

Trace elements and the control limits in ductile iron

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Since the invention and start of production of ductile iron in the 1940's people working in the area have tried to find a way to easily control the final properties of the cast product. For this several different equations calculating the effect of trace elements have been developed. There are equations trying to predict nodularity, pearlite percentage (and thus ferrite), segregation, balancing harmful trace element content and so on. This paper reviews some of these equations and discusses their appropriate fields of use. Equations for predicting the appearance of degenerate and chunky graphite and how to balance the harmful trace elements are also discussed.

Keywords: ductile iron, trace elements, pearlite, segregation

Introduction

Ductile iron is composed of elements that can be divided into four groups: major, minor, trace^{1,2} and alloying elements. The major elements are iron, carbon and silicon, minor elements are magnesium, oxygen and sulphur, alloying elements are typically copper, manganese and nickel (excluding Ni-hard and Ni-resist) while the rest of the elements are called trace elements. Trace elements are also often called tramp elements as in the ASM casting handbook³: "Contaminant in the components of a furnace charge, or in the molten metal or castings, whose presence is thought to be either unimportant or undesirable to the quality of the casting", while the Indian handbook defines trace elements as of such small quantity, usually too small for quantification.⁴ Not all trace elements can be classified as deleterious as some of them have a beneficial influence on the mechanical properties of the final casting. The common trace elements in ductile cast iron (Ce, Bi, As, Sb etc) appear in amounts appropriate for chemical determination while others are hard to determine (Sr, Ba) due to their segregation behaviour. Some of the elements have an additive effect (Bi, Sb, As, Pb)^{3,5} while others do seem to act alone (Zr, Sr).

Examples of typical trace elements and the change in the maximum amount found in ductile cast iron during a period of 30 years are given in Table 1. The content is based on Thielemann for years 1967 and 1998⁶ in Germany while the numbers (average values) from 2009 are from Europe, based on samples processed by Elkem AS. The empty boxes in the table are due to no values reported. For some elements, like Mo, the value is reported for ductile cast iron not intended for high temperature use (i.e. SiMo cast irons are excluded). Thielemann reported concentration limits for avoiding the detrimental influence of trace elements, as found in literature.⁵ These limits are listed in Table 2, where they are complemented with the maximum amount as recommended by Elkem AS.⁷

Equations developed for predicting nodularity are presented in the two next sections while those dealing with matrix structure as function of both trace elements and alloying elements are described in the following two sections.

Trace element effects on graphite structure

During the 1960's Thielemann⁵ studied the influence of different elements by using raw material from different suppliers and adding the elements he was interested in. The different melts were cast into samples with thicknesses 8-45 mm. He specifically studied the influence of Pb, Bi, Al, Sb, Sn, As, Ti, Cu, Mg and the rare earths since the rest of the trace elements were present in such small amounts that they were found to have no noticeable influence on the final ductile iron casting. He found that Pb and Bi are additive i.e. together they have a higher negative influence on the graphite morphology, while Bi alone in small amounts will have a positive influence on the nodule number. Pb and Bi have negligible solubility in iron while Sb, Sn, As and Cu have a low solubility in austenite while decreasing the carbon solubility in liquid iron.^{3,5} These latter elements have an additive effect as well. Ti and Al are depending on the cooling rate for their detrimental influence.

Thielemann developed a trace element evaluation number S_b for assessing the ability of the charge (i.e. this equation is only valid for calculations on the steel scrap, pig iron and returns used for producing the base iron) to give well-formed nodules:⁵

$$S_b = 4.4 \cdot w_{Ti} + 2.0 \cdot w_{As} + 2.3 \cdot w_{Sn} + 5.0 \cdot w_{Sb} + 290 \cdot w_{Pb} + 370 \cdot w_{Bi} + 1.6 \cdot w_{Al} \quad (1)$$

where w_i stands for the content in i elements, expressed in wt.%.

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Table 1: Reported typical maximum amounts of trace elements (wt.%) for 1967, 1998 and 2009

Element	1967 Thielemann ⁵	1998 Thielemann ⁶	2009 (Elkem AS)
Ti	0.2	0.013	0.017
Cr	0.08	0.177	0.121
Ni	0.07	0.843	0.073
V	0.11		0.010
W	0.012	0.026	0.004
Te	0.005		0.002
Mo	0.05		0.061
Co	0.012		
Nb		0.007	0.003
Al	0.014	0.041	0.008
Sb	0.009		0.004
As	0.038		0.006
Sn	0.012	0.041	0.005
Zn	0.006	0.093	0.005
Bi	0.0009	0.008	0.004
Pb	0.005	0.008	0.001
B		0.005	
Ce		0.008	0.006

Table 2: Concentration limits for detrimental influence of trace elements (wt.%) according to Thielemann⁵ and Elkem AS.

