

THE ROLE OF SLAG CHEMISTRY IN DEPHOSPHORIZATION:
AN EQUILIBRIUM AND KINETIC STUDY

by

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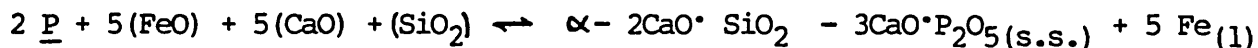
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ABSTRACT

The liquid solution behavior of phosphorus in iron-phosphorus alloys and steelmaking slags is reviewed with emphasis placed on characterizing alloy solute and slag component interactions. Complex metal-oxide phase relationships are discussed in an attempt to explain slag-metal reaction behavior and demonstrate significant interactions which occur within the liquid phase in specific composition regions. Reaction behavior is explained with reference to prominent features such as miscibility gaps, saturation surfaces and elevated liquidus temperatures, where regions of saturation with refractory-type reaction products occur.

Using levitation melting, slag component interactions were clarified by performing slag-metal equilibrations with a variety of slag systems ranging from the most simple basic oxides to more complex silico-oxyfluorides and synthetic basic oxygen steelmaking slags. In light of the results of the present study, existing dephosphorization correlations are critically evaluated in terms of both their regions of validity and accuracy in predicting equilibrium distribution behavior. A new equilibrium correlation is proposed based on a reaction model which takes into account present understanding of the complex slag phase relationships and microstructural observations of slag samples.

In the vicinity of dicalcium silicate saturation surface of basic steelmaking slags, the proposed dephosphorization reaction is given as follows:



At 1600°C, the value of the equilibrium quotient for this reaction is 1.30×10^{-12} in the region of the solid solution saturation surface. Slag component interactions are discussed in relation to their influence on the slag liquidus temperatures and silico-phosphate saturation surfaces of these slags.

Previous studies of dephosphorization reaction kinetics are critically reviewed in light of slag phase relationships and the dephosphorization reaction model presented in this study. The relative importance of thermodynamic equilibrium and metastable non-equilibrium states is discussed in regard to the proposed reaction mechanism and observed refining behavior. Experiments were performed to study the interactions of phosphorus, silicon, and carbon during oxidation with basic slags. Providing that a sufficient thermodynamic driving force is initially present for phosphorus, by proper choice of slag compositions, phosphorus was found to react simultaneously and competitively with these solutes. These results are discussed with reference to refining of hot metal in both basic oxygen steelmaking furnaces as well as with regard to current interest in preliminary external refining treatments.

A novel method for producing high density and high purity magnesia and calcia refractory labware was developed and optimized using lithium halides as sintering aids. Densities approaching theoretical values were obtained at low sintering temperatures with rapid firing schedules.

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PART A: SLAG-METAL DEPHOSPHORIZATION EQUILIBRIA

I. INTRODUCTION

With recent developments in solid-state microanalytical and surface analysis technology, particularly with advancement in Auger spectroscopy, increasing attention has focused on the metallurgical role of residual elements in alloy steels and the requirement for producing ultra-pure steels in order to improve both the mechanical properties and service life of these alloys.

As a major trace element in steels, phosphorus has long been recognized as a ferrite former and ferrite strengthener. Traditionally, due to its pronounced influence in decreasing ductility and causing embrittlement in low carbon steels, phosphorus is considered to be a hardening agent.¹ Additions of phosphorus cause a general raising of ductile-brittle transition temperatures in alloys and, as a molecular hydrogen recombinant poison, phosphorus induces hydrogen embrittlement² and promotes stress corrosion cracking.³

Recent microstructural studies have shown that phosphorus is very active at grain boundaries.⁴ During tempering, phosphorus segregates to grain boundaries and is a major factor in temper embrittlement.^{5, 7} It is known to lower grain boundary surface energies and promote intergranular fracture.^{6, 7} Because of this, phosphorus tolerances are restrictive in welding since segregation occurs within the heat-affected zone, causing embrittlement-susceptible weld regions and occasional eutectic composition formation within enriched regions.⁸

Utilizing Auger spectroscopy, advanced microstructural studies of fracture surfaces have demonstrated that even minute traces of phosphorus play an active role at grain boundaries.⁴ Due to strong interactions with alloying elements such as chromium, nickel, manganese, molybdenum and their precipitated carbides,^{9, 10} considerable cosegregation or promoted

segregation is observed and undesirable mechanical properties have been directly correlated to effective grain boundary phosphorus concentration rather than bulk concentrations.¹¹⁻¹⁴ While current HSLA standards call for phosphorus specifications of $<0.02\%$, impurity-induced failure mechanisms have been observed at bulk phosphorus concentrations of 0.005% .

As increasingly greater percentages of steel production are being continuously cast, interest in residual element control during processing is growing. The behavior of phosphorus within continuous casting streams is of particular interest, and control of residual phosphorus is particularly problematic. Since casting streams require higher tapping temperatures, phosphorus refining in furnaces will be adversely affected due to the observed temperature dependence of the refining reaction. During ladle transfer, deoxidizers are sometimes added to "kill" the steel, and these tend to promote reversion of phosphorus from slag to metal. In addition, considerable macrosegregation occurs in the casting strand due to the nature of the solidification process, and localized enrichment of phosphorus can lead to major structural defects and problems with subsequent tempering and mechanical working.¹⁵

This increasing awareness of the metallurgical effects of trace phosphorus levels in alloy steels has spawned considerable current interest in alloy refining processes for producing ultra-pure steels, particularly in Japan. Renewed interest in basic steelmaking slag chemistry and refining behavior has developed. Novel external refining treatments with a variety of fluxes have been the subject of an increasing number of investigations. Alternative approaches to steel converting have been suggested in order to improve product quality and reduce refining costs. It is within this current climate that the present study was initiated with the intention of clarifying slag refining chemistry in basic oxygen

steelmaking processes. Particular emphasis was given to understanding dephosphorization refining behavior and the role of slag components in the reaction chemistry. Ultimately, it was desired to identify optimum slag composition regions where maximum refining capacity is achieved and to establish the extent to which magnesia can be utilized as a lime substitute in steelmaking practice.

Historically, considerable emphasis has been placed on the dominant influence of slag lime content on refining at the expense of understanding the relative importance of other constituents. As a direct result, current understanding of slag refining chemistry is based primarily on empirical observation and very little is known regarding component interactions and their influence on the phosphorus reaction. Attempts to evaluate the relative benefits of slag component substitution are plagued with difficulties in making meaningful comparisons, and the literature of steelmaking is filled with conflicting claims as to the merits of a particular component addition.

Generally, within the confines of basic steelmaking practice, there is not a great deal of flexibility in the choice of slag composition, since this depends primarily on the hot metal charge and the oxygen blowing rate and duration which is ultimately determined by the grade of steel being produced. For a given furnace practice, slag lime, silica, phosphorus and iron oxide contents are fairly consistent. Endpoint slags are usually saturated with dicalcium silicate and most liquid compositions tend to lie on this saturation surface. However, during the course of refining, slag development paths are quite variable depending on individual practice, and the rate and path of slag formation are rather important variables in controlling refining behavior. This is why so much attention has been given to studies of lime dissolution rates and the effect of various fluxes

on lime solubility and slag development kinetics.

