High Temperature Modification of Steelmaking Slag by Addition of Fayalite Slag to Create a Volumetrically Stable Aggregate

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ABSTRACT

This study investigates high temperature modification of molten steelmaking slag by the addition of granulated fayalite slag for reuse as a volumetrically stable pavement aggregate. Reuse of steelmaking slag as a high-quality asphalt aggregate is hampered by the in-service hydration of free lime (CaO). The addition of fayalite slag (primarily FeO and SiO_2) to molten steelmaking slag inhibits the precipitation of free lime during solidification and cooling. It acts similar to the 'early' slag in steelmaking by dissolving lime flux. Physical testing and mineralogical investigation of modified slag from industrial trials with additions of approximately ten percent fayalite slag are discussed.

INTRODUCTION

Steelmaking slag was used in the Province of Ontario, Canada, as an aggregate in hot-mix asphalt aggregate for premium road surfaces since 1971. Its high strength, good rutting resistance and excellent anti-skid properties [1], which are superior to natural aggregate in asphalt pavement surfaces, make it particularly suitable for the Canadian winter climate. In 1990, over 488,000 tonnes of steelmaking slag aggregate was used in hot-mix asphalt, which accounted for over half of the province's total steelmaking slag generation for that year [2]. However, recent premature deterioration of road pavements constructed with steelmaking slag has resulted in a 1991 Ministry of Transportation Ontario (MTO) moratorium on its use [3]. Suddenly, three quarters of a million tonnes of annual by-product production became waste, and without any other high-volume secondary market readily available for its reuse, was destined for stockpiling or landfill. This research involves high-temperature modification of steelmaking slag in order to restore this by-product to the premium hot-mix asphalt pavement market.

BACKGROUND

The suspected cause of the premature pavement deterioration in certain areas of the provincial highway system is the volumetric instability of the steelmaking slag aggregate, which is a result of the in-service hydration of 'free' lime (and to a lessor extent, MgO) in the slag [4]:

$$CaO_{(s)} + H_2O_{(l)} \rightarrow Ca(OH)_{2(s)} \ . \tag{1}$$

The hydration is accompanied by an increase in unit volume, which creates internal stress within the steelmaking slag aggregate. The stress leads to aggregate deterioration, and ultimately pavement failure.

The source of free lime in steelmaking slag is twofold [5]:
(a) lime precipitated from the melt during solidification and subsequent solid-state reactions; and,
(b) lime from undissolved flux and from limestone (or dolomite) added as coolant.
The former manifests itself as micro-sized grains, while the latter ranges in size from macroscopic particles to micrometer-sized grains in the slag microstructure. The nature of origin of each type of free lime is explained in further detail.

Precipitated free lime arises due to solid state reactions upon slag cooling. Monaco and Lu [6,7] and Monaco [8] investigated the origin of free lime in industrial steelmaking slag specifically manufactured with negligible amounts of undissolved lime (that is, slag produced under well-defined conditions). For the slag under study, any precipitated free lime found was produced from the solid-state transformation of tricalcium silicate to dicalcium silicate and free lime upon cooling,

$$Ca_3SiO_{5(s)} \rightarrow Ca_2SiO_{4(s)} + CaO_{(s)} \ . \tag{2}$$
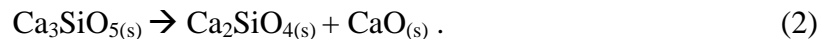
This decomposition manifests itself as a striped pattern of CaO grains within a Ca_2SiO_4 field. This solid state reaction occurs at approximately 1250°C in the Ca-Si-O system [9].

A significant conclusion of the study [7,8] is that for industrial steelmaking slag with negligible amounts of undissolved lime, hydraulic expansivity of the slag increases with increasing $[CaO]/[SiO_2]$, or V-ratio. The greater the ratio of $[CaO]/[SiO_2]$, the more likely tricalcium silicate is formed over dicalcium silicate. The more tricalcium silicate formed initially, the more free lime that is transformed upon its subsequent decomposition.

The study [7,8] determined that for slag with a V-ratio below a certain value, no appreciable amount of tricalcium silicate initially appears; therefore, no appreciable amount of free lime is subsequently formed. Thus, the slag expansivity is negligible for slag below the critical V-ratio. For slag with a V-ratio above a certain value, the amount of tricalcium silicate formed initially becomes more appreciable, and so does the amount of free lime formed upon the subsequent solid-state transformation. Thus, the slag expansivity is appreciable for slag above the critical V-ratio. The critical $[CaO]/[SiO_2]$ is approximately 3.0 for the particular slag of the investigation, but is probably dependent upon steelmaking shop practice.

In traditional BOF steelmaking, calcined lime is charged into the slag in aggregate-sized pieces and heated rapidly. Liquid iron-silicate (Fe_2SiO_4) at approximately 1400°C penetrates into the pores of the solid lime and attacks it according to the path marked in Figure 1 where the product is liquid iron-calcium silicate. When the concentrations of FeO and MnO are very low, solid dicalcium silicate may form, often selectively precipitating on the still dissolving lime particle. A liquid (slag)/solid (lime) interface must exist for reasonable lime dissolution. This solid dicalcium silicate layer, which acts as a kinetic barrier, should be minimised for further lime dissolution.

This calcium-silicate layer can be attacked, or prevented from forming altogether, by a more aggressive liquid phase, such as one containing more FeO, MnO and Al_2O_3. Even though bulk slag chemistry may predict that free lime should not exist, localised deficiencies of certain elements around dissolving lime particles may result due to a slow mass transfer process in the liquid phase.

The steel and construction industries are at odds over lime requirements of steelmaking slag: steelmakers require high lime activity in the slag for effective impurity removal, while users of steelmaking slag aggregate in the construction industry demand a low lime content to control volumetric instability. Since it is impractical for the steelmaker to reduce the amount of lime necessary to ensure refining, the only feasible approach for use in both applications is to reduce the lime activity between applications; that is, to lower the activity of lime after the steel is tapped from the vessel but before its use as an aggregate.

Lime activity after steel tapping can be lowered by two means: (a) ambient or low-temperature processing (slag ageing), or high temperature processing (slag modification).

Slag ageing, the processing of slag to reduce volumetric instability at ambient and low temperatures, is the traditional method of achieving aggregate stability. Simply, the slag is put into contact with water to pre-hydrate any exposed free lime prior to service. However, the process is land, labour and time intensive. In addition, the cold Canadian winter climate requires hot water or steam, which presents further energy demands and processing challenges.

Slag modification, on the other hand, involves targeting the desired slag mineralogy and chemical composition through the appropriate additives at high temperatures. This processing takes place while the slag is still molten in order to take advantage of the available superheat for incorporation of the addition. In order to minimise the amount of free lime in the modified slag, the addition should have two desired effects:

(a) the addition should lower the $[CaO]/[SiO_2]$ ratio to minimise the formation of tricalcium silicate, thereby reducing the amount of precipitated lime; and,

(b) the addition should react with any undissolved lime to produce hydraulically stable mineral phases.

Silica is the obvious addition to reduce the $[CaO]/[SiO_2]$ ratio; however, the use of silica alone as an additive presents many kinetic limitations. Figure 1 is the CaO-SiO_2-Fe_nO quasi-ternary phase diagram superimposed with the association between pure lime and potential additions. The thermodynamic equilibrium between pure silica and pure lime can ultimately result with hydraulically stable mineral phases, such as dicalcium silicate; however, the kinetic path to this equilibrium is fraught with a number of intermediate high melting-point phases.

A recent modification process [10] involving injection of silica sand as a modifying additive overcomes the kinetic limitations by using oxygen as a carrier gas. The oxygen produces heat by oxidising FeO to Fe_2O_3, which facilitates SiO_2 dissolution. However, the aforementioned study by Monaco [8] suggests that the 'wustite' or $Fe(Mg,Mn)O$ phase in steelmaking slag may act as a crucial contributor to the slag's strength. The wustite phase forms the matrix of the polycrystalline slag microstructure, and appears to act as a predominant crack arrestor.

It is well known that the best solvent to dissolve lime is the 'early' slag of the steelmaking process; that is, an iron-manganese-silicate melt. Fayalite slag, a predominately iron-silicate slag from non-ferrous metals refining, is close to the composition of this 'early' slag. Table 1 gives a typical chemical composition of the fayalite slag used in this study, obtained from a Canadian nickel producer. As superimposed on Figure 1, the equilibrium between fayalite slag and lime is not kinetically restricted by intermediate high-temperature phases. In comparison to the addition increasing slag fluidity and overcoming localised flux deficiencies. Unlike SiO_2 alone, iron silicate works to dissolve high-melting point calcium silicate phases that act as kinetic barriers to lime dissolution. Finally, greater FeO concentrations in the slag lowers its melting point [11]. A reduced melting point grants more superheat available for addition dissolution.

Our research group arrived at the use of fayalite slag after conducting industrial trials using silicate glass as a high-temperature addition to steelmaking slag. Three industrial trials were completed, each of which consisted of approximately one tonne of silicate glass shards added to 12 to 15 tonnes of molten steelmaking slag in the steelmaking converter after the steel had been tapped. The linear expansivity of the modified slag was, on average, 55% lower than the control slag; however, it was still several percent higher than the unofficial provincial acceptance standard of 1%. The limiting factor was the addition incorporation. Remnants of undissolved glass shards were found within the solidified slag. The silicate glass softens and becomes very viscous, and does not an effective additive alone. Based on this work with silicate glass addition, acidic oxide additions which result in wider ranges in melting compositions and temperatures,

such as fly ash and fayalite slag, were recommended. This work involves industrial-scale high-temperature modification of steelmaking slag by the addition of fayalite slag[†].