Element	Concentration	Elkem recommended maximum
Ti	0.04-0.10	0.2
Cr		0.1
Ni		0.2
V	0.05	0.02
W		0.03
Te	0.002-0.08	0.005
Mo		0.1
Co		
Nb		0.01
Al	0.08-0.3	0.2
Sb	0.002-0.026	0.01
As	0.02-0.125	0.01
Sn	0.005-0.13	0.15
Zn	0.01-0.10	0.05
Bi	0.001-0.03	0.01
Pb	0.002-0.011	0.005
B	0.005-0.01	0.01
Ce	0.02	0.02
Cu	0.5-4.0	1.5
Cd	0.01	
Se	0.03	0.002
Mg	0.08-0.10	0.03-0.06
Zr	0.01-0.10	0.01

Equation (1) is valid for residual Mg content 0.04-0.08 wt.% while the maximum concentration for the other elements is shown in Table 3. Comparing the maximum concentration limits for the validity of equation 1 with the numbers shown in Tables 1 and 2 the following can be remarked: lead is the only element where Elkem has a higher recommended maximum level in ductile cast iron. The other elements listed in Table 3 have a higher upper limit for the validity of equation 1 than the typical maximum levels listed in Tables 1 and 2 and thus equation 1 should still be valid for calculations for modern castings. When $S_b=1\pm 0.0625$ no correction of the charge is necessary for obtaining a ductile iron with a nodularity above 85%. As earlier mentioned the equation was developed during the 1960's by experiments on castings with wall thicknesses 8-45 mm for different pig irons (37 different variants, where 17 were specifically aimed for production of ductile iron, from around the world) in combination with returns and steel scrap. The work is based on 200 industrial heats and 163 laboratory melts. Within the different groups, containing either Bi and Pb, or Sn and As and Sb, or else Ti by itself, the effect of the elements was found to be additive. This synergy and the effect between the different groups were taken into account when equation (1) was developed.

Table 3: Concentration limits (wt.%) of the various elements for the use of equation (1).⁵

Element	Maximum
As	0.14
Sb	0.10
Sn	0.15
Pb	0.002
Bi	0.002
Ti	0.12
Al	0.27

Equation (1) is sometimes found in literature with the denomination “anti-nodularising”⁸ and almost always used for a final composition instead for a charge composition.⁹ For some publications it is difficult to assess the calculations of S_b due to insufficient information, and it is sometimes unclear what the trace element evaluation equation is used to assess.⁸ When the trace element evaluation number S_b is high ($> \sim 1.1$) balancing the amount of deleterious elements is necessary. Javaid and Loper, Jr. did extensive work in this area,¹⁰ since somewhat modified by Hansen et al.,¹¹ balancing the deleterious elements with the help of rare earths. The number of deleterious elements considered in the work by Javaid and Loper, Jr.¹⁰ has been increased by Labrecque and Cabanne.⁹

Using rare earth elements to control nodularity

It was quite early clear that it is possible to balance the deleterious trace elements by rare earth additions. Most of this work has been concentrated on Ce or Ce in combination with La. Javaid and Loper, Jr.¹⁰ and Lacaze et al.¹² investigated the ratios $(Ce+La)/(Sb+Bi+As+Pb+Te+Ti)$ and $(Ce+La)/Sb$ respectively, and found the balancing ratio to be 1 in the first case and 0.8 in the latter. Javaid and Loper, Jr. report the optimum amount of RE to be ~1.5 of the amount of added subversive elements or ~1 of the residual level of the final iron.¹⁰ Lacaze et al. present a developed expression as $(Sb+La)/(Mg+Ce) \approx 0.05$.¹² None of these seems to be able to give a reasonable result when checked against foundry trials. This might be due to the difficulty in determining the low level of Sb, as well as the rare earths. Looking back at Table 1 it is seen that a typical maximum level of Sb is in the range of 0.004. Often the reporting limit for this element is set at 0.003 meaning the detection limit is around 0.0003. The difficulty is obtaining calibration standards for the lower concentration range. The numbers for the rare earths/trace elements ratio are very often misquoted in literature i.e. the number mostly quoted is 1.5 for Javaid and Loper, Jr.¹⁰ while for Lacaze et al.¹² only 0.8 is mentioned. Javaid and Loper, Jr. pointed out the problem in using published work for reviews:¹⁰ incomplete data on processing, incomplete chemistries, etc, but still managed to produce balancing equations for subversive elements. Note however that there was a drawback in their reasoning in one point: the trace elements considered have an additive effect and thus the amount of rare earths needed for balancing should not decrease but increase, as pointed out by Hansen et al.¹¹ According to these latter authors, the equation describing balancing of trace elements by rare earths should write:

$$w_{RE} = 0.5037 \cdot \sum w_{sub,i} + 0.0037 \quad (2)$$

where w_{RE} is the sum of added RE (wt.%) and $w_{sub,i}$ is the content in subversive element i (wt.%). The subversive elements are Sb, Pb, As and Ti, whereas it is unclear in the work by Javaid and Loper, Jr. if Bi and Te should be included.