There are a variety of practical reasons for considering the use of magnesia as a slag fluxing agent and a lime substitute in basic oxygen steelmaking practice. As pure calcitic lime sources become depleted, dolomitic lime becomes an attractive and economic substitute. Lime dissolution in slags is generally inhibited by the formation of a refractory calcium orthosilicate reaction layer on the lime surface. The presence of magnesia in slags has been known to reduce the tendency to form an impermeable product layer and thus promotes early basic slag development by reducing the slag liquidus temperature and increasing slag fluidity.¹⁶⁻¹⁸ Because of this, magnesia additions eliminate problems of unfused lime and thus reduce lime charging requirements and the need for additional fluxing agents such as fluorspar.^{16, 17, 20}

Magnesia additions have other potential benefits due to their influence on slag physical characteristics. With controlled addition, below the saturation level, magnesia lowers the slag liquidus temperature and melt viscosity,^{17, 18} promoting rapid slag development and shorter blowing times.²⁰ Approaching saturation levels, additions of magnesia raise apparent slag viscosity and eliminate slopping during hard blowing.^{19, 20} Due to an endothermic heat of solution, dolomite addition can control excessive temperature increases during the course of a blow, acting as a cooling agent.²⁰

Magnesia addition to slags is generally preferred to the use of other fluxing agents due to its dramatic influence in prolonging furnace lining life and reduction in refractory corrosion.^{19, 20, 277, 281, 282} Virtually all basic oxygen furnaces are lined with magnesite refractories, and additions of magnesia early in the blow saturate the slag, thus reducing the chemical potential gradient between slag and refractory and limiting

the amount of corrosive attack. Further benefits are realized as the slag becomes saturated with magnesia and a highly viscous protective coating forms on the lining.^{18, 19} This impedes slag penetration and slows the kinetics of lining attack. In addition, due to its role as a fluxing agent in promoting early basic slag development, magnesia additions reduce the exposure time of the basic lining to initially formed acidic slag.

While dolomitic lime has never been considered as a replacement for calcitic lime, due to the previously mentioned advantages of magnesia additions to slags, various degrees of substitution practice have been tested. The extent of substitution has varied considerably depending on the grade of steel being produced and particular plant practice. Conflicting claims have been made as to the relative benefits of magnesia additions and optimum substitution levels. From early preliminary plant trials in the 1960's, substitution practice reached a maximum of 50% in the early 1970's and since then there has been a steady decrease to 20-30% substitution due to some undesirable side effects of high magnesia slag practice.¹⁹

With excessive additions of magnesia to basic oxygen steelmaking slags, super-saturated slags precipitate refractory-type compounds such as magnesio-wustite, olivine solid solutions, forsterite and spinels.²⁷⁷ Such phases cause rapid bottom build up in furnaces and significantly reduce both the effective furnace volume and throughput. In addition, as the magnesia solubility limit is exceeded, slags having very high apparent viscosities are produced and furnace operation becomes erratic due to problems with emulsion formation and foam stabilization caused by suspended precipitates within the slag.²⁷⁷ This results in increased losses of metallic iron suspended in the slag, slower reaction kinetics due to inhibited mass transfer and rapid slag set up time due to high viscosity and elevated

liquidus temperatures.²⁷⁷ While such operational problems can be minimized by developing a working knowledge of the particular handling characteristics of high magnesia slags, there is significant concern over the refining properties of these slags and possible loss of metallurgical control with both sulfur and phosphorus residuals.^{19, 20, 277-280}

The chemistry of magnesia-based slags and the role of magnesia in slag dephosphorization behavior is not well characterized either on a laboratory scale or in plant operations practice. However, with high carbon heats, magnesia slags have not been able to meet phosphorus specifications for certain alloy grades.^{19, 20} In addition, some reduction in sulfur removal has been observed.^{20, 280} Such observations have been explained, in the case of dephosphorization, by magnesia's role in neutralizing the effective oxidation potential of slags through formation of magnesio-wustite with iron oxide.¹⁹ Magnesia is also considered somewhat less reactive than lime on the basis of measured thermodynamic properties of the orthophosphates and their relative high temperature phase stabilities and the empirically determined compositional dependence of dephosphorization behavior. Thus, partial substitution of lime with magnesia would be expected to reduce slag refining power through a dilution effect and, naively, the best approach would be optimization of charging practice so as to reduce metallurgical losses to a minimum. Some industrial substitution trials have demonstrated improved dephosphorization with moderate additions of magnesia^{20, 277-9} and this may be due to the relative importance of slag development path and kinetic factors which permit early slag formation and better refining during the initial blowing period. Generally, the conventional view of reduced dephosphorization refining power with magnesia slags remains prominent and the question remains as to whether there is a kinetic or thermodynamic basis for understanding discrepancies in observed refining

behavior.

It is this uncertainty in current understanding of the refining chemistry of magnesia-based slags which inspired the present study. In order to obtain a sound footing, it was necessary to review the historical development of previous approaches toward dephosphorization reaction behavior and the various roles of other slag constituents in slag refining chemistry. It was necessary to approach the problem from several viewpoints. The role of solution thermodynamics and structural factors were considered with regard to potential interactions between various slag constituents. The importance of identifying the dephosphorization reaction product or form of dissolution of phosphorus in the slag was realized. An understanding of the complex phase relationships, miscibility gaps, saturation surfaces, elevated liquidus temperatures and extensive regions of heterogeneous phase stability was required.

In attempting to characterize the refining behavior of various slags on the basis of their dephosphorization capacity, it is desirable to select a correlation which adequately reflects this ability and serves as a useful means of comparison. There are many existing correlations from which to choose, all of which are essentially statistical-empirical in nature and rely on curve-fitting a pseudo-equilibrium quotient to available data through regression analysis. As such, these correlations have no fundamental thermodynamic basis and they offer little information as to the nature of the dephosphorization reaction mechanism. A major flaw in existing correlations is that they are not very sensitive in predicting either residual phosphorous levels in alloys or estimating phosphorous distribution on the basis of slag composition. Because of the relative insensitivity of existing correlations, they tend to ignore significant systematic compositional factors which produce subtle changes in refining

behavior and generally assume the essential equivalence of basic and acidic oxides in refining chemistry. Thus, it is considerably difficult to evaluate the influence of compositional changes on refining behavior using existing correlations and a new dephosphorization criterion is required for adequate comparison.

