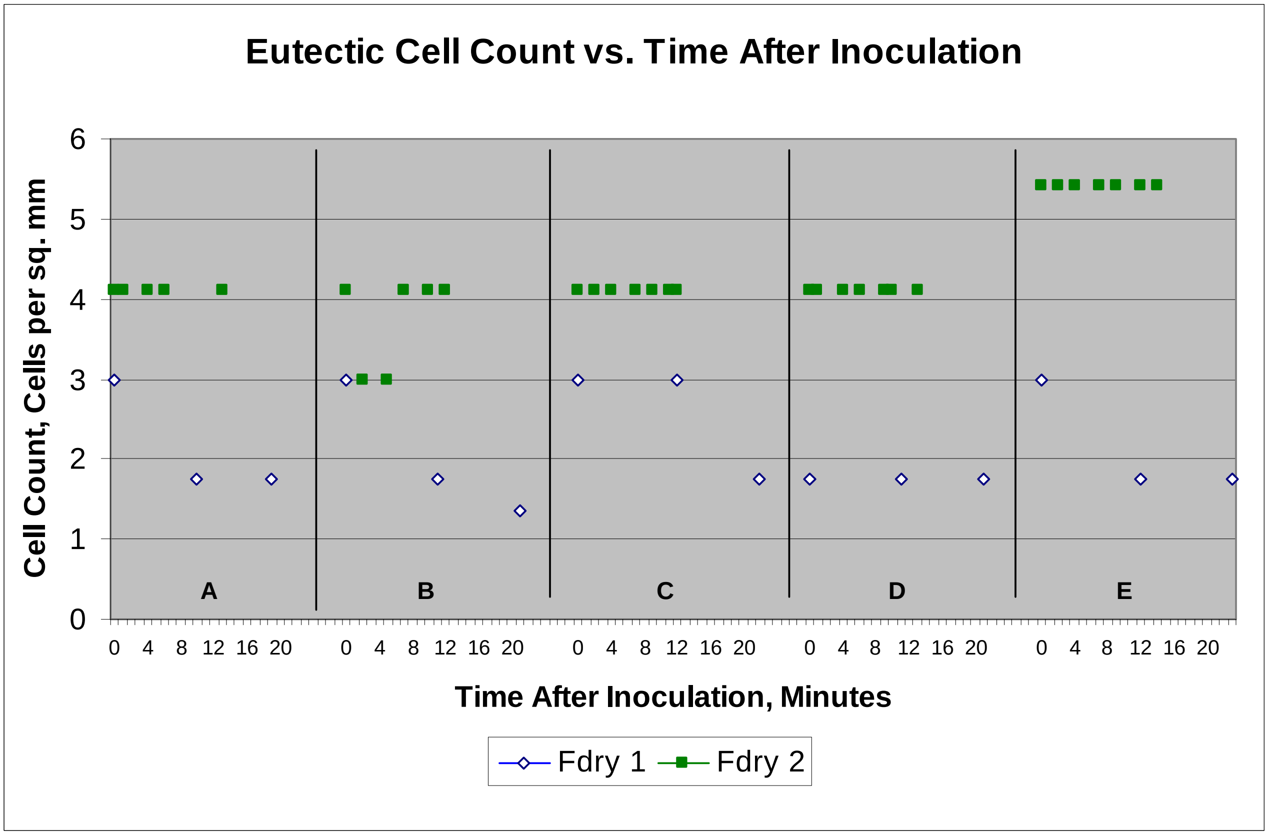

Fig. 9. Eutectic cell count over time is graphed.

Figure 10 illustrates the relationship between TElow and chill level at Foundry 1. Chill level clearly rises over time regardless of inoculant. Inoculant A provides the best chill resistance regardless of time interval with Inoculant C in second place. Inoculants B, D and E show inferior chill resistance in the short run as well as the long run. In general terms, Inoculant D provides the highest TElow and Inoculant B provides the lowest TElow at Foundry 1. Over time, TElow shows the most change over time when using Inoculants A and D and very little change with the other three inoculants. This discrepancy between TElow and chill level suggests a section size effect between the chill wedge and the thermal analysis cup.

There is some scatter in both data sets at Foundry 2. A rise in chill level corresponds with a drop in TElow for Samples B C, and E (Fig. 11). Again, Inoculant A showed the lowest tendency to chill both in the long and short runs. Inoculants B and C provided the least chill resistance. Inoculant E provides the highest TElow followed by inoculant A.