Javaid and Loper, Jr. did also calculate a more complex equation where wall thickness ϕ (expressed in inches) is taken into account:¹⁰

$$\frac{w_{RE}}{\sum w_{sub,i}} = 2.083 + 65.896 \cdot w_P + 0.783 \cdot w_{Si} - 39.09 \cdot w_{Mg} - 1.963 \cdot w_{Ni} - 0.176 \cdot \phi \quad (3)$$

Both of these equations give reasonable results as shown by Hansen et al. when calculated for a ductile iron.¹¹ It may be also worth mentioning that Wray found in his experiments that $0.1\%Ti = 0.7\%Si$, somewhat implicating that Ti could be tolerated if the Si content is decreased.¹³ Equation (3) could be amended accordingly.

Already in 1970 Thielemann⁵ found that overcompensation with Ce-mischmetal gave exploded graphite, as also recently reported by Ghergu et al.¹⁴ A simple evaluation of cerium adsorption on a graphite nodule is shown in the appendix. When comparing this calculation and assumptions with what seems to be a limiting amount of cerium in reality, when using charge material with low amounts of trace elements, the critical amount of cerium above which exploded or chunky graphite could appear seems to be of the order of 0.0029 wt.%. If the assumption that coverage of graphite by adsorption is the main mechanism for exploded or chunky graphite development, then a more precise calculation should account for all elements that can adsorb on it. Note however that chunky graphite does not evolve from exploded graphite, as seen in the paper by Ghergu et al.¹⁴

Löblich finds that Si, Cu, Ni, Ca and Ce will give chunky graphite in heavy section castings.¹⁵ Ni will give chunky graphite even in thin sections, while Ca will only give chunky graphite if added late in the melting process. Ce-mischmetal added to a heavy section casting free of Ce in the charge will give chunky graphite in the centre of the casting. Löblich also found that chunky graphite will always appear when the undercooling of the eutectic reaction is 4-10 K while normal nodules will be formed at an undercooling of 1-2 K.¹⁵ This is contradictory to the findings by Lacaze et al.¹⁶ Löblich concludes that the following factors influence the formation of chunky graphite:¹⁵ level of trace elements, number of nuclei, Si, Mn and S segregation, Ni level and long solidification time. The specific elements studied were Ce, Ca, Pb, Sb and As. It was concluded that these elements do not segregate at the casting scale. Finally, Löblich finds that Ce will be compensated by the presence of Pb, Sb and As and that the Si content (wt.%) in a 200x200 mm casting should be limited to a maximum value $w_{Si,limit}$ according to:¹⁵

$$w_{Si,limit} = \frac{2.26 - 1.5 \cdot \frac{w_{Ce}}{w_{Pb} + w_{Sb} + w_{As}}}{1.0 - 0.64 \cdot \frac{w_{Ce}}{w_{Pb} + w_{Sb} + w_{As}}} \quad (4)$$

This equation is valid for solidification times up to 50 minutes when the silicon content is lower than $w_{Si,limit}$. If the Si content is above this limit there is a danger for formation of chunky graphite. When checking this equation with other castings with or without chunky graphite no correlation between Si content and the appearance of chunky graphite can be found. Section size has an influence on acceptable limits of trace elements so that the level of cerium has to be lower in thick sections to avoid degenerated graphite.

Effect of trace and alloying elements on the matrix structure of ductile iron

A number of relations have been proposed to relate the composition of cast irons with the amount of ferrite or pearlite, at given cooling conditions. Björkegren¹⁷ has reviewed some of the works available at the beginning of the 1980's, listing those by Weis,¹⁸ Motz and Orths,¹⁹ Campomanes and Goller²⁰ and Thielemann.⁵ The first two works seem to have been dedicated to ferritic-pearlitic grades. Weis looked at the effect of low level elements on the mechanical properties of a standard nodular cast iron and tried to optimize the composition so that the product $A \cdot (R_m)^2$ —where R_m is the rupture strength and A elongation at rupture - would be either lower than 41,000 or higher than 48,000.¹⁸ As the ratio of ferrite and pearlite changed depending on the alloying content, Weis proposed the following expression for the pearlite fraction (% , with reference to the matrix only as all following relationships) in the matrix:¹⁸

$$f_{\text{pearlite}} = -2.45 + 768 \cdot w_{\text{Sn}} - 5.2 \cdot w_{\text{Si}} + 106 \cdot w_{\text{Mg}} - 142 \cdot w_{\text{Co}} + 138 \cdot w_{\text{Cr}} - 549 \cdot w_{\text{N}} + 101 \cdot w_{\text{Al}} + 51.6 \cdot w_{\text{P}} \quad (5)$$

Motz and Orths studied the detrimental effect of some elements on the ferrite fraction and obtained:¹⁹

$$f_{\text{ferrite}} = 92.3 - 96.2 \cdot w_{\text{Mn}} - 211 \cdot w_{\text{Cu}} - 14270 \cdot w_{\text{Pb}} - 2815 \cdot w_{\text{Sb}} \quad (6)$$

In a later work, Motz and Röhrig complemented their first study and provided the following relationship based on more than 100 heats:²¹

$$f_{\text{ferrite}} = -19.9 + 1.37 \cdot O_{\text{Gr}} - 3.01 \cdot [\% \text{SiO}_2] + 52.7 \cdot w_{\text{Si}} - 18.5 \cdot w_{\text{Mn}} + 814 \cdot w_{\text{S}} - 1818 \cdot w_{\text{Cr}}^2 - 11110 \cdot w_{\text{Pb}} \quad (7)$$

where O_{Gr} is the specific surface area of graphite and $[\text{SiO}_2]$ is the fraction of silica in the withdrawn slag.