In a study such as this, the relative importance of equilibrium and kinetic factors must be clarified. The comparison of equilibrium laboratory studies with a non-equilibrium reaction system such as a basic oxygen convertor is not particularly suitable, particularly when an equilibrium analysis leads to a contradiction of predicted and observed behavior. Traditionally, the equilibrium approach to steelmaking reactions has established itself as a historical bias of chemical metallurgists. This has evolved from the considerable interest in basic open hearth reactions which proceed close to equilibrium during the refining stage. Since the speed and efficiency in refining with basic oxygen steelmaking processes depend primarily on non-equilibrium contacting conditions, an equilibrium study alone cannot provide adequate information as to what actually occurs within the furnace during refining. For this reason the primary study of slag-metal equilibrium refining behavior presented in the following sections was supplemented by a kinetic study in Section B. This was necessary in order to clarify some of the present misconceptions which exist in the literature in regard to equilibrium and metastable, non-equilibrium states. This additional kinetic study, combined with the equilibrium approach proposed in this section, provides a self-consistent model of phosphorous refining behavior which is capable of explaining slag-metal reactions in basic oxygen convertors and some anomalous behavior observed with current studies of hot-metal pretreatment refining.

II. LITERATURE REVIEW

In this section the properties of binary and multicomponent iron-phosphorus alloys are reviewed with regard to phase equilibria and solution thermodynamics in Part A. Phase relationships and thermodynamic properties of pertinent slag systems are discussed in Part B. In Part C, slag-metal phosphorus distribution studies and dephosphorization correlation development are critically reviewed.

A. Properties of Iron-Phosphorus Alloys

1. Binary Phase Equilibria

Recently, the iron-phosphorus binary phase diagram has been critically reviewed by Schurmann²¹ and Kubaschewski²² and the thermodynamic properties of various phases have been evaluated so as to provide consistency with reported phase boundaries. The iron-rich region of the binary system has been studied by several authors and, at steelmaking temperatures, a region of complete miscibility is present as shown in Figure 2.1. The limit of solubility of phosphorus in austenite and ferrite is 0.306 and 2.56 %, respectively, and phosphorus is generally considered to be a ferrite former. Both of the iron phosphides demonstrate high temperature stability and are indicative of the rather strong interactions between iron and phosphorus. Phosphorus has a correspondingly low activity in liquid binary alloys in these composition regions.

2. Alloy Solution Thermodynamics

a. Binary Alloys

In high temperature x-ray diffraction studies of liquid iron-phosphorus alloys, Waseda found short range order in the liquid state with nearest neighbor type distances similar to the Fe_3P arrangement.²³ This would imply relatively strong interactions between iron and phosphorus in the liquid state.

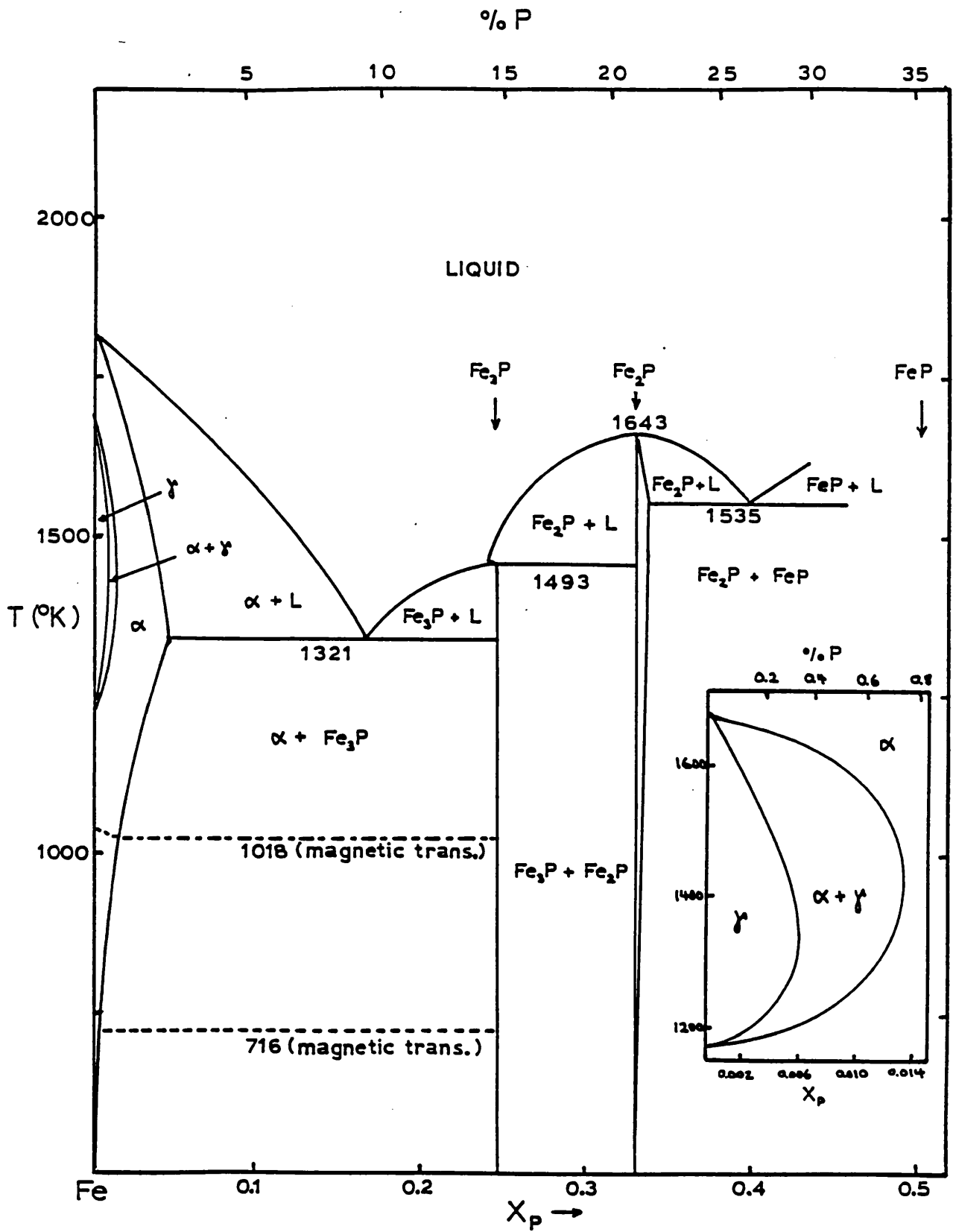


Figure 2.1 Iron-Phosphorus Binary Phase Diagram (22).

The solution behavior of phosphorus in iron-phosphorus alloys has been studied by numerous workers. Urbain,²⁴ Froberg²⁵ and Banya²⁶ investigated the phosphorus distribution equilibria between liquid silver and iron-phosphorus alloys. Schenck²⁷ utilized a pseudo-isopiestic method. Both transpiration studies and modified transpiration studies were used by Granowskaya,²⁸ Banya²⁹ and Bookey.³⁰ Langmuir evaporation was used by Polyakov.³¹ Schurmann³² utilized differential thermal analysis and high-temperature calorimetry. E.M.F. Studies were used by Fisher³³ and Esin.³⁴ Yamada and Kato^{35, 36} utilized a Knudsen-effusion mass spectrometry technique.