EXPERIMENTAL

To date, three industrial trials have been completed at a local steel company using granular fayalite slag as a high-temperature addition to molten steelmaking slag. In each trial, approximately one tonne of fayalite slag is placed into the slag pot prior to tapping of the steelmaking slag from a BOF which is designed to contain 136 tonnes of liquid steel. In Trial #1, 30 kg bundles of fayalite slag are laid in the bottom of the pot. In Trial #2, the fayalite slag is placed in a metal-framed cage, approximately 2 m high and 1 m square, and this cage was placed in the slag pot. In Trial #3, a 2.2 m tall metal framed annulus, with an outer diameter of 1.2 m and an inner diameter of 0.9 m, is filled with fayalite slag and placed in the slag pot. The improvement in distribution method from Trial #1 to Trials #2 to #3 is done in order to facilitate mixing for incorporation of the fayalite slag.

The addition is incorporated into the steelmaking slag as it is being poured from the BOF into the slag pot. Initially, a reference steelmaking slag sample, referred to as the 'control slag', is tapped from the furnace into a slag pot during the first turndown of the steelmaking vessel. Approximately 3 to 7 tonnes of slag are poured into the control slag pot at this time, depending on operational concerns. Due to the limitation in the overall number of slag pots available, the control slag is usually tapped into a pot already containing layers of previously solidified slag.

After first turndown, the steelmaking process may resume with the oxygen blow. Once completed, liquid steel is tapped from the tap-hole. Finally, the vessel is turned and the remaining steelmaking slag is poured through the vessel's mouth into the fayalite slag-laden slag pot. Between 8 to 15 tonnes of steelmaking slag is tapped onto the one tonne of fayalite slag. This amount of fayalite slag results in a range of addition of 6 to 11 percent. The exact percentage of addition is undeterminable beforehand as it is unknown how much slag is present in the vessel for any particular heat, and how much slag will be tapped out as control slag during at vessel turndown.

Both slag pots, containing the control slag and the fayalite slag-modified slag, are taken to the slag yard. In normal operations, the still largely molten slag would be poured out of the slag pot into the slag pits, where the slag would solidify and be made available for crushing and separation of metallics. For this study, however, the two pots are moved to an isolated region of the slag yard, where the slag is allowed to solidify in the pots over a week-long period. The pots are then inverted and the slag falls out, more or less as an intact dome.

Slag samples are systematically sampled from different regions of these slag domes. These samples are then tested and compared to identify the extent of addition incorporation. Figures 2(a) and 2(b) show two-dimensional cuts through a slag pot schematic that indicates the approximate sampling regions of both the control and modified slags respectively. The sampling regions are radially distributed from the centre of the slag pot. In the case of the control slag

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[†] Component of U.S. Provisional Patent Application, filed September, 1999

(Figure 2(a)), samples are collected from the centre of the slag pot, halfway from the centre to the edge, and around the edge of the slag pot. In the case of the fayalite slag-modified slag (Figure 2(b)), samples are collected both vertically and radially: at the top of the slag pot, samples are collected all along the subsurface; at the middle of the slag pot, samples are collected from the centre, one third of the way outward, two thirds of the way outward, and at the edge; and at the bottom of the slag pot, samples are collected in the middle. Slag samples are not collected from the 'steel button' region, where the entrapped steel has accumulated by gravity segregation.

In total, over 500 kg of slag is sampled for each trial. The slag is crushed and sieved to appropriate sizes for the two different aggregate gradations commonly used by Ontario pavement contractors, which will be referred to as (a) coarse gradation, and (b) coarse + fine gradation. Particle size for the coarse gradation of aggregates ranges from −16mm to +4.75mm, while that for the coarse + fine gradation consists of particles less than 26.5 mm. The particle size distribution for both gradations is found in Table 2.

The industry-accepted accelerated test method to measure volumetric stability of aggregates is the ASTM D4785-88, *Standard Test Method for Potential Expansion of Aggregates From Hydraulic Reactions*. From 5 to 7 kg of aggregate is compacted into a proctor mould − a cylinder closed at one end. A 2.2 kg piston is placed on top and the whole assembly is submerged in 71°C water over a number of days. The only direction that the aggregate can swell (if any swelling occurs) is upward, and the linear measure of this upward expansion as a percentage is termed the linear expansion. Currently, the unofficial provincial acceptance standard is 1% linear expansion or less.

Linear expansion testing is performed twice on each gradation of slag from each region sampled. In addition, chemical analysis is performed on three samples from each region sampled. Chemical analyses were determined using x-ray fluorescence methods, except for the sulphur contents, which were determined by a standard combustion method, and FeO contents, which were determined by wet chemical analysis.

Selected samples are also retained for microstructural investigation. Samples were mounted, ground and polished eventually to a 0.5μm suspended diamond solution. Kerosene was used as the lubricant during the preparation to prevent free lime hydration. Samples were analysed using a JOEL Model 733 electronprobe microanalyser.

RESULTS

In order to establish the mass percent addition of fayalite slag, mass balances on selected components between the Control Slag and Fayalite-Modified Slag for each Trial were performed. In total, 28 chemical analyses for each Trial were performed. Examples of the chemical analyses for the turndown samples of each Trial are shown in Table 3.

As previously mentioned, operational variations make it impossible to know the exact amount of steelmaking slag which is to be tapped in the final discharge; therefore, the fayalite addition percentage has to be calculated after the fact. The target is a 10 % addition. The calculated

addition ranges, established by mass balances on CaO, SiO$_2$ and Fe, are shown in Table 4. Addition ranges were between 6.3 to 11.3 %. In general, the addition ranges fell just short of the target, except for Trial #2, where the range spans the target.

Ranges of the linear expansion results at 10 days are summarised for each gradation for all Trials in Table 5. Linear expansion results for each sampling region are shown in much greater detail in the Tables and Figures that follow. Tables 6a, 6b and 6c show the 10-day linear expansion range results and [CaO]/[SiO$_2$] ranges for Trials #1, #2 and #3 respectively. These linear expansion and [CaO]/[SiO$_2$] results are presented by sampling region.

Graphs of linear expansion by sampling region are for Coarse Gradations and Coarse + Fine Gradations presented in Figures 3 to 5 and 6 to 8 respectively.   Figure 3(a) shows the linear expansion results for each of the two samples (labelled A and B) taken from the three sampling regions for Trial #1, Control Slag, Coarse Gradation. Figure 3(b) shows the results for each of the two samples (labelled A and B) for each of the 6 sampling regions for Trial #1, Fayalite Modified Slag, Coarse Gradation. The same corresponding results for Trials #2 and #3 are shown in Figures 4 and 5. Figures 6 to 8 show the corresponding results in the same fashion but for the Coarse + Fine Gradations.

Reductions in free lime content after fayalite slag modification for Trials #2 and #3 are demonstrated in the typical photomicrographs of Figures 9 and 10. Figure 9 represents a photomicrograph of a typical microstructure for Control Slag prior to modification. Free lime content, in this case precipitated rivulets of free lime within dicalcium silicate grains resulting from the tricalcium silicate decomposition of Equation (2), is evident. Figure 10 represents a typical microstructure after fayalite slag treatment; that is, no observable free lime content.

DISCUSSION

In all Trials, fayalite slag modifcation did result in a decrease in linear expansion. However, this reduction was far more significant for Trials #2 and #3 than for Trial #1. In addition, linear expansivity of the coarse + fine gradation was significantly greater than for the coarse gradation in all cases. This result is expected for two reasons. First, the fines have more surface area exposed to potential hydration than the coarse particles alone. Second, the fines cause the aggregate packing to be more dense, as the fines fill the voids between the coarser particles, which were potential areas that could incorporate the any expansion.

Trial #1

Results from Table 5 show that linear expansivity for Trial #1 improved from a range from 16-18% to 7-12% for the coarse gradation, and from +20% to 12 to 18% for the coarse + fine gradation. While the linear expansion results did show a significant improvement after fayalite slag modifications, these results were still far from the unofficial acceptance standard of 1%.

The suspected reasons for this include:

- Incomplete mixing, due to the fact that all the nickel slag was placed on the bottom of the slag pot. An appreciable amount of undissolved fayalite slag was found in the slag pile during sampling.

- An unusual slag composition, with a higher initial V-ratio, or $[CaO]/[SiO_2]$, than anticipated. The initial V-ratio for slag of this grade of steel had traditionally ranged from 3.2 to 3.7. In this Trial, it ranged from 4.3 to 4.5, as shown in Table 6a. Mineralogical investigation revealed a significant amount of both precipitated and undissolved free lime in the slag. This resulted in the high linear expansion results for the Control Slag. In fact, as shown in Figure 6(a), the linear expansivity for the coarse + fine slag was over 20%, which exceeds the equipment's range, by the third day.

- Subsequently, the tonne of fayalite slag addition did not reduce the V-ratio of the modified slag below 3.0, which is necessary, based on our experience, to eliminate precipitated free lime. It is concluded that not enough fayalite slag was incorporated into the melt to prevent precipitated lime from forming.

Trials 2 and 3

The linear expansion results of Trials #2 and #3 show further improvement over Trial #1. For at least the coarse gradation, linear expansion of fayalite slag-modified slag has been reduced from an unacceptable range (5 to 7% for Trial #2, and 6 to 8% for Trial #3) to an acceptable level (0.2 to 0.6% in Trial #2, and 0.4 to 1.0% in Trial #3). As shown in Tables 6b and 6c, the $[CaO]/[SiO_2]$ ratios were reduced from values over 3.4 to mostly between 2.4 to 2.8. Only in a few sampling locations was this reduction not under 3.0.

Although the results for the coarse + fine gradation (0.4 to 2% for Trial #2 and 1% to 2.5% for Trial #3) do not fall within the 1% mark, they show great improvement and promise for further trials. In any respect, the linear expansion results for coarse+fine gradations are always greater for all aggregates with respect to coarse gradation alone.

In terms of government regulatory position, as long as a gradation standard can meet consistant expansion levels of of 1% or less, it can be considered for full-scale trials in the field. Modification allows the coarse gradation to meet these levels, even though the coarse+fine gradation has yet to meet this level with this series of industrial trials.