For studying the effect of alloying elements in the case of ferritic grades, it has been suggested to use the product $w_{\text{Si}} \cdot S_{\text{C}}$, where S_{C} is called the degree of carbon saturation and is given by the product of the alloy content in carbon and the carbon equivalent CE: $S_{\text{C}} = w_{\text{C}} \cdot \text{CE}$.²² To the best of the knowledge of the authors, this suggestion has not found useful applications.

Campomanes and Goller studied the effect of carbide promoters on the microstructure of bars with different diameters.²⁰ They analysed 46 heats, using a small sized bar for evaluating the amount of carbide and a medium sized bar (1 in) for ferrite fraction. In this latter case, three bars showed an amount of carbide at 1% or less while all others were carbide free. Statistical analysis was first performed to look at the main effect of each element, and then multiple analyses were performed to characterize interactions. Though these latter analyses got a better correlation coefficient at 0.82 instead of 0.77 for the former, further use of their results will be made easier by considering the simpler linear analysis that gave:²⁰

$$f_{\text{ferrite}} = -7.565 - 13.187 \cdot w_{\text{Mn}} + 11.293 \cdot w_{\text{Si}} - 68.546 \cdot w_{\text{Ti}} - 13.546 \cdot w_{\text{Cr}} - 16.37 \cdot w_{\text{V}} \quad (8)$$

In the same lines of looking at the effect of pearlite promoting elements on ferrite fraction, some more recent works are worth of mention. Yu and Loper, Jr. investigated the effect of Cu, Mo and Ni on the formation of ferrite in as-cast nodular cast iron containing 0.5 wt.% Mn.²³ For this, they cast bars with diameters D ranging from 0.5 to 2.5 in, and their results show that no bainite or martensite was observed in any bars with diameter equal or larger than 1.5 in. Regression analysis showed a high sensitivity to the cooling rate leading to the following equation:

$$f_{\text{ferrite}} = 15.6 + 19 \cdot D - 11.9 \cdot w_{\text{Mo}} - 13.6 \cdot w_{\text{Cu}} - 8.1 \cdot w_{\text{Ni}} \cdot D - 15.9 \cdot w_{\text{Cu}} \cdot D \quad (9)$$

Yu and Loper, Jr. noticed that Cu is the most efficient of these three elements to decrease ferrite fraction, followed by Ni the effect of which increases significantly with section thickness as for Cu. Mo is seen to favour pearlite, but close examination of Yu and Loper, Jr. data shows this effect slightly decreases with section thickness. The effect of Mo on ferrite fraction is indeed controversial, as mentioned by Yu and Loper, Jr.²³ and later by Venugopalan and Alagarsamy.²⁴ These latter authors studied the effect of the same elements plus Mn and P on the microstructure of 15 heats of nodular cast iron. These alloys were cast in keel blocks (1x1.5x8 in) and were all found free of carbides in the as-cast state. The authors report two regression analyses, with or without accounting for P, which both show some cross terms. The regression including P writes:²⁴

$$f_{\text{ferrite}} = -86 + 66 \cdot w_{\text{Si}} + 721 \cdot w_{\text{P}} + 226 \cdot w_{\text{Mo}} - 29 \cdot w_{\text{Mn}} - 100 \cdot w_{\text{Cu}} - 16.5 \cdot w_{\text{Ni}} - 234 \cdot w_{\text{Mo}} \cdot w_{\text{Ni}} - 113 \cdot w_{\text{Cu}} \cdot w_{\text{Mo}} \quad (10)$$

It is here seen that Mo favours ferrite, in contradiction with the finding by Yu and Loper, Jr.²³ According to Venugopalan and Alagarsamy, this complex effect of Mo is related to the fact it increases temperatures for both ferrite and pearlite formation and shifts also both reactions to longer times. As a consequence, Mo favours ferrite at low cooling rate and pearlite at high cooling rates. It was very tempting to check if the two above works on Cu, Mo and Ni could be analysed together. Following Venugopalan and Alagarsamy, only their 12 first castings were used because their last melts had much larger nodule count. Their results were added to those obtained by Yu and Loper, Jr. for the 2.5 in bars. Multi-variable analysis was performed that gave a very high correlation factor $R^2=0.98$ but with several cross terms that decreased significantly the number of freedom of the analysis. It was thus decided to restrict the analysis to cross terms invoking Cu which, as already stressed, is the most efficient element effecting ferrite fraction. This procedure again led to a high correlation factor $R^2=0.98$ with the following equation:

$$f_{\text{ferrite}} = 135.8 + 18.1 \cdot w_{\text{Si}} - 1566 \cdot w_{\text{Mg}} - 52.1 \cdot w_{\text{Mo}} - 30.7 \cdot w_{\text{Mn}} - 27.6 \cdot w_{\text{Ni}} - (260 - 81.1 \cdot w_{\text{Cu}} - 1703 \cdot w_{\text{Mg}} - 62.0 \cdot w_{\text{Mo}} - 30.9 \cdot w_{\text{Ni}}) \cdot w_{\text{Cu}} \quad (11)$$

Measured versus predicted values are plotted in Fig. 1 where it is seen that both series of results span a large domain of ferrite fractions, and are thus intertwined. Looking at equation (11), it is seen that the apparent first order effect of all elements but Si is to decrease the amount of ferrite. However, writing the cross terms as done shows that Cu, Mg, Mo

and Ni do level off the effect of Cu. In other terms, adding several pearlite promoter elements will rapidly saturate the effect. Also, it is seen that at low level of Mg, Mo or Ni, the cross term invoking either of these elements may overtake the first order term if the Cu content is high enough. In a simple analysis this would lead to conclude that these elements are ferrite promoters, but this will not be true if the Cu content is low enough.

The works presented so far were mostly concerned with the effect of alloying additions on ferrite fraction. Other works as the one by Thielemann were more focused on pearlitic grades and the effect of impurities. Thielemann expressed the residual ferrite fraction (%) as:⁵

$$f_{\text{ferrite}} = 961 \cdot \exp(-Px) \quad (12)$$

with:

$$Px = 3.00 \cdot w_{\text{Mn}} - 2.65 \cdot (w_{\text{Si}} - 2.0) + 7.75 \cdot w_{\text{Cu}} + 90.0 \cdot w_{\text{Sn}} + 357 \cdot w_{\text{Pb}} + 333 \cdot w_{\text{Bi}} + 20.1 \cdot w_{\text{As}} + 9.60 \cdot w_{\text{Cr}} + 71.7 \cdot w_{\text{Sb}} \quad (13)$$

Note that this evaluation is meaningful for grades with some pearlite as it should be ensured that f_{ferrite} is lower than 100%, or equivalently that P_x is larger than about 2.3. Furthermore, if a fully pearlitic structure is considered to be obtained when the cast contains a maximum of 2% ferrite, the equation shows that P_x should be higher than 6.2.

Predicting the matrix structure of ductile iron

The relationships listed above have been most often obtained for given cooling conditions which however may vary from one work to another. The effect of cooling rate and of nodule count on the amount of ferrite or pearlite is well documented, and it is in particular known that the ferrite fraction is much less sensitive to cooling rate at high nodule count than at low nodule number. In analysing literature data as done below, it appeared possible to show the effect of cooling rate and then to illustrate the effect of alloying or trace elements by selecting data corresponding to similar cooling conditions. However, it appeared hardly possible to separate the effect of nodule count.

The information included in equation (13) could be complemented by data from literature, where use is often made of Sn equivalent and Mn equivalent. Eventually, the coefficients giving the Sn or Mn equivalent of an element are obtained as the ratio of the corresponding coefficients in the listed equations. Table 4 shows the values for the Sn-equivalent obtained from the equation by Weis¹⁸ and by Thielemann,⁵ as well as other data proposed by Else²⁵ and Lacaze et al.²⁶ It is seen than apart for As, the proposed Sn-equivalent values are generally of the same order. Also, Neumeier et al. used 0.10 for Cu which is well in the range of the values reported in table 4.²⁷

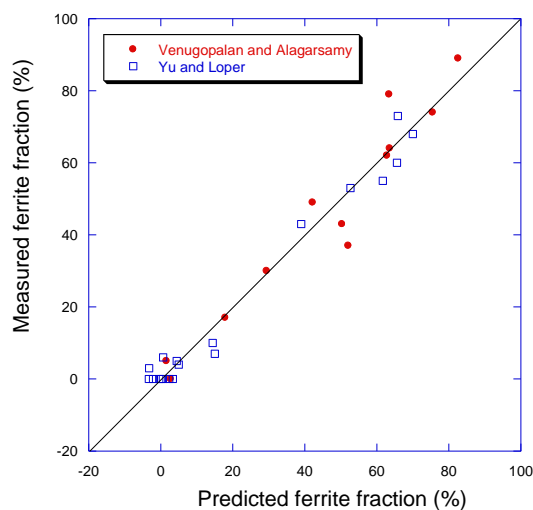


Fig.1: Measured^{23,24} versus predicted ferrite fractions. The line is the bisector.