Results of these studies indicate that phosphorus solution behavior demonstrates strong negative deviation from Raoult's Law and correspondingly strong positive deviation from Henry's Law. Virtually all of these studies have examined the concentration range from 0.1 to 0.4 mol fraction of phosphorus and the data have been extrapolated to lower concentration regions for estimating the phosphorus self-interaction parameter as well as the Henrian activity coefficient in the dilute solution region. Since deviations from Henrian behavior are observed at levels as low as 0.3 %P, such extrapolations are prone to considerable error. This accounts for the lack of agreement in the various studies as shown in Table 2.1. Since the phosphorus levels encountered in actual refining practice generally fall below those regions where large deviations are present, the assumption of Henrian solution behavior is generally valid in equilibrium treatment of slag-metal reactions.

The solubility of phosphorus gases in iron alloys and the phosphorus vapor pressure of binary alloys has been measured by several investigators and these results are shown in Table 2.2. Only the results of Bookey³⁰ and Banya²⁹ show good agreement. In all of these studies, the temperature

Table 2.1: Self Interaction Parameter for Phosphorus in Iron-Phosphorus Alloys

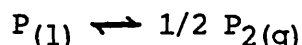
Study (Ref.)	Temperature Range (°C)	%P	e_p^p		Measurement Technique
			Reported	Recalculated	
Esin (34)	1470	1.5-23	0	0	E.M.F
Granowskaya (28)	1540-1620	0.1-1.0	-	0	Tracer Effusion
Urbain (24)	1355-1600	5-22	-	0.040	Ag/Fe Distribution
Schenk (27)	1515-1540	9-30	0.122 (0.039)	0.122	Isopiestic (Graphite Saturation)
Fischer (33)	1650	.034-20	-	0(< 1.1 %P) 0.044(> 1.1 %P)	E.M.F.
Frohberg (25,48)	1600	6-16	0.062 (0.024)	0.061	Ag/Fe Distribution (Graphite Saturation)
Aratani (43)	1540-1600	0.05-2.0	0.01-0.04	-	CaO/4CaO·P ₂ O ₅ Equilibrium
Banya (26)	1300-1600	4.7-22	0.030	0.047	Ag/Fe Distribution
Polyakov (31)	1550-1600	0.3-6.0	-	0.036	Vacuum Effusion
Yamada (35)	1600	0.7-3.2	0.054	0.051	Mass Spectrometer and Knudsen Cell
Banya (29)	1200-1500	4.5-18.7	0.022	0.044	Transpiration
Elliott (38)	1600	-	0.062	-	Data Review

Table 2.2: Solution Behavior of Phosphorus Gases and Henrian Activity Coefficient of Phosphorus in Liquid Iron Alloys

Study (Ref.)	Temperature Range (°C)	%P	Reaction	ΔG_T° (KJ/mol)	$\gamma^\circ(1525^\circ\text{C})$
Bookey (30)	1540–1580	0.008–1.00	$1/2 \text{ P}_2(\text{g}) = \underline{\text{P}}_{(1\text{w/o})}$ $\text{P}_{(1)} = \underline{\text{P}}_{(1\text{w/o})}$	$-122.44 - 0.019T$ $-64.192 - 0.070T$	3.2×10^{-6}
Schenk (27,61)	1515–1650	9–30	$1/2 \text{ P}_2(\text{g}) = \underline{\text{P}}_{(1\text{w/o})}$ $\text{P}_{(1)} = \underline{\text{P}}_{(1\text{w/o})}$	$-463.48 + 0.173T$ $-404.72 + 0.122T$	4.9×10^{-6}
Yamamoto (36)	1590–1580	1–3	$1/2 \text{ P}_2(\text{g}) = \underline{\text{P}}_{(1\text{w/o})}$ $\text{P}_{(1)} = \underline{\text{P}}_{(1\text{w/o})}$	$-157.81 + 0.005T$ $-99.564 - 0.045T$	6.0×10^{-6}
Banya (29)	1200–1500	4.5–18.7	$1/2 \text{ P}_2(\text{g}) = \underline{\text{P}}_{(1\text{w/o})}$ $\text{P}_{(1)} = \underline{\text{P}}_{(1\text{w/o})}$	$-131.83 - 0.018T$ $-73.573 - 0.068T$	2.1×10^{-6}
JANAF (37)	–	–	$\text{P}_{(1)} = 1/2 \text{ P}_2(\text{g})$	$58.22 - 0.054T$	–

dependence of the reaction is subject to significant error since only limited temperature ranges were investigated. Within the range of 1500 to 1600°C fairly good agreement is found.

By combining the results of these studies and using data available for the vaporization of pure liquid phosphorus³⁷ where



and

$$\Delta G_T^O = 58.22 - 0.0504T \quad (\text{KJ/mol}) ,$$

the standard free energy change can be calculated for the change of standard state from Raoultian to the hypothetical 1 w/o standard state or Henrian standard state. Henrian activity coefficients can be estimated. These values are listed in Table 2.2 for each of the investigations. With such low values for the Henrian activity coefficient and large negative enthalpy of solution, it is obvious that phosphorus has a remarkable stability in solution and presents a major problem in removal during refining of steel.

b. Ternary and Multicomponent Alloys

In Table 2.3 phosphorus interaction parameters are listed for major solute elements encountered in steelmaking practice. Solute interactions in phosphorus-carbon and phosphorus-oxygen alloys have been studied by numerous workers and for phosphorus-carbon alloys good agreement is found. For phosphorus-oxygen alloys, experimental and sampling difficulties have produced considerable scatter in the data. Virtually all common solute elements, of either substitutional or interstitial type, tend to raise the activity of phosphorus in an iron matrix with the effect of silicon and chromium being most pronounced. It is important to note that, in the presence of carbon, moderate or strong carbide forming solutes such as chromium and molybdenum have rather complex interactions with phosphorus

Table 2.3: Solute Interaction Parameters for Iron-Phosphorus Alloys

Solute Element	Study (Ref)	Temperature Range	%P	%i	e_p^i	Equilibration Method
Oxygen	Schenk (39)	1600-1650	0.12-1.05	.03-0.2	-(0.277-0.292)	Co/Co ₂ gas
	Dutilloy (40)	1600	0.53-2.78	0.011-0.045	0.11	H ₂ /H ₂ O gas
	Fischer (41)	1600	0.25-4.0	0.035-0.12	0.005	EMF
	Banya (42)	1510-1610	0.5-5.5	0.035-0.12	-0.010	Co/Co ₂ gas
	Aratani (43)	1540-1600	0.048-1.99	0.006-0.035	0.05	H ₂ /H ₂ O gas
	Pearson (44)	1572-1660	0.05-1.71	0.025-0.05	-0.040	H ₂ /H ₂ O gas
	Chipman (45,60)	1600	-	-	-0.159	Estimated
	Sanbongi (46)	1540-1625	0.1-2.4	0.014-0.026	0.09	H ₂ /H ₂ O gas
	Levenetz (47)	1500-1650	0.05-3.2	0.012-0.032	-0.0635	H ₂ /H ₂ O gas
Carbon	Frohberg (25,48)	1600	4-20.4	0.4-5.4	0.0975-0.126	Graphite Solubility
	Schenk (39)	1600	0.12-1.05	0.8-1.25	0.142	Co/Co ₂ gas
	Mori (49)	1550	0.44-5.51	3.37-5.01	0.256	Graphite Solubility
	Banya (42)	1510-1610	0.5-5.5	0.030-.185	0.06-0.152	Co/Co ₂ gas
	Schenk (50)	1515	5.76-28.7	0.012-0.419	0.250	Graphite Solubility
	Banya (26)	1500	4.96-18.9	0.003-3.33	0.079	Ag/Fe Distribution
	Turkdogan (51)	1290-1575	0-4.18	3.07-5.25	0.114-0.126	Graphite Solubility

Table 2.3 (Cont.)