The two highest curves in each of fayalite slag-modified slag graphs of Trial #2, Figures 4(b) and 7(b), and Trial #3, Figures 5(b) and 8(b) have been excluded from the ranges in the Table 5. The slag from these sources originates from the *bottom centre* location in the slag pot. Both observation and chemical analysis confirms that slag from this region did not benefit from full incorporation of fayalite slag. An appreciable amount of undissolved fayalite slag was found in this region. Thus, it is concluded that this region did not benefit from fayalite slag addition and is not indicative of fayalite slag-modified steelmaking slag aggregate. Thus, the results from these locations were not included in summary of Table 5.

The improved method of addition in Trials #2 and #3 over Trial #1 is still not completely adequate. The V-Ratio and linear expansion results for the *bottom centre* region of the fayalite slag-modified slag is significantly greater than for other sampling regions. As previously mentioned, undissolved fayalite slag was still found in the bottom section of the slag pot during sampling; however, the amount was much less appreciable than in Trial #1. Thus, even in Trials #2 and #3, this region has the excess of fayalite slag addition, which does not entirely dissolve into the molten steelmaking slag. Subsequently, the desired modification does not occur to the extent necessary for acceptance as an aggregate.

The lack of complete additive dissolution resulting non-uniformity in modified slag performance, reflects limitations on dissolution kinetics. It is due to the simple additive delivery system used in these experiments. Even though fayalite slag is of lower melting point, it still presents a formitable heat sink to the molten slag. An improved additive delivery system will avoid excessive cooling locally and promote complete dissolution and uniformity in concentrations.

A simplified heat balance confirms that for the conditions under study, enough superheat is available in the steelmaking slag to incorporate the fayalite addition and still keep the system in a liquid state. If one uses 0°C as a reference point, then the enthalpy of the mass of steelmaking slag, M, at the temperature of fayalite addition, T_0, and the enthalpy of the fayalite slag, m, at ambient temperature, 25°C, equates to the enthalpy of the modified slag at its resulting uniform temperature, T:

$$C_p(T_0) \times M \quad + \quad c_p(25) \times m \quad = \quad \overline{C}_p T \times (m+M) \tag{3}$$

where C_p, c_p and $\overline{C}_p$ are the heat capacities of steelmaking slag, fayalite slag and the modified slag respectively. Assuming that the heat capacities are equal, Equation (3) simplifies to

$$T_0 + 25\frac{m}{M} \quad = T(1+\frac{m}{M}) \tag{4}$$

where *m/M* is the weight fraction of fayalite slag addition. A plot of Equation (4) for fayalite slag additions of 5%, 10% and 15% is found in Figure 11. It shows that for a steelmaking slag tap temperature of approximately 1650°C, at a fayalite addition of 10%, the resulting system temperature is 1500°C. Although heat loss to the surroundings and the heat abosrbed by the slag pot will be appreciable, there is sufficient superheating for the system to remain in the liquid state as observed in these trials.

Visual observations indicate that fayalite slag-modification leads to less fines generation in routine handling and during the crushing of slag samples. Coarser slag is more desirable for reuse as an aggregate, for recycling in the Blast Furnace, or for materials handling in general.

CONCLUSIONS

The premise of fayalite slag addition to steelmaking slag, in respect to both the liquid-phase reaction path as shown in Figure 1 and the heat balance shown in Figure 11, is fundamentally

sound. What remains is to overcome the limitations inherent in its industrial application; that is, to ensure more thorough mixing with a better system to deliver granular fayalite slag. Based on the three trials to date, the following conclusions are given:

- Fayalite slag is an effective modifier for BOF slag that overcomes many kinetic limitations of solid-state intermediate compounds that exist when using silica alone;

- Fayalite slag-modified steelmaking slag aggregate obtained in Trials #2 and #3 fell within unofficial industry acceptance standard for the coarse gradation; and,

- The effectiveness of the modification at the present time is limited by the additive delivery system. An improved additive delivery system, which disperses the fayalite slag more evenly throughout the molten slag to overcome localised kinetic deficiencies of additives and/or heat, is necessary for more uniform improvement.

ACKNOWLEDGEMENTS

REFERENCES

1. J.J. Emery, CIM Bulletin, Dec. 1975, 60-68.
2. John Emery Geotechnical Engineering Limited, Mineral Aggregate Conversation − Reuse and Recycling. Prepared for the Aggregate Resources and Petroleum Section, Ontario Ministry of Natural Resources, Queen's Printer for Ontario, 1992, 25-28.
3. B.L. Farrand and J.J. Emery, In Proceedings of the International Symposium on Resource Conservation and Environmental Technologies in Metallurgical Industries, The Canadian Institute of Mining, Metallurgy and Petroleum, 1994, 99-106
4. F. Wachsmuth, et al., Canadian Metallurgical Quarterly, Vol.20, No.3 (1995) 561-571.
5. J. Geiseler, Slag Atlas, 2nd edition, Ed. Verein Deutscher Eisenhüttenleute, Verlag Stahleisen GmbH, Germany, 1995.
6. A. Monaco and W-K. Lu, In Proceedings of the International Symposium on Resource Conservation and Environmental Technologies in Metallurgical Industries, The Canadian Institute of Mining, Metallurgy and Petroleum, 1994, 107-116.
7. A. Monaco and W-K. Lu, In 1996 Steelmaking Conference Proceedings, Iron and Steel Society, 1996, 701-711.
8. A Monaco, M.Eng Thesis, McMaster University, Hamilton, Ontario, Canada, 1995.

9. M. Kowalski, *et al*., <u>Slag Atlas</u>, 2nd edition, Ed. Verein Deutscher Eisenhüttenleute, Verlag Stahleisen GmbH, Germany, 1995.
10. Peter Drissen and Michael Kühn, 4th ASM International Conference and Exhibition on "The Recycling of Metals", <u>ASM no. 34</u>, June 1999.
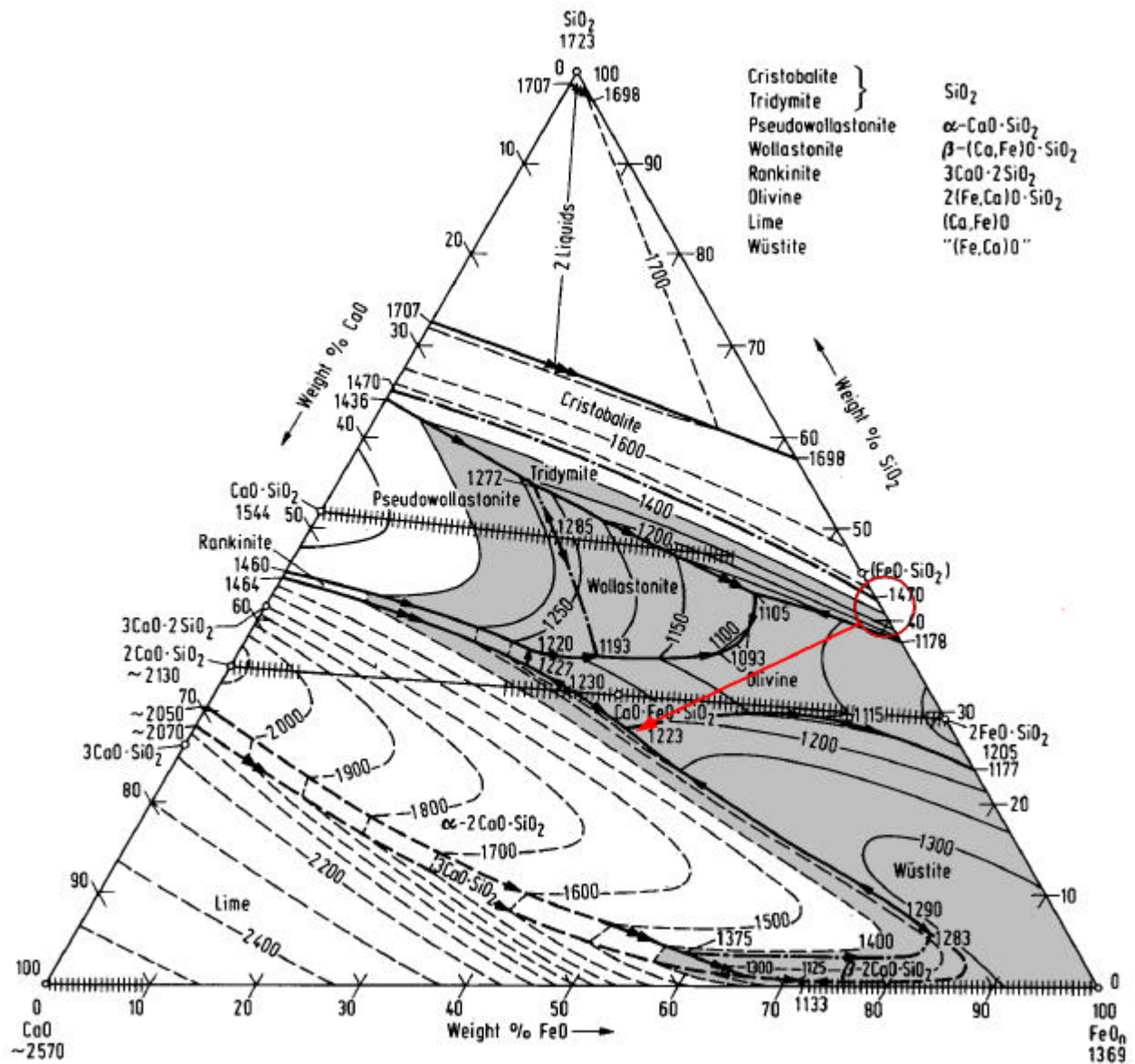11. H. Preβlinger, *et al*., <u>Steel Research</u> 70 (1999) No. 6, 209-214.