Figure 12 shows the relationship between recalescence and time. Inoculant B appears to display an increase in recalescence at both foundries, as compared to the other inoculants studied. Inoculant D displays a decrease in recalescence over time at both foundries. No firm trends are apparent with the other inoculants.

Figure 13 represents a scatter chart made with data points from both foundries. The heats selected for this chart, by definition, were heats in which a valid chill wedge and a valid thermal analysis sample were both taken. Despite the discrepancy between TElow and chill discussed above, Fig. 13 suggests that a larger data sample might generate a clearer relationship between TElow and chill level independent of inoculant choice. This relationship is clearly stronger at Foundry 2 than at Foundry 1.

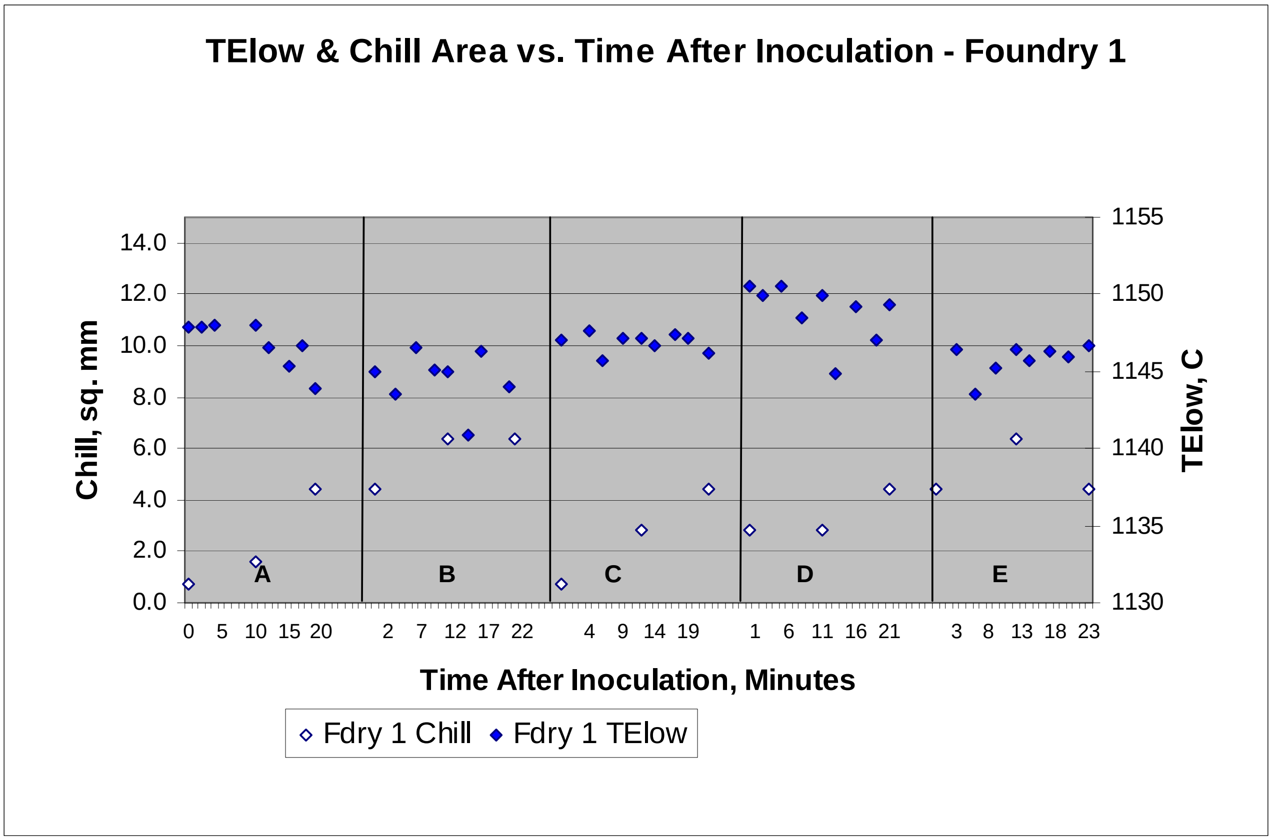

Fig. 10. This graph illustrates TElow and chill over time at Foundry 1.