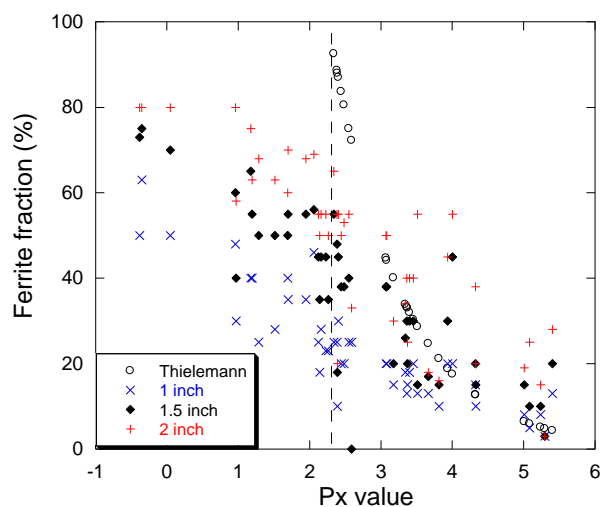


Fig. 2: Comparison of experimental ferrite fraction²⁰ with prediction equation (12) plotted versus amended P_x parameter, equation (14).

The same data and other²⁸ can be used to evaluate a Mn-equivalent as shown in Table 5. It is seen that the values of some coefficients are scattered, with a factor of 8 for V. This scattering may be understood because some of the studies were focused on pearlitic irons while others investigated ferritic irons. Accordingly, linear relationships that have been used between composition and matrix structure fail to describe the transition between mainly ferritic and mainly pearlitic matrices. On the contrary, the exponential function used by Thielemann predicts that addition of any of the pearlitic-promoter elements above a critical level leads to an abrupt decrease of the ferrite fraction down to a value at which the effect of further additions levels off. This result has been confirmed recently for the case of Cu, Mn and Sn. At given cooling conditions, the critical level was found to be 0.6 wt.% for copper²⁹ and 0.05 wt.% for tin.²⁶

Table 4: Sn-equivalent for several elements favouring (+) or preventing (-) pearlite.

Al	As	Bi	Co	Cr	Cu	Mg	Mn	N	P	Pb	Sb	Si	Reference
0.132			-0.185	0.180		0.138		0.715	0.067			-0.007	[17]
	0.22	3.7		0.107	0.086		0.033			3.97	0.797	-0.029	[5]
	2				0.083		0.042						[25]
					0.125		0.075						[26]

Table 5: Mn-equivalent for several elements favouring (+) or preventing (-) pearlite.

As	Bi	Cr	Cu	Mo	Ni	Pb	Sb	Si	Sn	Ti	V	reference
6.7	111	3.2	2.6			119	24	-0.9				[5]
48			2.0						24			[25]
		1.0						-0.9		5.2	1.2	[20]
			2.2			148	29					[19]
		4.0	0.5		1.5						10	[28]
			1.7						13.3			[26]
				1.7	0.9			-0.6				Equation (11)

It appeared then of some interest to attempt to use the data in tables 4 and 5 to complement the proposal by Thielemann and check predictions against results from literature. Merging information from both tables, a tentative amended Px value could be written:

$$Px = 3.00 \cdot [w_{Mn} + 1.5 \cdot w_{Ni} + 5.2 \cdot w_{Ti} + 1.2 \cdot w_V + 1.7 \cdot w_{Mo}] - 2.65 \cdot (w_{Si} - 2.0) + 7.75 \cdot w_{Cu} + 90.0 \cdot [w_{Sn} - 0.185 \cdot w_{Co} + 0.138 \cdot w_{Mg} + 0.75 \cdot w_N + 0.067 \cdot w_P] + 357 \cdot w_{Pb} + 333 \cdot w_{Bi} + 20.1 \cdot w_{As} + 9.60 \cdot w_{Cr} + 71.7 \cdot w_{Sb} \quad (14)$$

The first attempt was performed using the results by Campomanes and Goller,²⁰ plotting the reported ferrite fraction values for 1, 1.5 and 2 inches cylindrical bars against predictions made with the amended Thielemann's Px expression. As expected, it is seen in Fig. 2 that the experimental ferrite fraction does increase with the diameter of the bar, though the scattering of the data is quite significant. When compared to the predictions (open circles), which should be limited to values of Px higher than 2.3 (vertical interrupted line in the graph), it is seen that the agreement is within $\pm 20\%$ of ferrite, for ferrite fractions lower than 40%.