Figure 1: CaO-SiO$_2$-Fe$_n$O quasi-ternary phase diagram [9] demonstrating fayalite slag attack on solid lime in liquid phase field of 1400°C − similar to lime dissolution in 'early' slag.
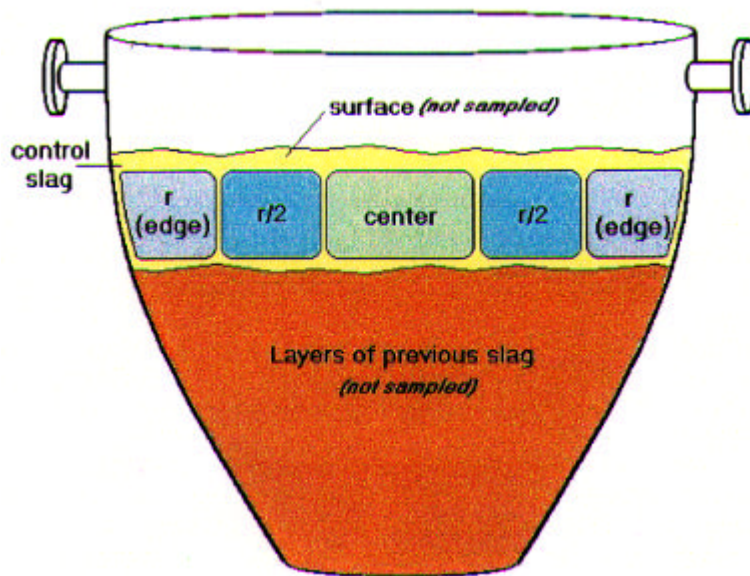
Figure 2(a): Sampling regions in slag pot for Control Slag.
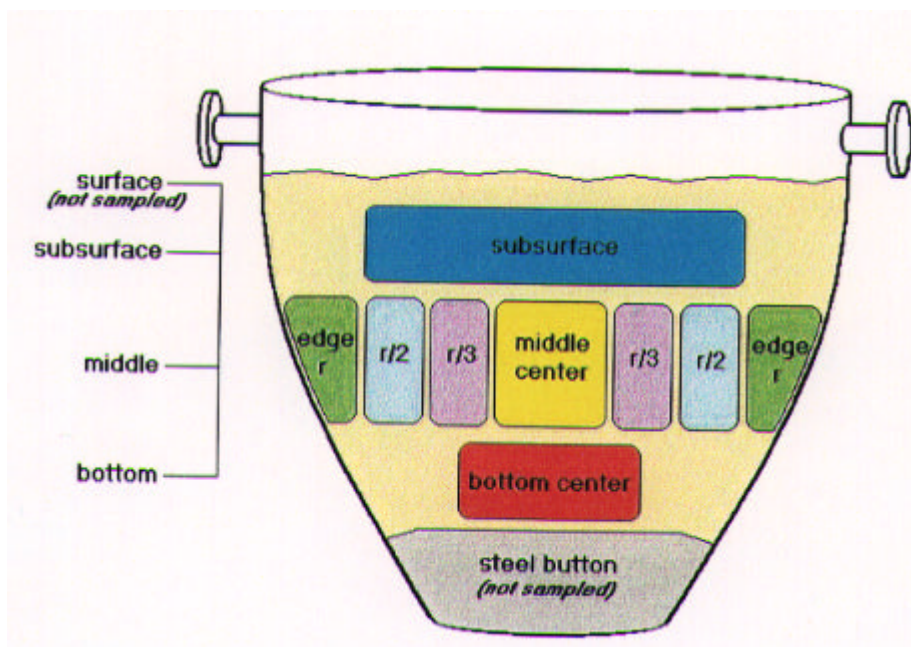
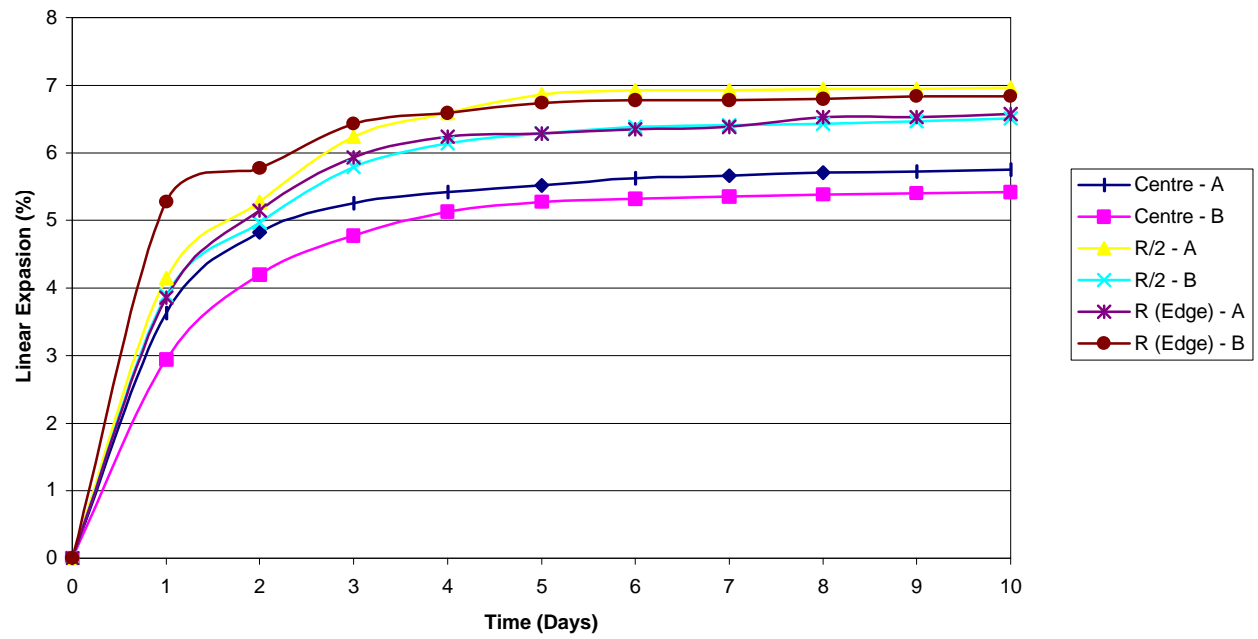Figure 2(b): Sampling regions in slag pot for Fayalite-Modified Slag.
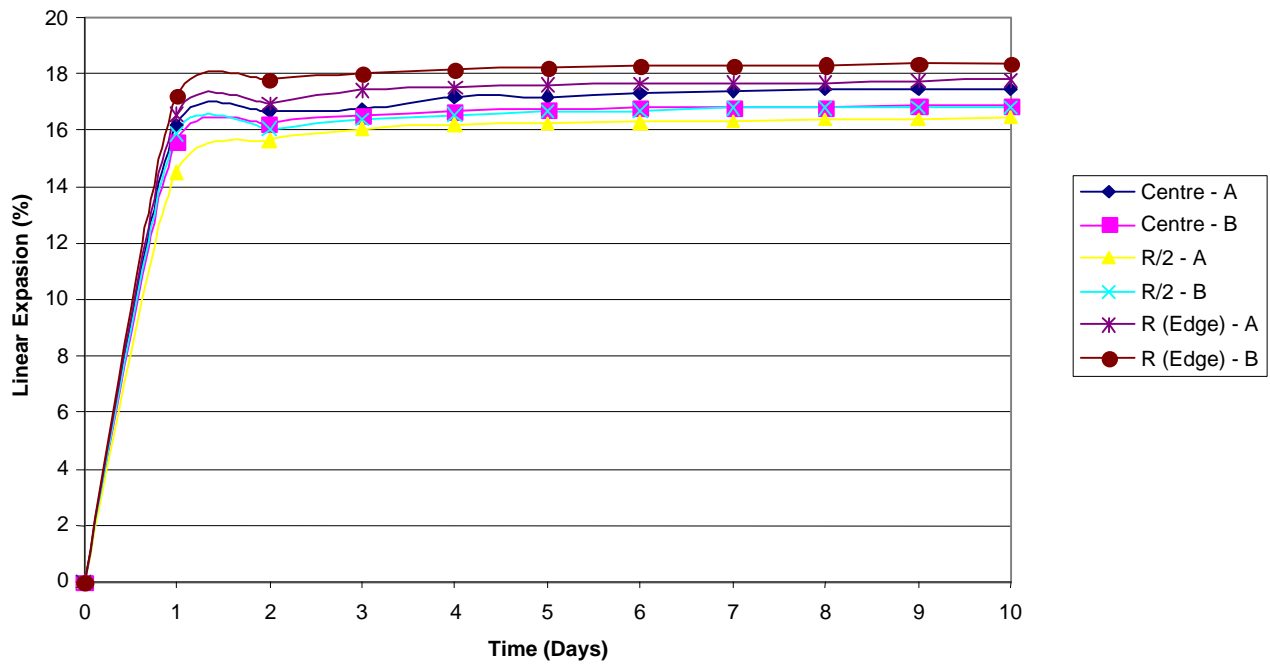
Figure 3(a): Linear expansion results, Trial #1, Control Slag, Coarse Gradation
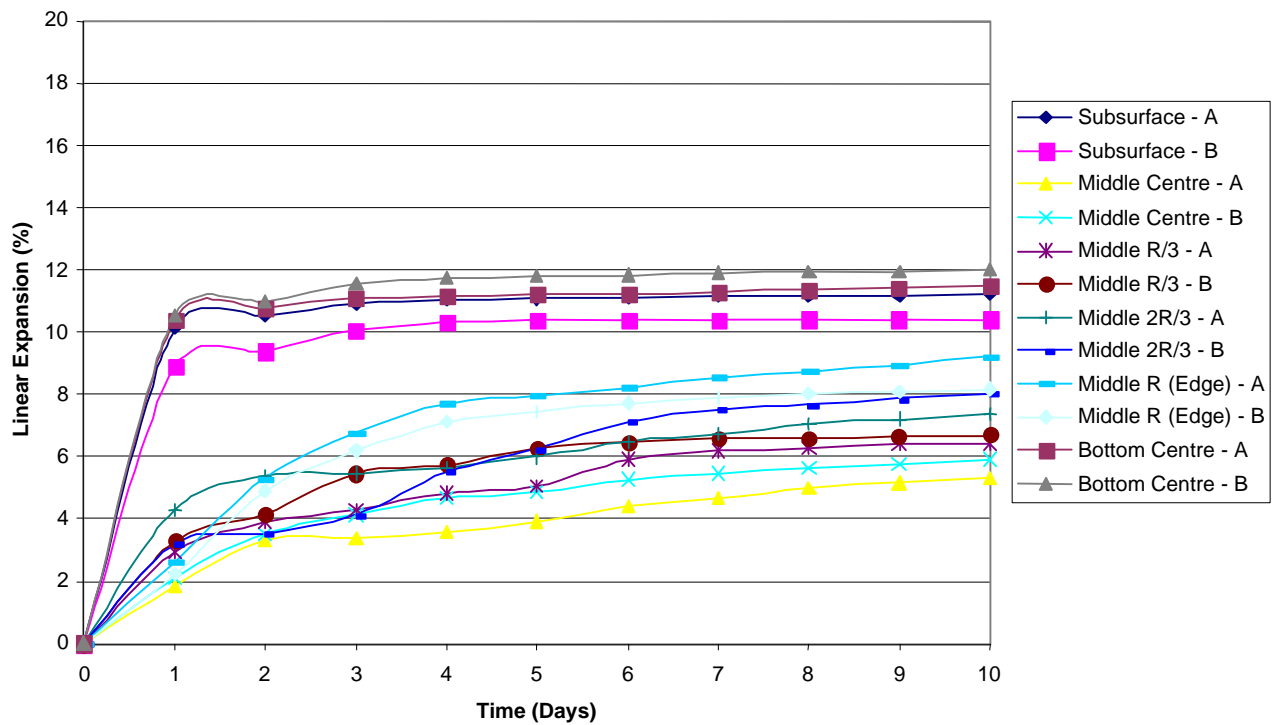
Figure 3(b): Linear expansion results, Trial #1, Fayalite-Modified Slag, Coarse Gradation