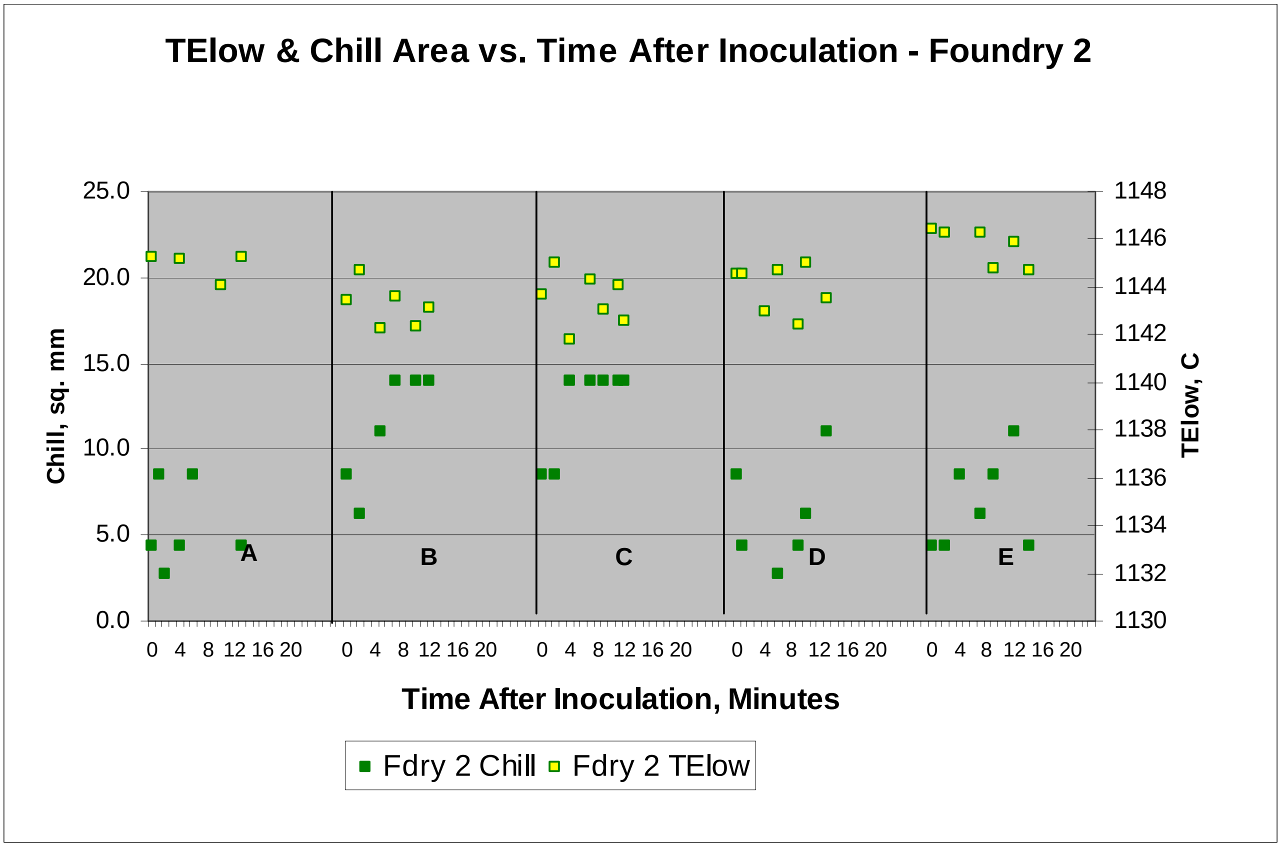

Fig. 11. This graph illustrates TElow and chill over time at Foundry 2