Solute Element	Study (Ref)	Temperature Range	%P	%i	e_p^i	Equilibration Method
Silicon	Schenck (52)	1515	14.6-26.5	1.20-11.96	0.118	Isopiestic
	Schenck (61)	1550	0-6.2	0-5.0	0.064	Isopiestic (Graphite Saturation)
	Yamada (55)	1600	1.0	1.0-7.0	0.099	Mass Spectrometer and Knudsen Cell
	Girilli (56)	-	-	-	0.178	-
	Chipman(45,59)	1600	-	-	0.092	Estimated
Sulfur	Sherman (57)	1600	0.76-8.04	0.133-0.312	0.038	H ₂ /H ₂ O gas
	Banya (58)	1550	1.92-14.0	0.63-5.62	0.028	H ₂ /H ₂ O gas
Nickel	Schenck (61)	1550	-	0-100	0.0	Isopiestic
		1550	-	7-66	0.006	Isopiestic (Graphite Saturation)
	Yamada (55)	1600	1.0	3-10	0.003	Mass Spectrometer and Knudsen Cell

Table 2.3: (Cont.)

Solute Element	Study (Ref)	Temperature Range	%P	%i	e_p^i	Equilibration Method
Chromium	Schenck (61)	1550	-	2-11	0.087	Isopiestic
		1550	-	11-20	-0.039	Isopiestic
		1550	-	2-5	0.056	Isopiestic (Graphite Saturation)
		1550	-	5-15	-0.017	Isopiestic (Graphite Saturation)
	Yamada (55)	1600	1.0	3-10	-0.018	Mass Spectrometer and Knudsen Cell
	Frohberg (25,48)	1600	3-16	2-18	-0.025	Ag/Fe Distribution
Manganese	Schenck (61)	1550	-	5-16	0.0	Isopiestic
		1550	-	5-16	0.0	Isopiestic (Graphite Saturation)
Molybdenum	Yamada (55)	1600	1.0	6-16	0.001	Mass Spectrometer and Knudsen Cell
Cobalt	Yamada (55)	1600	1.0	4-10	0.004	Mass Spectrometer and Knudsen Cell

which are dramatically influenced by precipitation of carbides from solution.^{49, 50} As will be shown later, most solute interactions with phosphorus can be generally neglected with the notable exception of silicon and chromium.

B. Slag Phase Relationships and Thermodynamic Properties

Whether considering basic Bessemer, basic open hearth or basic oxygen steelmaking processes, any comprehensive study of the dephosphorization reaction in steelmaking must consider the extremely complex slag phase relationships of associated phase systems. Perhaps no other reaction provides such a remarkable and interesting example of phase diagrams applied to fundamental understanding of the refining chemistry of steelmaking slags. In this section relevant slag and oxide phase systems are presented and evaluated with the intent of providing a basis for further discussion of slag refining chemistry. Each system is discussed with reference to prominent phase relationships and solution thermodynamic properties when these are available. The various slag systems are grouped under the following headings: basic oxides and silicates, basic phosphates, silico-phosphates and fluoride containing slags.

1. Basic Oxides and Basic Silicates

The compositions of most basic oxygen steelmaking slags generally fall within the $\text{CaO}-\text{'FeO'}-\text{SiO}_2-\text{MgO}$ pseudo-quaternary system since these four components account for over 90% of slag composition with the balance provided by P_2O_5 (1-3%), Al_2O_3 (0-5%), MnO (0-5%) and TiO_2 (0-3%). The phase relationships in the quaternary and ternary boundary systems are well-characterized and the liquid phase volume is shown in Figure 2.2 together with the associated ternary systems in Figure 2.3 for the 1600°C isotherm.⁶²⁻⁶⁵ The distinctive features of the quaternary system are the bordering saturation surfaces of the slag phase volume and limited