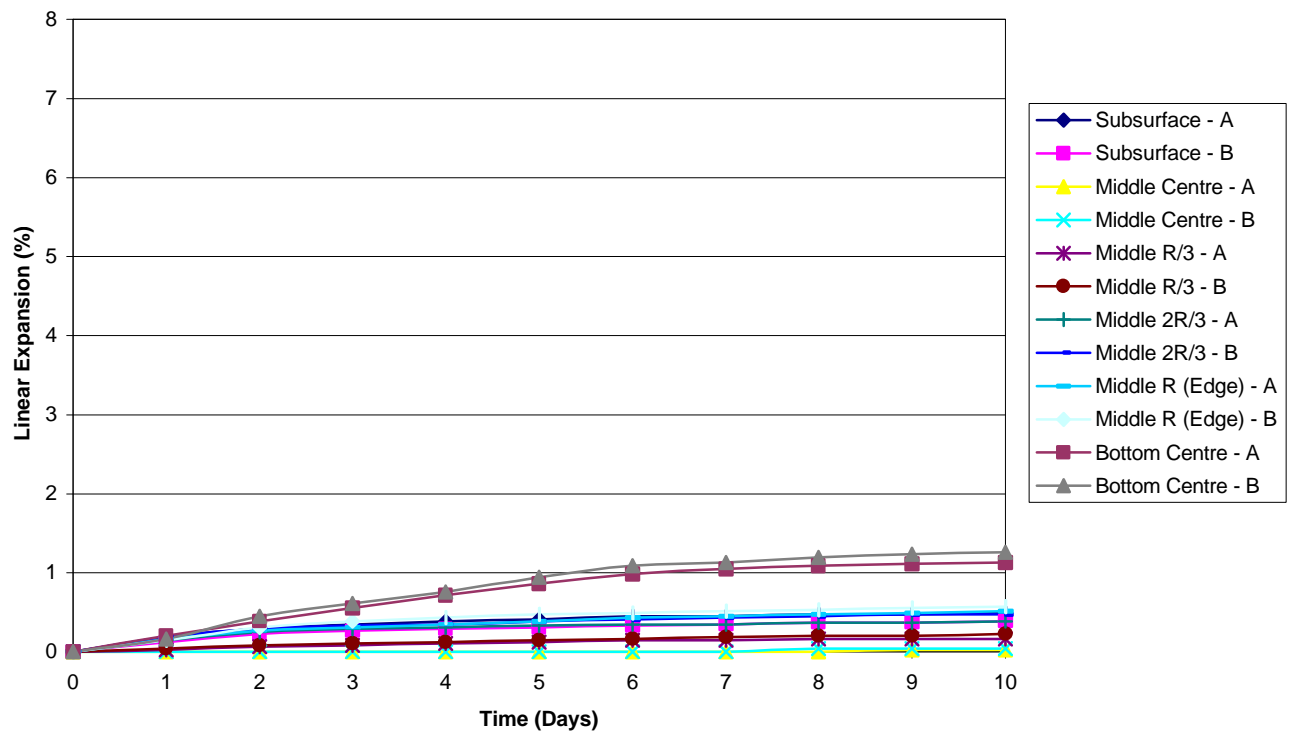Figure 4(a): Linear expansion results, Trial #2, Control Slag, Coarse Gradation

Figure 4(b): Linear expansion results, Trial #2, Fayalite-Modified Slag, Coarse Gradation
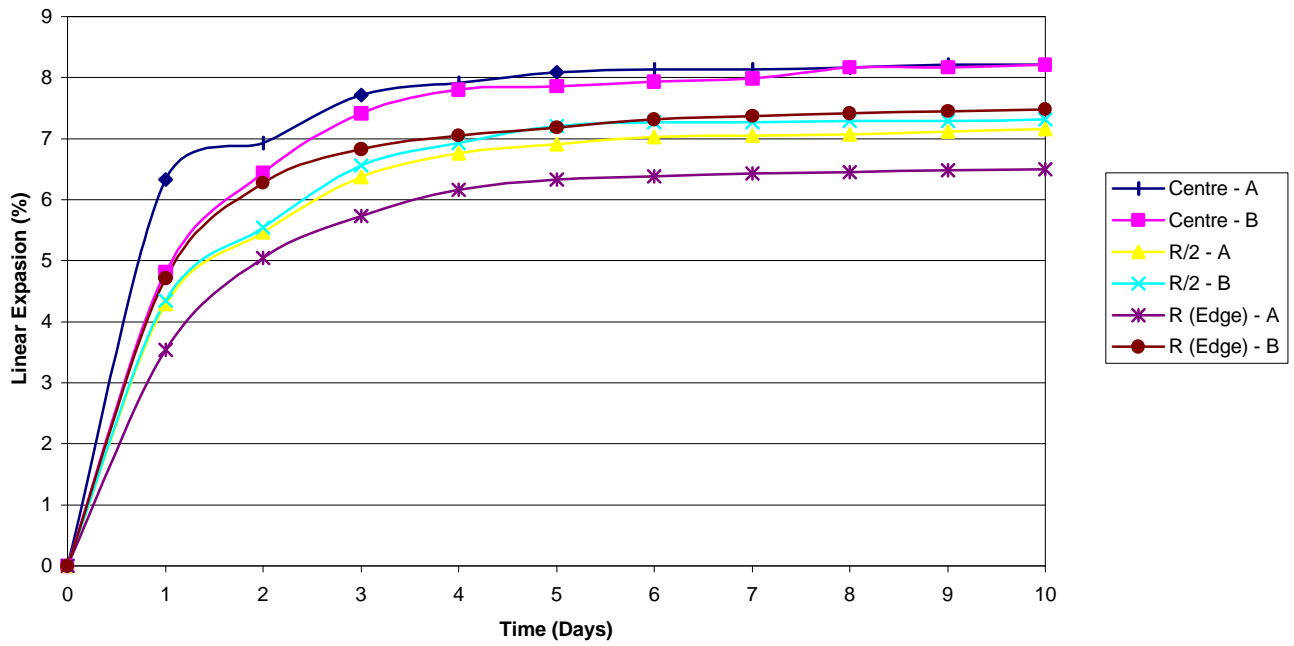
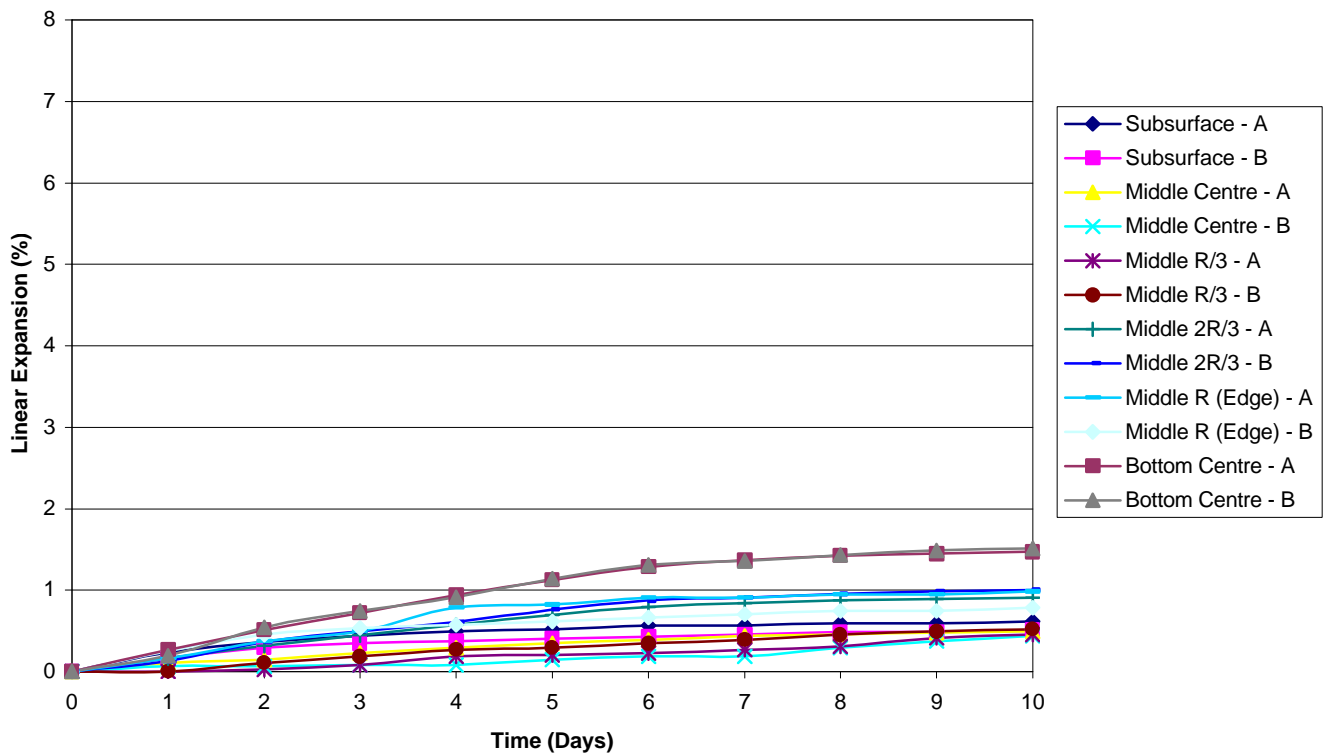Figure 5(a): Linear expansion results, Trial #3, Control Slag, Coarse Gradation