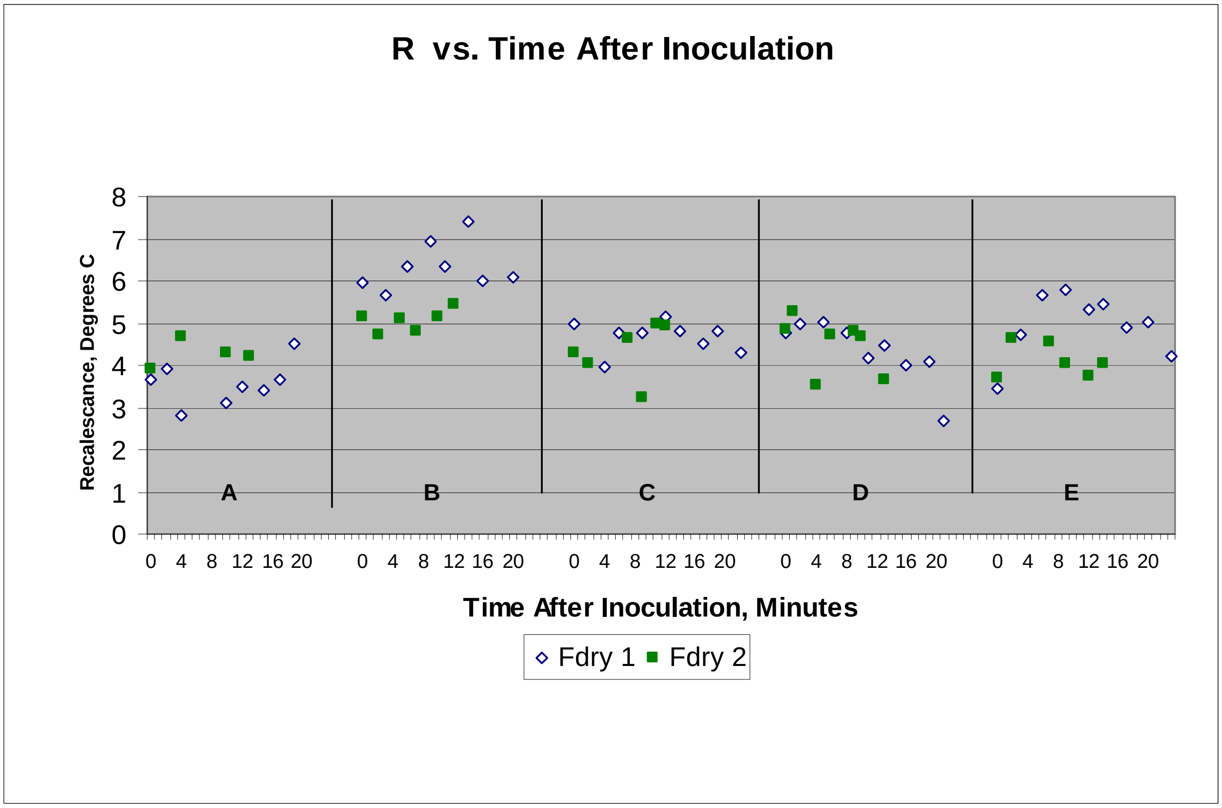

Fig. 12. Recalescence over time is graphed.