The next attempt concerned data reported by Pan et al. on the effect of Cu, Sn and Mn on the pearlite fraction measured in keel-block legs cast with both nodular and flake cast iron grades.³⁰ Their results are reported in Fig. 3 against the amended Px value, and compared with predictions made with Equation (12) using the corrected Px value given by equation (14). Data from Venugopalan and Alagarsamy²⁴ and Yu and Loper²⁵ used for plotting Fig. 1 have also been reported in Fig. 3, as well as results reported by Kovacs for 2 in thickness of a step casting in which 20 heats have been cast to study the effect of Mn, Sn and Sb on pearlite fraction of nodular and flake cast irons.³¹ Though the scatter in the experimental results is here also quite high, it is seen that the transition from a ferritic-pearlitic matrix to a nearly fully pearlitic matrix is well reproduced. This has been emphasized by drawing the solid line corresponding to Thielemann's approach with around a greyed area ($Px \pm 2$) that is intended to account for differences in nodule count, cooling conditions and uncertainties in chemical analysis. Two remarks are relevant here: i) it has been noticed that accounting for Mg content is of importance, the agreement would have been otherwise much worse with higher scatter, at least for the results by Pan et al.³⁰; ii) data for lamellar graphite are all located in the fully pearlitic area so that it can hardly be concluded if they agree or differ from results for nodular iron. It is however worth mentioning that Pan and Loper showed convincingly that flake graphite irons are more pearlitic than compacted/nodular cast iron of similar composition.³³

Buhr³² studied the effect of low level elements Pb (up to 0.013 wt.%), Sb (up to 0.023 wt.%) and Bi (up to 0.009 wt.%) in 5 inch thick castings of nodular iron inoculated with three inoculants differing by their Ce content (high, medium and nil). Buhr used the sum of the contents in residual elements (Pb, Sb and Bi) to discuss the results and found their effect varies with the Ce content. Reanalysing these results shows that the pearlite content decreases when the nodule count increases at low level of residual elements, as expected. High levels of residuals increases the amount of pearlite for both nil and medium Ce contents, while it decreases it at high level of Ce. It may thus be inferred that this high Ce content was enough to counteract the effect of residuals, when this was not the case for the two lower levels. Buhr's results are plotted as function of the amended Px values in Fig. 4. Again, it was noticed that accounting for Mg and P through the amended Px expression is of importance. In fig. 4, it is thus seen that the results for nil and medium Ce contents do overlap and show the same trend when this was not the case when using the sum of the residuals as done by Buhr.³² Excluding the high Ce series, this means that the weighting factors proposed by Thielemann are appropriate in the present case as well. Also, the curve calculated with equation (12) has been drawn in Fig. 4 and shows a trend similar to experimental data for low Ce levels. At high Ce level, a totally different process takes place that was not explained by Buhr.

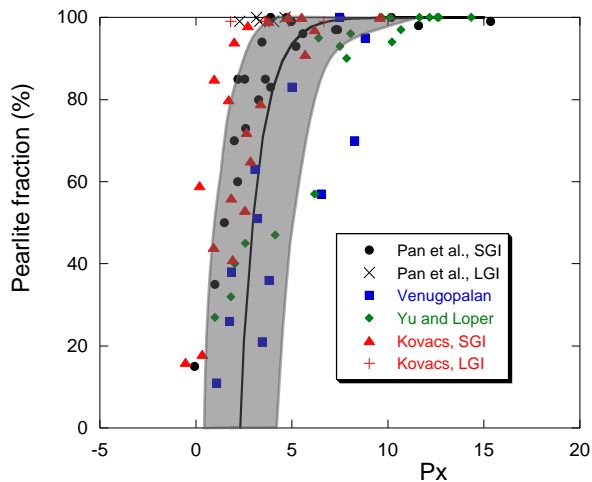


Fig. 3: Comparison of measured pearlite fractions for nodular (closed symbols) and lamellar (crosses) irons^{23,24,30,31} with predictions made with Thielemann's approach (solid line), reported versus the amended Px value.

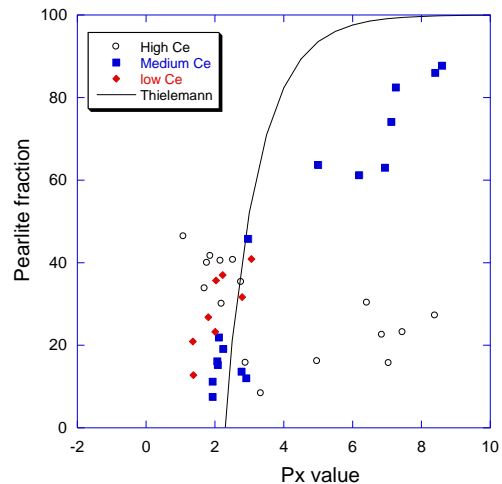


Fig.4: Plot of Buhr's data and predicted pearlite fraction as function of the amended Px values.³²

Discussion - Conclusion

Thielemann's trace element evaluation equation for the charge of pig iron, steel scrap and returns is giving an indication of if the base iron will have to be adjusted for production of nodular cast iron. The trace element evaluation equation is however not made for evaluation of a final casting, as often seen in publications, and the equation has defined limits for its validity, as shown in the original paper and in Table 3.

Several of the trace elements used to develop equation 1 have drastically decreased, as seen in Table 1, during the 40 odd years covered in the table. The most detrimental element, Bi, has however increased. When the trace element evaluation equation indicates a value above 1, typically when the amount of returns increases, corrective actions by adding rare earth elements to the melt have to be taken. Thielemann did experiments with corrective additions of cerium-mischmetal but unfortunately did not produce any equations for this.