Figure 5(b): Linear expansion results, Trial #3, Fayalite-Modified Slag, Coarse Gradation
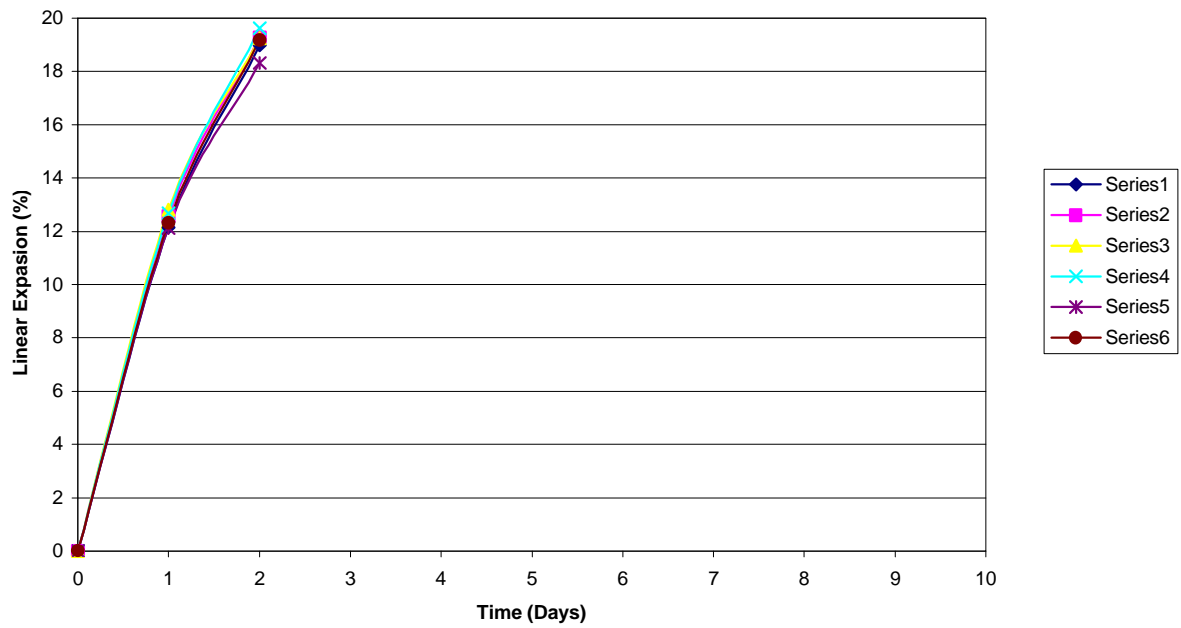
Figure 6(a): Linear expansion results, Trial #1, Control Slag, Coarse+Fine Gradation
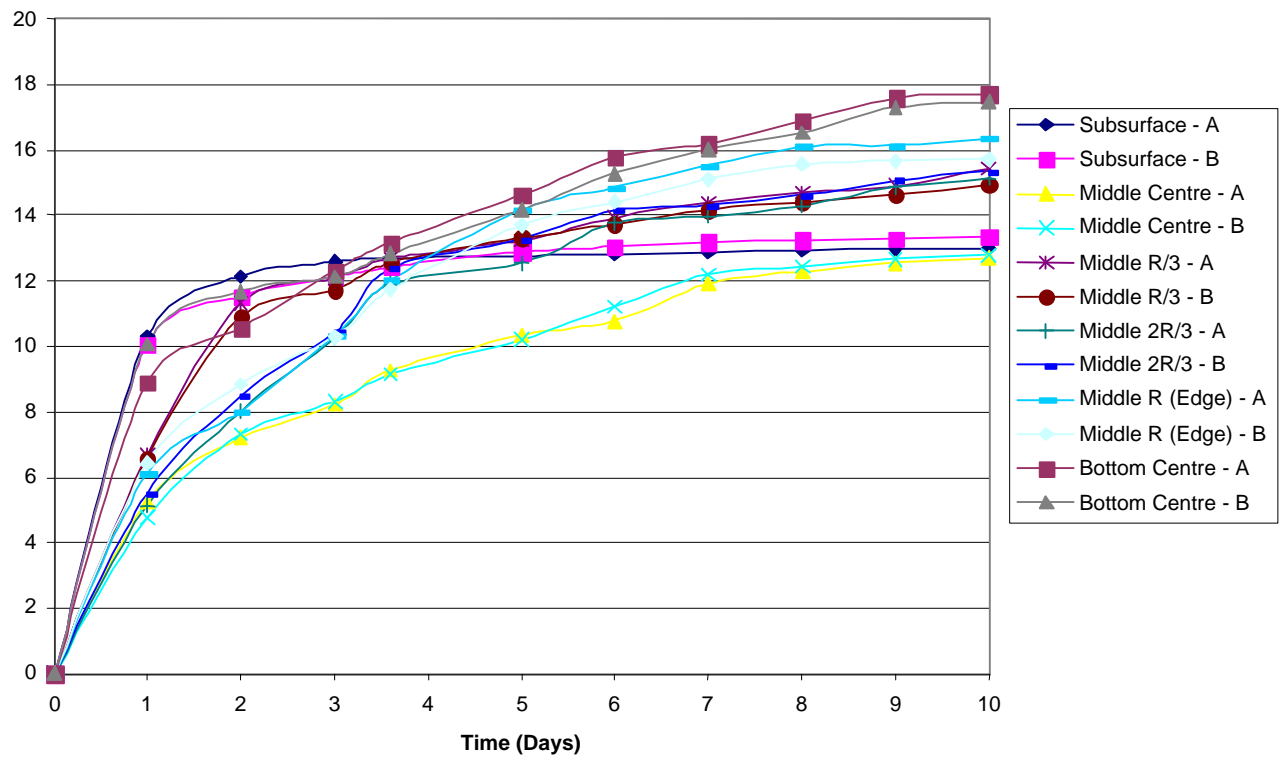

Figure 6(b): Linear expansion results, Trial #1, Fayalite-Modified Slag, Coarse+Fine Gradation

Figure 7(a): Linear expansion results, Trial #2, Control Slag, Coarse+Fine Gradation