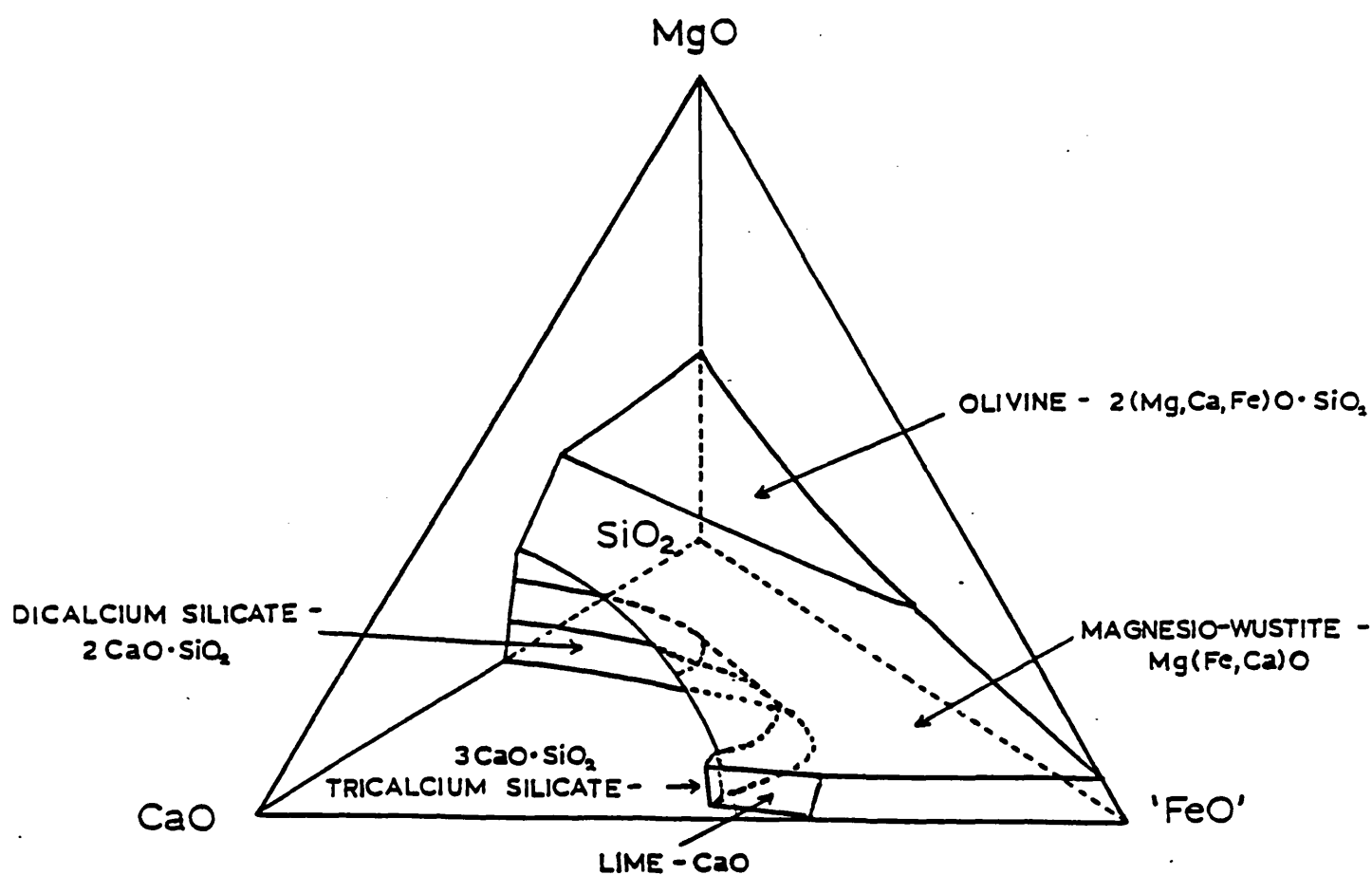


Figure 2.2 The CaO-'FeO'-SiO₂-MgO Pseudo-quaternary Liquid Phase Field at 1600°C. (62-65)

solubility of lime and magnesia in the liquid due to formation of high temperature silicates and solid solutions. Of particular interest to steelmaking refining is the region of the lime-rich apex and protrusion of the dicalcium and tricalcium silicate phase regions into the liquid phase volume.

While the solution thermodynamics of quaternary liquids have not been thoroughly studied, the $\text{CaO}-\text{'FeO'}-\text{SiO}_2$ pseudo-ternary and associated binary systems have been investigated by a number of workers⁶⁸⁻⁸³ and iso-activity lines have been derived.⁸¹⁻³ A distinctive feature of $\text{CaO}-\text{FeO}-\text{SiO}_2$ ternary melts is the pronounced maxima in iron oxide activities along the iron oxide-dicalcium silicate join. This type of behavior has been explained on the basis of structural arguments.⁸⁴ It is interesting to note that slag compositions along this join have traditionally demonstrated optimum refining properties. In more complex multicomponent liquids, thermodynamic studies have been generally limited to evaluating the relative effect of basic and acidic oxides on iron oxide activities and slag oxidation potential.^{68-72, 77, 82} This approach has been used to evaluate the influence of magnesia additions on slag oxidation potential.^{69-71, 85, 86} The results of a recent study by Banya⁸⁶ are shown in Figure 2.4 where magnesia additions are shown to decrease the oxidizing character of a slag at constant basicity.

Magnesia solubilities in synthetic steelmaking slags have been studied by Chipman,^{66, 70} Banya⁸⁷ and Obst.⁸⁸ These workers derived simple empirical relationships between magnesia solubility and slag basicities and oxidation state. While these workers failed to correlate solubility data with slag phase relationships, Tromel and co-workers^{62, 63, 65} studied the surfaces of saturation in quaternary slags and provided detailed data for both magnesio-wustite and olivine saturated slags. Their results are

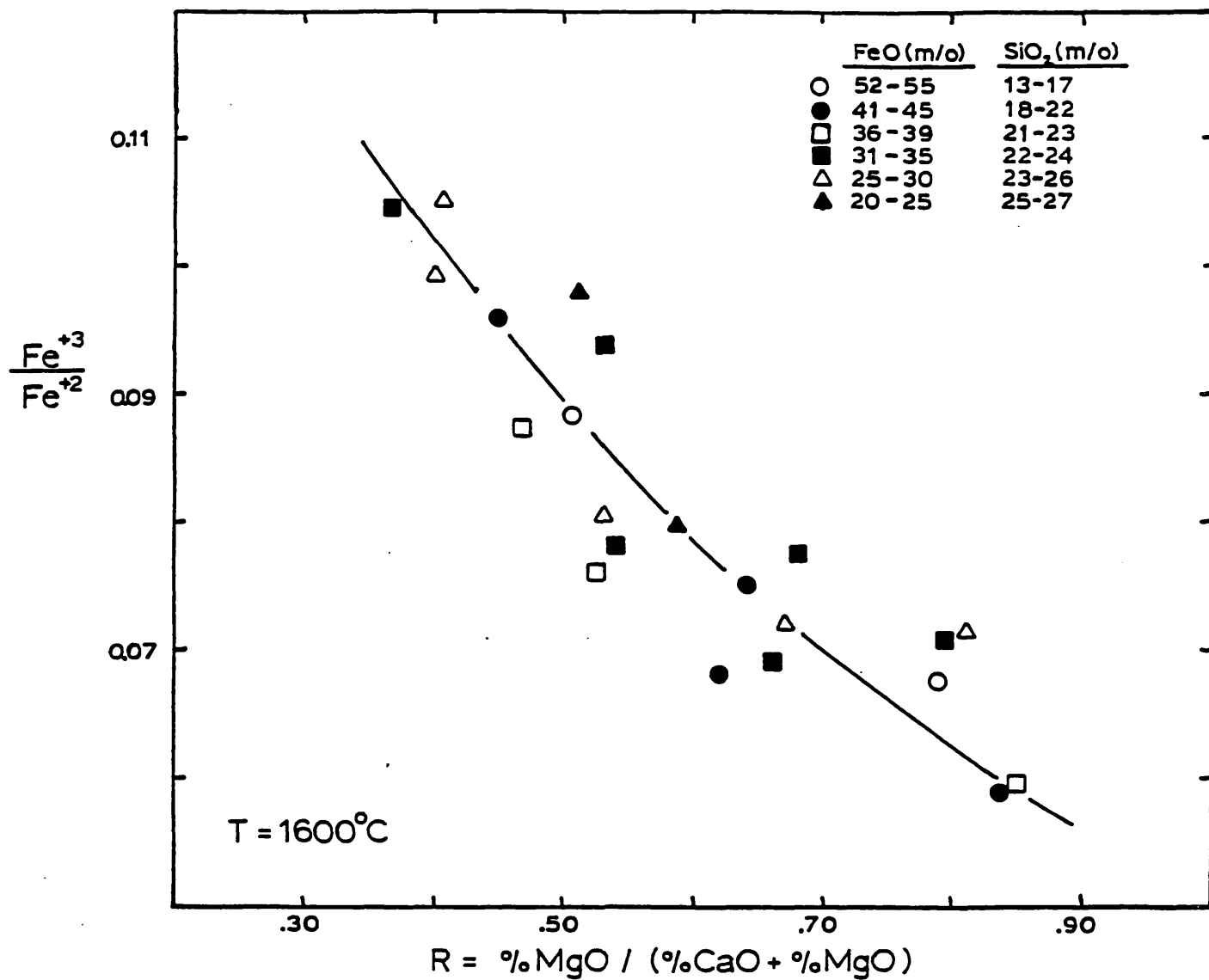


Figure 2.4 The Influence of Magnesia Content on Slag Oxidation Potential (86).