The balancing equations are found in the thorough work by Javaid and Loper, Jr., who analysed large amounts of data. The result is a simple equation easily used in a foundry. This equation, somewhat corrected by Hansen et al., gives reasonable results for modern ductile iron.

Javaid and Loper, Jr., as well as Lacaze et al. developed simple equations (ratios of rare earths to subversive elements) for correction of subversive elements. None of these equations did give any reasonable result when checked against foundry trials. This could, however, be due to the difficulty in determining the low levels of the trace elements.

Löblich tried to correlate the amount of subversive elements and cerium to a limiting level of silicon. The equation was developed for castings of size 200•200 mm² with a solidification time lower than 50 minutes. When calculating this silicon limit for foundry castings, comparing with actual silicon level and checking against defects like chunky graphite no correlation could be found.

When calculating the possible amount of cerium adsorbed on a graphite surface and comparing with foundry trials an upper cerium limit of 0.0029 wt.% seems reasonable to avoid the formation of chunky graphite in a cast iron with low level of trace elements.

Thielemann's equation expressing the fraction of ferrite as a function of a parameter which is a linear function of composition variables has been found to describe in most cases properly, though semi-quantitatively, the transition from ferritic-pearlitic to fully pearlitic microstructures. Some of the discrepancy may come from the fact that this equation does not account for casting size. The equation for Px has been here extended using Sn and Mn equivalents to account for elements that have not been studied by Thielemann. This may explain part of the scattering as well, but most of it certainly comes from interactions between alloying and trace elements for which very little is known and would be worth of further study. Also, check of a few results on lamellar graphite irons seems confirming these alloys are more prone to give pearlitic matrix than nodular cast irons, and this would certainly be worth of further study as it could give some valuable insight about the mechanisms by which trace elements affect solid-state graphite growth.

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Appendix

Let assume that nodules have precipitated with a density N_V around nuclei having a radius r^o . The graphite fraction when the nodules have reached a radius r^g is:

$$V^g = \frac{4}{3} \cdot \pi \cdot \left[(r^g)^3 - (r^o)^3 \right] \cdot N_V \quad (A-1)$$

The number n_i of atoms of element i that were in the volume now occupied by graphite is $n_i = C_i \cdot V^g$, where C_i is the molar concentration of i in the initial liquid, which writes:

$$C_i = \frac{\rho_i}{M_i} = \frac{\rho \cdot w_i^0}{M_i} \quad (A-2)$$

with ρ_i the mass concentration ($\text{kg} \cdot \text{m}^{-3}$) of i in the liquid, ρ the density of the liquid, w_i^0 the nominal mass fraction of element i in the material and M_i the atomic mass of element i . Assuming that all i atoms in the V^g volume adsorb at the surface of the growing graphite nodules, the coverage is given by:

$$\Gamma_i = \frac{n_i \cdot (r_i)^2}{4 \cdot \pi \cdot (r^g)^2 \cdot N_V} = \frac{\rho \cdot w_i^0}{M_i} \cdot \frac{\left[(r^g)^3 - (r^o)^3 \right] \cdot (r_i)^2}{3 \cdot (r^g)^2} \quad (A-3)$$

where the surface occupied by a i atom has been taken as $(r_i)^2$, where r_i is the atomic radius of element i . With ρ set at $7200 \text{ kg} \cdot \text{m}^{-3}$ and r^o at $0.5 \text{ } \mu\text{m}$, M_i set at $140 \text{ g} \cdot \text{mol}^{-1}$ and r_i at $2 \text{ } \text{Å}$ as for cerium, one gets the solid curves shown in

Fig.A-1 for three values of w_i^0 , 10, 100 and 1000 ppm per mass. As growth proceeds, more and more i element accumulates at the surface of the nodules until full coverage is achieved. This is readily done for 1000 ppm at the very start of growth while this will be achieved for a radius of $8 \text{ } \mu\text{m}$ for 100 ppm and even larger for 10 ppm. The case where some of i element gets incorporated in graphite is illustrated with the dotted lines that assumes a "partition" coefficient of 0.25 as reported for lanthanum.³⁴

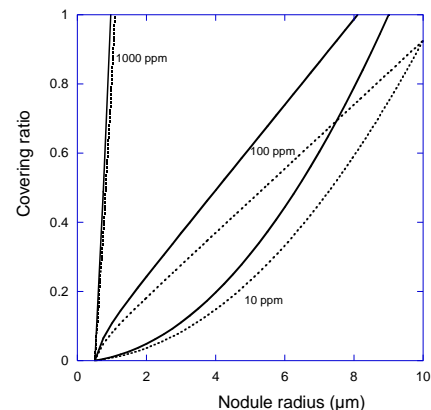


Fig.A-1: Calculation of graphite nodule coverage for various nominal amounts of adsorbed element.