Figure 7(b): Linear expansion results, Trial #2, Fayalite-Modified Slag, Coarse+Fine Gradation
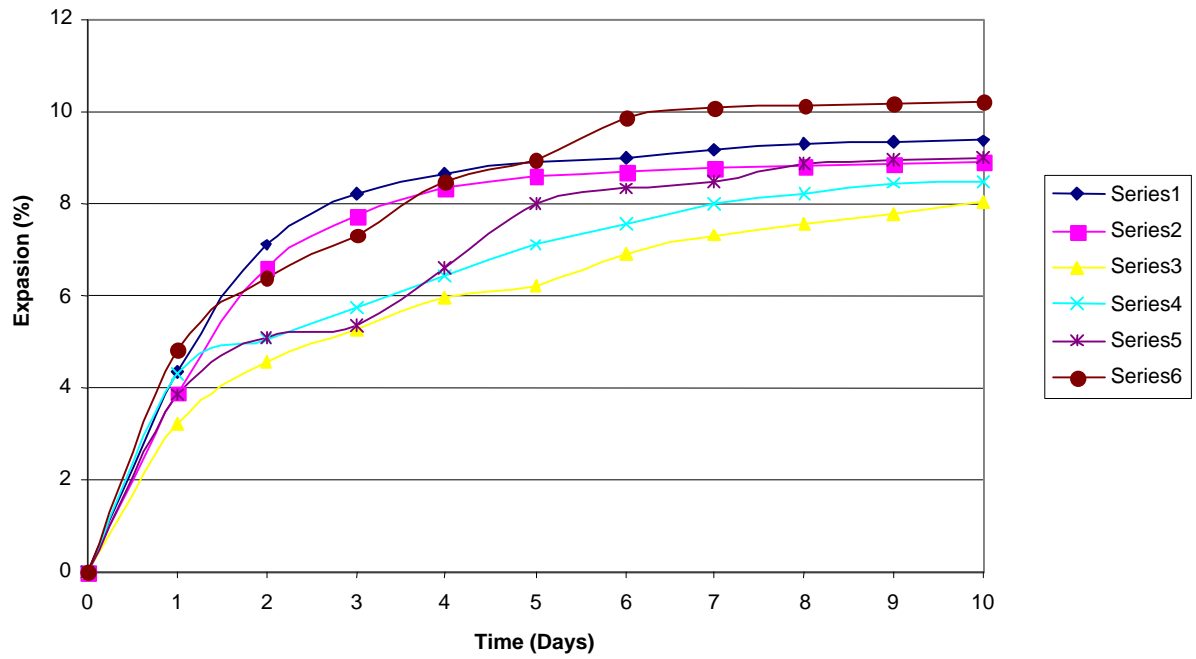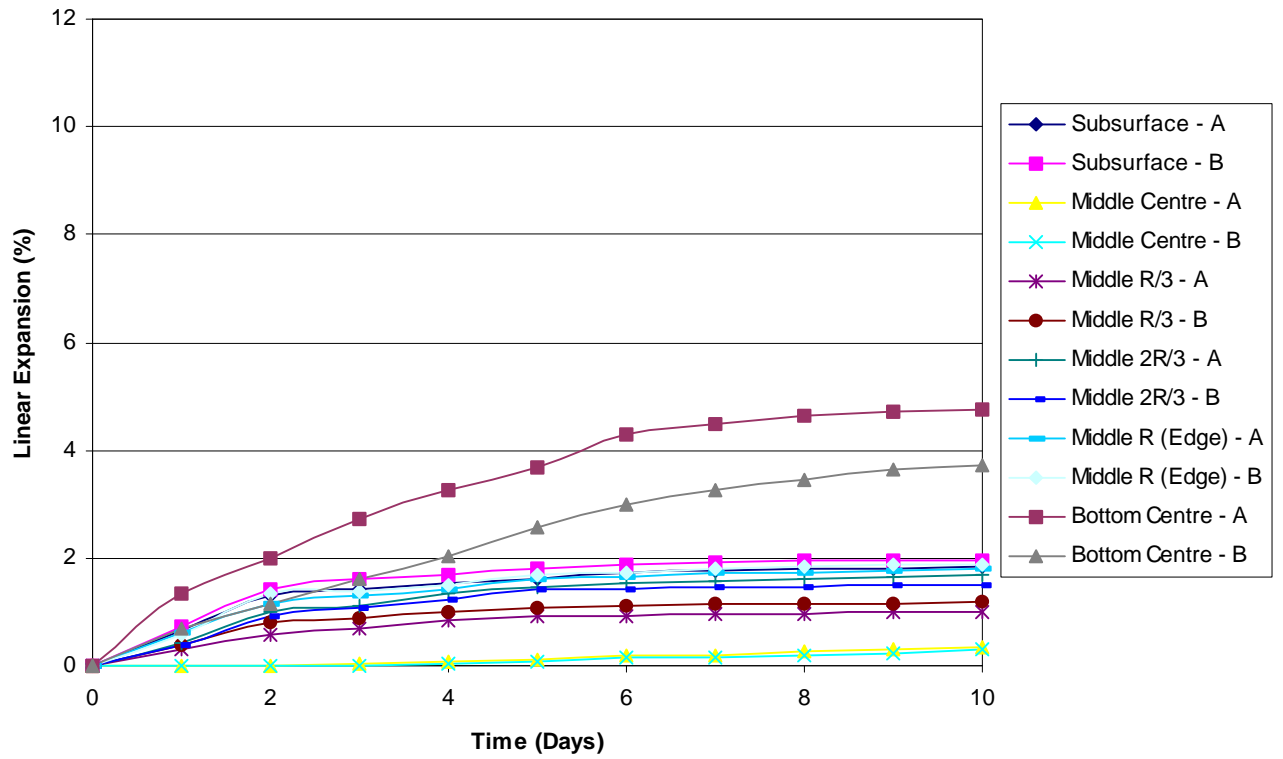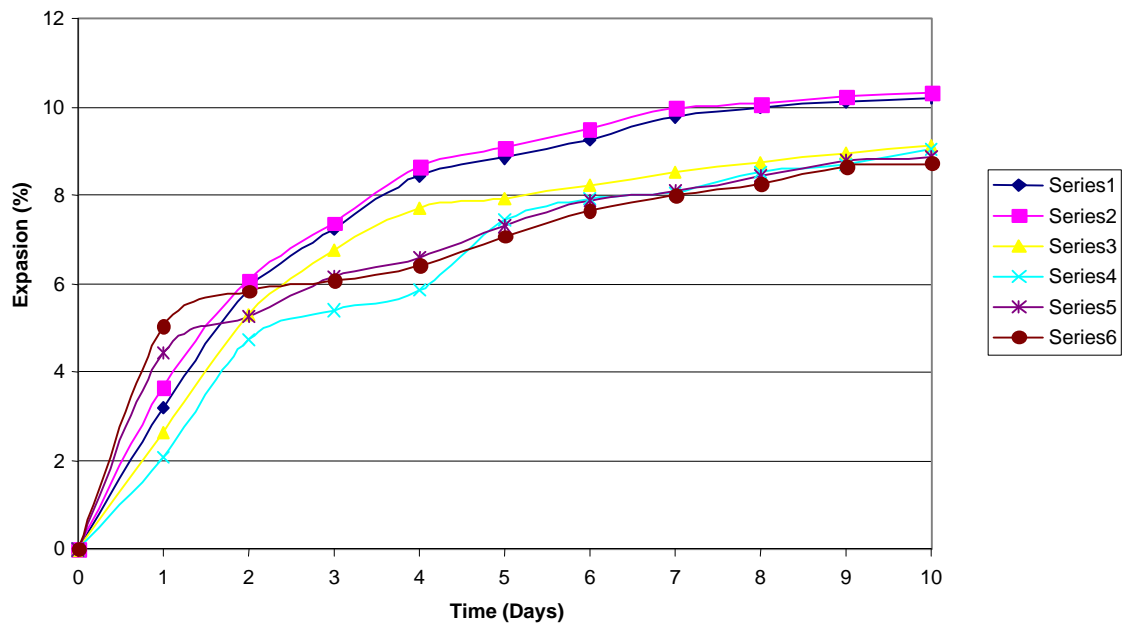
Figure 8(a): Linear expansion results, Trial #3, Control Slag, Coarse+Fine Gradation
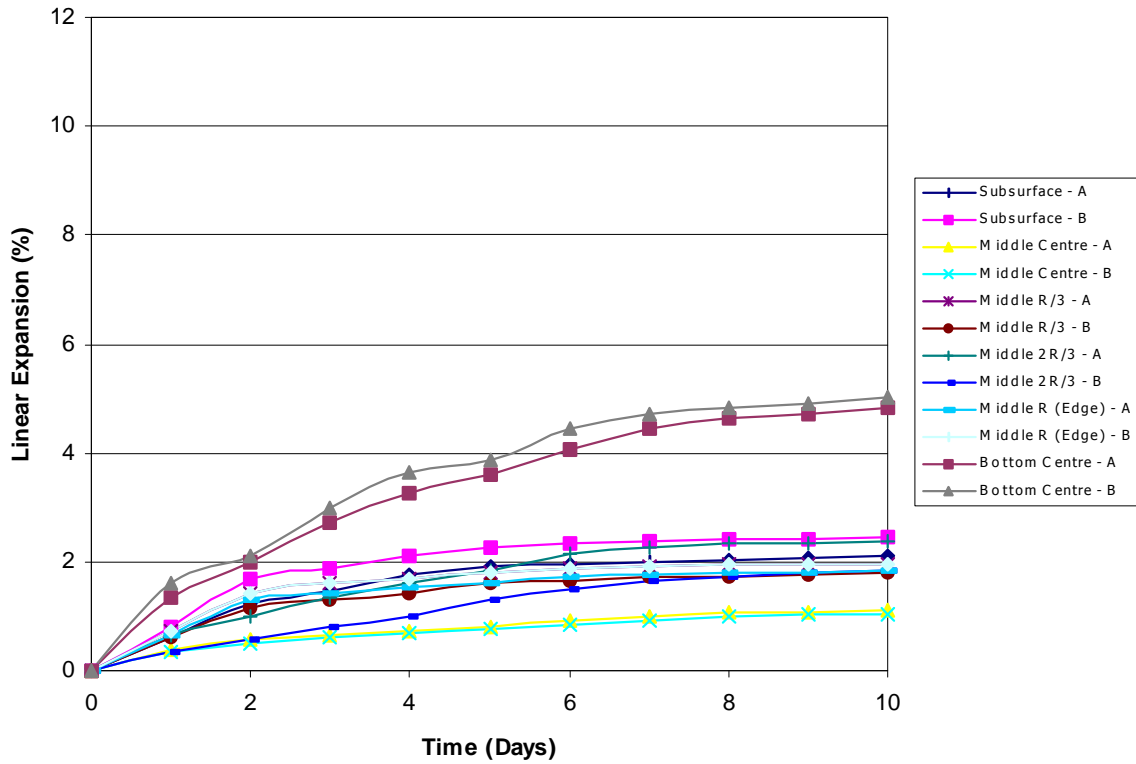
Figure 8(b): Linear expansion results, Trial #3, Fayalite-Modified Slag, Coarse+Fine Gradation
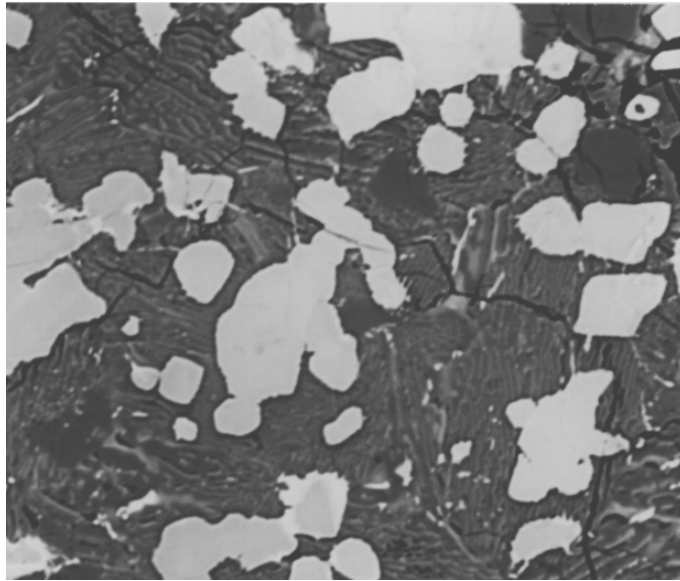
10 µm