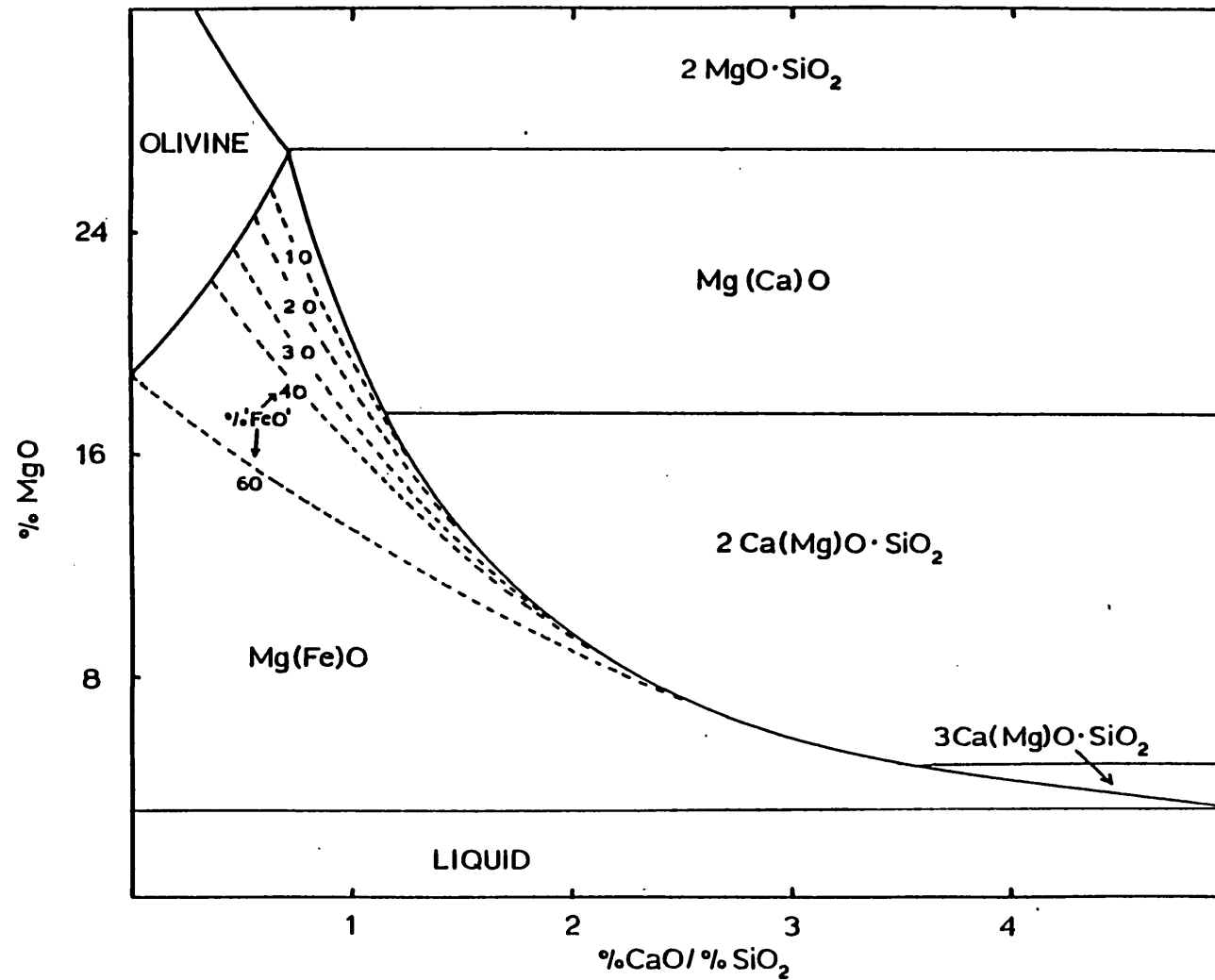


Figure 2.5 Magnesia Solubilities in Pseudo-Quaternary Slags at 1600°C (62, 63, 65, 67).

shown in Figure 2.5 where solubilities are shown as a function of basicity and oxidation state at various regions within the quaternary. As clearly demonstrated in this diagram, magnesia solubility is inversely proportional to slag basicity and oxidation potential.

2. Basic Phosphates

a. Binary Phosphates

The exceptional high temperature stability of the binary phosphates has traditionally been considered a major factor in slag refining behavior. Tromel,⁸⁹ Nurse,¹¹⁷ Riboud¹²³ and co-workers studied high temperature phase equilibria for the calcium phosphate system. Schwerdtfeger and Engell⁹⁰ measured phosphorus pentoxide activities in the binary system using an e.m.f. method. The phase diagram shown in Figure 2.6 is taken from Nurse¹¹⁷ and Riboud.¹²³

The free energy of formation of the calcium phosphates has been studied by Bookey,⁶⁰ Fischer,³³ Banya⁴² and Aratani.⁴³ While these studies are in general agreement, the temperature dependence of the reaction is subject to considerable error due to the narrow range of temperatures studied. Other investigators have studied the reaction equilibria for the manganese⁹¹ and magnesium⁹² phosphates. Tromel⁹³ has studied the stability of the iron phosphate at lower temperatures. Thermodynamic data for the hypothetical pure binary liquids has been estimated by Elliott.⁹⁴ The relative stabilities of solid and liquid phosphates are presented in Table 2.4 where free energy data are included. It is clear from the data given that the calcium phosphates possess the greatest thermodynamic stability.

b. Ternary Phosphates

Oelsen and Maetz⁹⁵ pioneered studies of the alkali and alkaline earth metal phosphate ternary systems. They developed schematic phase diagrams for many of these systems and discovered systematic similarities in all of