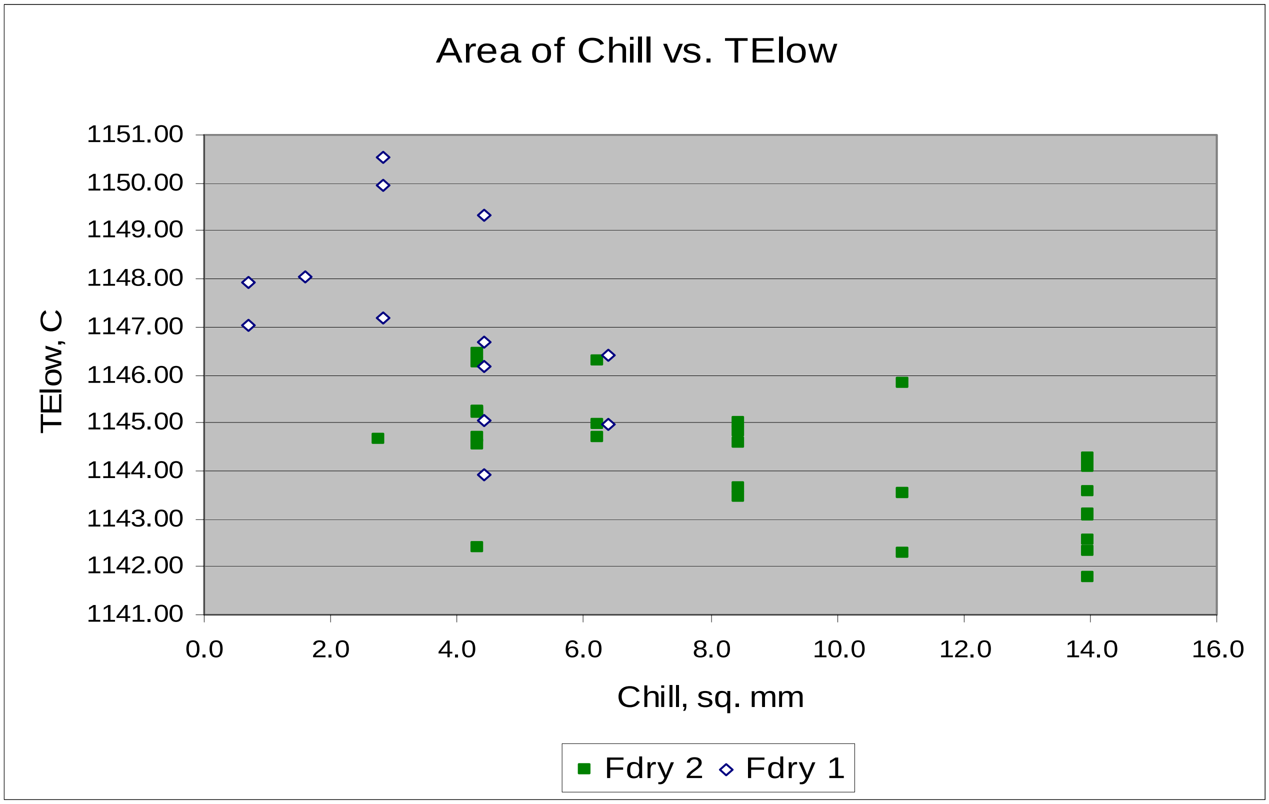

Fig. 13. Scatter chart of TElow Chill, independent of time and inoculant, is illustrated.

CONCLUSIONS

- This study has clearly shown that the selection of the correct inoculating system has an influence on the fading characteristics of the nucleation level in the iron. Two sets of conditions have been studied and these have given significantly different results. One of the main variables between the foundries was the base sulfur (S) level of the iron.
- Many factors affecting inoculation have been documented. However, advances in measurement techniques, such as thermal analysis methods, have enabled more accurate measurement to be made. Much more work needs to be done industry wide in this field, although it is apparent from this study that each individual foundry has it's own set of unique circumstances which dictate the choice of an inoculant.
- Foundry 1 experiences more temperature loss than does Foundry 2, but no definitive conclusion can be readily drawn from the effect of pouring temperature on inoculant fade. This is because pouring and inoculation temperature, while quantified here, is only one of the different operating conditions between the plants. This parameter could be an avenue of further research.
- At both the medium and high S levels, the rate of loss of UTS appears to be fairly consistent. Inoculant C shows the lowest rate of UTS deterioration. With three of the inoculating systems, including inoculant C, there appears to be a slight increase in the UTS during the first few minutes following the addition of the inoculant. While one could postulate that this is due to the greater rate of heat loss from the iron during this period, no conclusion may be drawn from the number of results available. Further work in this area needs to be done.
- Inoculant B provided a lower level of graphitization relative to the other inoculants at Foundry 1. This is reflected in the values seen for TL, GRF1 and ACEL. This artificially low ACEL led to a higher UTS value for Inoculant B. However, Inoculant B also generated higher chill levels and recalescence.
- The Foundry 1 iron displayed a clearer correlation between TL and UTS than did the Foundry 2 iron.
- ACEL is clearly impacted by inoculant choice at Foundry 1, and this impact appears to be smaller at Foundry 2.
- This study did not show a meaningful correlation between maximum flake size and UTS, even though the study by Bates found otherwise (Bates,1991). Conclusions about changes in flake size between inoculants, foundries and over time are uncertain.
- As stated earlier, the correlation between cell count and properties (such as chill) is problematic already and this study does not suggest any relationship between cell count and any other characteristic.

- Inoculant A performed best in chill resistance at both shops. There is a relationship between TElow and chill level in both foundries, though this is much clearer at Foundry 2 than at Foundry 1.
- Recalescence is a good measure of the effectiveness of an inoculant. As explained by Sillen earlier in this paper, too high a recalescence can result in mold wall movement and subsequent penetration and/or shrinkage problems (Sillen, 2003). In the examples examined in this study, inoculants A, C and E showed lower recalescence values. Inoculant E gave a good set of values at the lower S level.
- Foundries need to decide on their priorities, such as chill, UTS, shrinkage and fade as the main charateristics normally in deciding the choice of inoculant. This study, while limited, indicated that fading is to be taken seriously because chill, UTS and other properties will alter over time to a greater or lesser degree dependant on the choice of inoculant.
- Consistency in castings poured from a single ladle will vary as demonstrated and it is the job of the foundry engineer to minimize these differences to reduce costs and variation in post foundry operations.

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