Figure 9: Photomicrograph of typical microstructure for Control Slag, Trial #2
        light solid phase − magnesio-wustite, Fe(Mg,Mn)O
        dark phase − dicalcium silicate, Ca_2SiO_4
        light rivulets − free lime, CaO
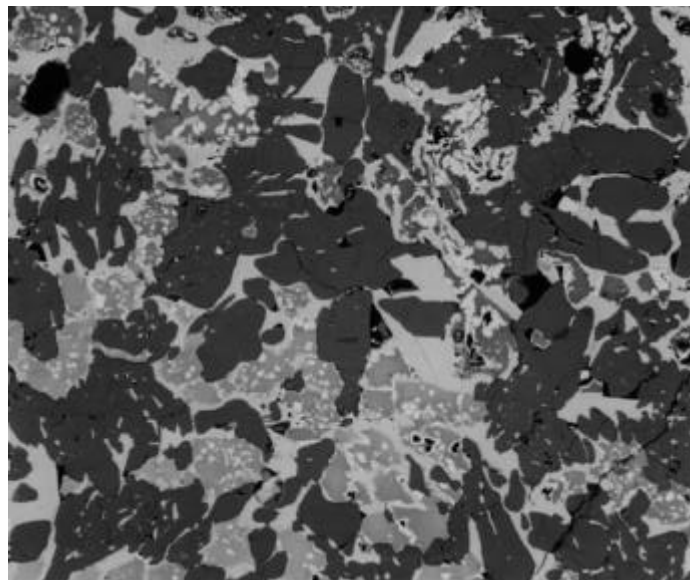
20 µm

Figure 10: Photomicrograph of typical microstructure for Fayalite-Modified Slag, Trial # 2
        light solid phase − magnesio-wustite, Fe(Mg,Mn)O
        dark phase − dicalcium silicate, Ca_2SiO_4
        medium phase − dicalcium ferrite, $2CaO \cdot Fe_2O_3$

Figure 11: Final modified slag temperature based on steelmaking slag temperature at time of fayalite addition as derived by heat balance calculations for varying addition percentages (wt.%).

Table 1: Typical chemical composition of granulated fayalite slag used in this study.

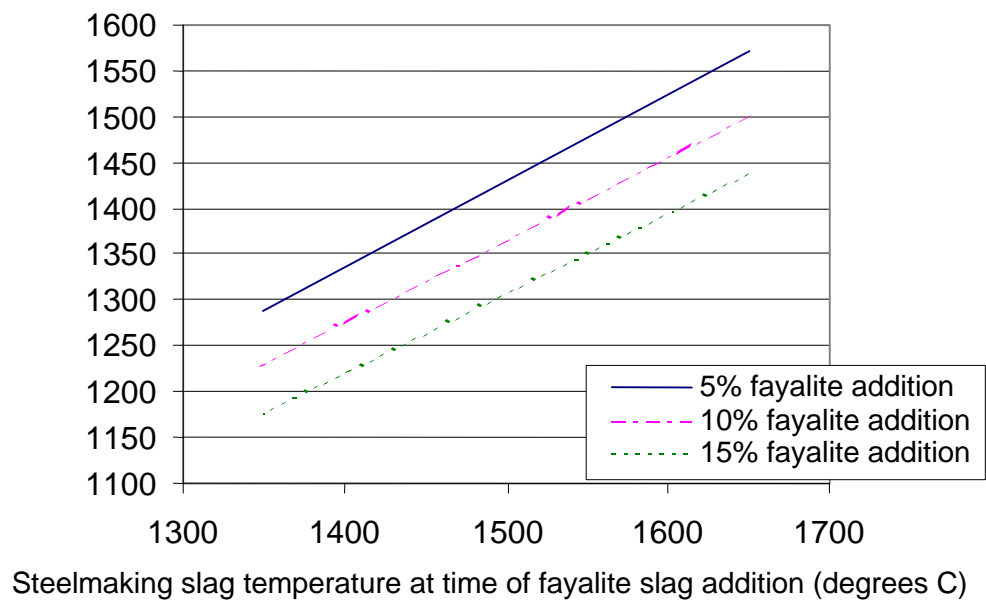| Component	FeO	Fe_3O_4	SiO_2	MgO	Al_2O_3	S	Cu	Ni	Co	CaO
Weight %	39.4	10.2	37.9	2.37	4.71	0.98	0.50	0.52	0.20	1.61

Table 2: Particle size distribution for the two aggregate gradations used in this study.

Metric Sieve Size	Percent Passing	
	Coarse Gradation	Coarse + Fine Gradation
26.5 mm		100 %
19.0 mm		95 %
16.0 mm	100.0 %	
13.2 mm	97.7 %	75 %
9.5 mm	58.6 %	60 %
6.7 mm	29.3 %	
4.75 mm	0.0 %	40 %
2.36 mm		
1.18 mm		20 %
600 μm		
300 μm		12 %
150 μm		
75 μm		4 %

Table 3: Example of chemical analysis results for slag samples.

Trial	Weight percent of component for first turndown (control) steelmaking slag sample.											
	FeO	CaO	MgO	SiO_2	Al_2O_3	Fe_{total}	MnO	P	Cr_2O_3	TiO_2	S	V-ratio
# 1	26.0	31.8	12.4	7.9	0.84	27.0	7.9	0.22	0.41	0.73	0.07	4.0
# 2	21.0	33.5	12.6	10.1	0.70	24.4	7.6	0.21	0.51	0.73	0.16	3.3
# 3	28.2	28.9	12.4	8.2	1.2	29.9	8.3	0.19	0.43	0.72	0.11	3.5

Table 4: Fayalite slag addition range ($^{wt}/_o$) established by component mass balance.

Trial #	Fayalite slag addition based on component mass balance ($^{wt}/_o$)			Addition Range ($^{wt}/_o$)
	CaO	SiO_2	Fe	
1	6.3 %	7.8 %	9.2 %	6.3 – 9.2 %
2	7.1 %	6.8 %	11.3 %	6.8 – 11.3 %
3	9.5 %	7.4 %	9.6 %	7.4 – 9.6 %

Table 5: Range of 10-day linear expansion results for all three trials.

Gradation	Trial #1	10-day linear expansion range	
		Control	Fayalite-Modified
Coarse	#1	16 to 18 %	7 to 12 %
	#2	5 to 7 %	0.2 to 0.6 %
	#3	6 to 8 %	0.4 to 1.0 %
Coarse + Fine	#1	20+ %	12 to 18 %
	#2	8 to 10 %	0.4 to 2 %
	#3	9 to 10 %	1 to 2.5 %

Table 6a: Trial #1 linear expansion results and [CaO]/[SiO₂] by sampling region.

Slag Type	Sampling Region in Slag Pot	10-Day linear expansion (%)		[CaO]/[SiO₂]
		Coarse Gradation	Coarse+Fine	
Control	Edge (r)	17.8 to 18.3 %	+20 %	4.3 to 4.5
	Half (r/2)	16.4 to 16.8 %	+20 %	4.3 to 4.4
	Centre	16.9 to 17.5 %	+20 %	4.3 to 4.4
	Subsurface	10.4 to 11.2 %	13.0 to 13.4 %	3.2 to 3.5
	Edge (r)	8.2 to 9.2 %	12.7 to 12.8 %	3.5 to 3.9
	Half (r/2)	7.4 to 8.0 %	15.0 to 15.4 %	3.6 to 3.9
	Edge (r/3)	6.4 to 6.7 %	15.1 to 15.4 %	2.6 to 2.9
	Middle Centre	5.3 to 5.9 %	15.7 to 16.4 %	2.6 to 3.0
	Bottom Centre	11.5 to 12.0 %	17.5 to 17.7 %	3.9 to 4.5

Table 6b: Trial #2 linear expansion results and [CaO]/[SiO$_2$] by sampling region.

Slag Type	Sampling Region in Slag Pot	10-Day linear expansion (%)		[CaO]/[SiO$_2$]
		Coarse Gradation	Coarse+Fine	
Control	Edge (r)	6.6 to 6.8 %	8.9 to 9.4 %	3.4 to 3.7
	Half (r/2)	6.5 to 7.0 %	8.0 to 8.5 %	3.5 to 3.7
	Centre	5.4 to 5.8 %	8.9 to 10.2 %	3.4 to 3.6
Fayalite-Modified	Subsurface	0.4 to 0.5%	1.8 to 2.0 %	2.7 to 3.1
	Edge (r)	0.5 to 0.6 %	0.31 to 0.35 %	2.5 to 2.9
	Half (r/2)	0.4 to 0.5 %	1.0 to 1.2 %	2.5 to 2.7
	Edge (r/3)	0.2 to 0.3 %	1.5 to 1.7 %	2.4 to 2.6
	Middle Centre	0.02 to 0.04 %	1.8 to 1.9 %	2.2 to 2.7
	Bottom Centre	1.1 to 1.3 %	3.7 to 4.7 %	2.9 to 3.3

Table 6c: Trial #3 linear expansion results and [CaO]/[SiO$_2$] by sampling region.

Slag Type	Sampling Region in Slag Pot	10-Day linear expansion (%)		[CaO]/[SiO$_2$]
		Coarse Gradation	Coarse+Fine	
Control	Edge (r)	8.1 to 8.2 %	10.2 to 10.3 %	3.7 to 3.9
	Half (r/2)	7.2 to 7.3 %	9.0 to 9.1 %	3.5 to 3.9
	Centre	6.5 to 7.5 %	8.7 to 8.9 %	3.5 to 3.8
Fayalite-Modified	Subsurface	0.5 to 0.6 %	2.1 to 2.5 %	2.6 to 3.0
	Edge (r)	0.4 to 0.5 %	1.0 to 1.1 %	2.5 to 2.7
	Half (r/2)	0.4 to 0.5 %	1.8 to 2.0 %	2.6 to 2.8
	Edge (r/3)	0.9 to 1.0 %	1.9 to 2.4 %	2.7 to 3.0
	Middle Centre	0.8 to 1.0 %	1.8 to 2.0 %	2.6 to 2.9
	Bottom Centre	1.4 to 1.5 %	4.8 to 5.0 %	3.0 to 3.3