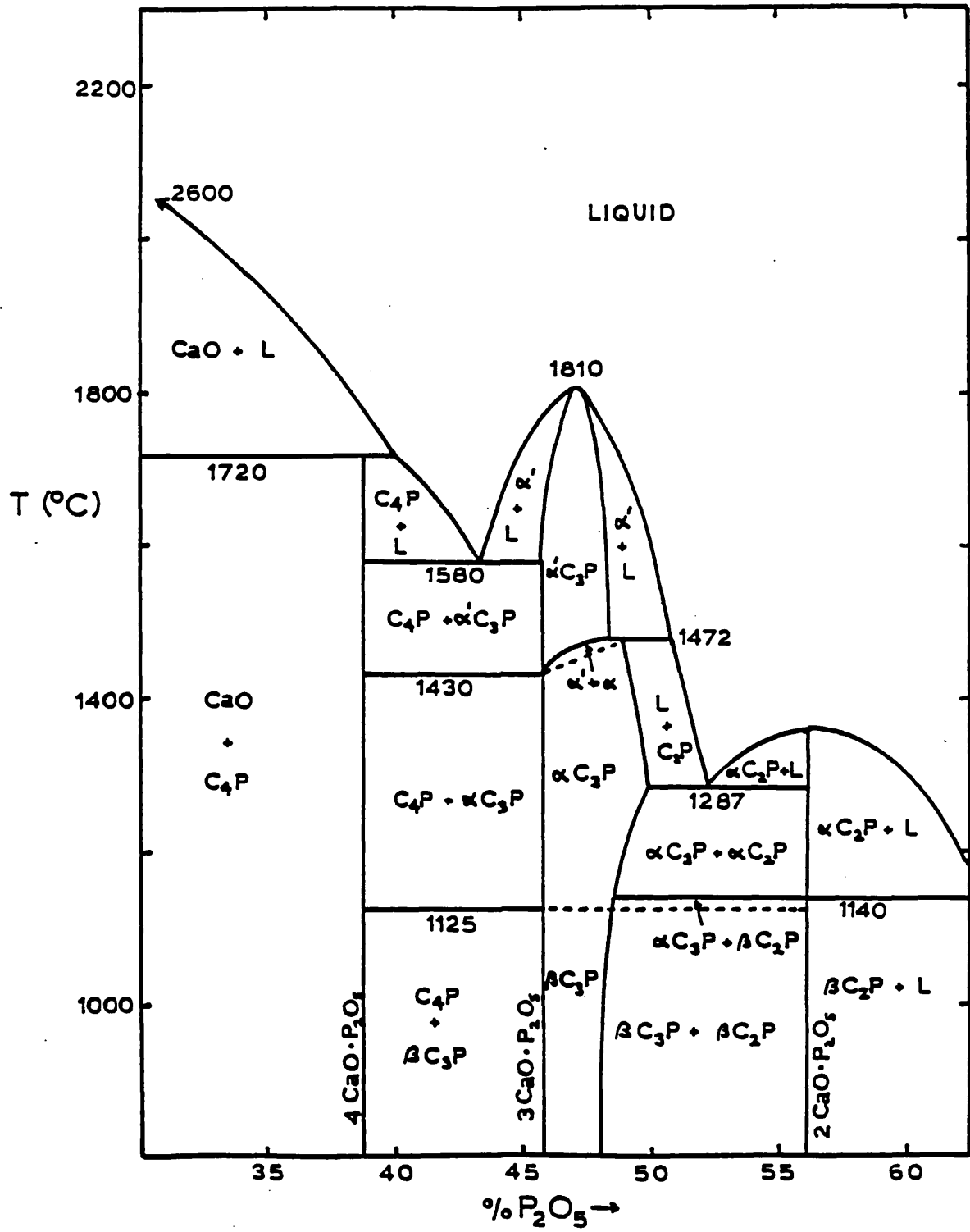
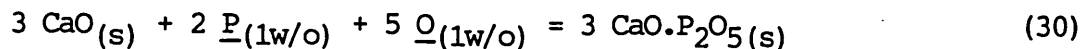


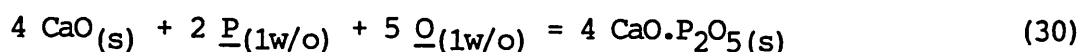
Figure 2.6 The CaO-P₂O₅ Binary Phase Diagram (117, 123).

Table 2.4: Free Energy of Formation of Some Basic Phosphates

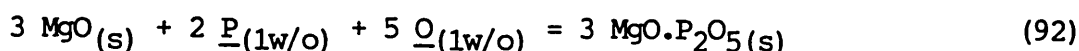
A. EXPERIMENTAL VALUES FOR SOLIDS

Reference

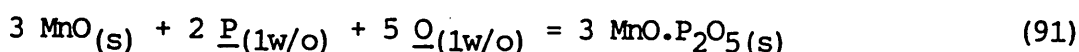
$$\Delta G_T^O = -1419 + 0.5920T \text{ (KJ/mol)}$$



$$\Delta G_T^O = -1437 + 0.5974T \text{ (KJ/mol)}$$

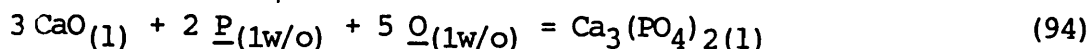


$$\Delta G_T^O = -1193 + 0.5936T \text{ (KJ/mol)}$$

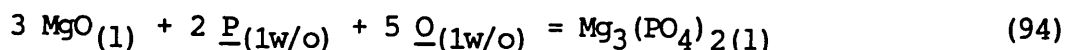


$$\Delta G_T^O = -1247 + 0.7033T \text{ (KJ/mol)}$$

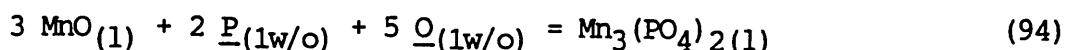
B. ESTIMATED VALUES FOR LIQUIDS



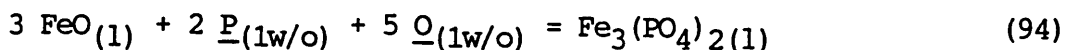
$$\Delta G_T^O = -1574 + 0.6551T \text{ (KJ/mol)}$$



$$\Delta G_T^O = -1279 + 0.4562T \text{ (KJ/mol)}$$



$$\Delta G_T^O = -1232 + 0.6592T \text{ (KJ/mol)}$$



$$\Delta G_T^O = -1135 + 0.6492T \text{ (KJ/mol)}$$

these systems. The predominant features of these ternaries are an extensive region of liquid immiscibility centered on the tribasic phosphate-iron oxide join and the exceptional high temperature stability of the basic phosphates.

In previous studies of phase equilibria pertinent to phosphorus refining behavior, major emphasis has been given to the $\text{CaO-P}_2\text{O}_5\text{-FeO}$ ternary system. This is particularly true in Europe where this ternary represents the idealized basic Bessemer or Thomas-type slag. The known phase equilibria for this ternary system were primarily the work of Tromel and co-workers⁹⁶⁻⁹ who made extensive studies of slag-metal equilibrium behavior. The phase diagram proposed by these authors is widely accepted and the 1600°C isotherm is shown in Figure 2.7. The system exhibits fairly complex regions of liquid saturation with both calcia and the two refractory phosphates, tricalcium and tetracalcium phosphate. A complex region of liquid immiscibility extends across the phase fields, separated by a tricalcium phosphate saturation surface. Since slag compositions in the Thomas process generally operated within the single liquid region, close to dual saturation with calcia and tetracalcium phosphate, slags saturated with respect to both of these phases have been the object of extensive studies in attempts to develop slag-metal dephosphorization correlations and reaction equilibrium constants.

Slag-metal phosphorus distribution behavior for this ternary and other basic phosphate ternary systems is discussed in a later section.

c. Multicomponent Systems

With quaternary and higher order systems, work has been restricted to evaluating the influence of small additions of a fourth or fifth component such as SiO_2 , MnO , Al_2O_3 , MgO or Cr_2O_3 on the $\text{CaO-FeO-P}_2\text{O}_5$ phase fields and slag-metal phosphorus distribution.⁹⁶⁻¹⁰⁴ This was done either to simulate

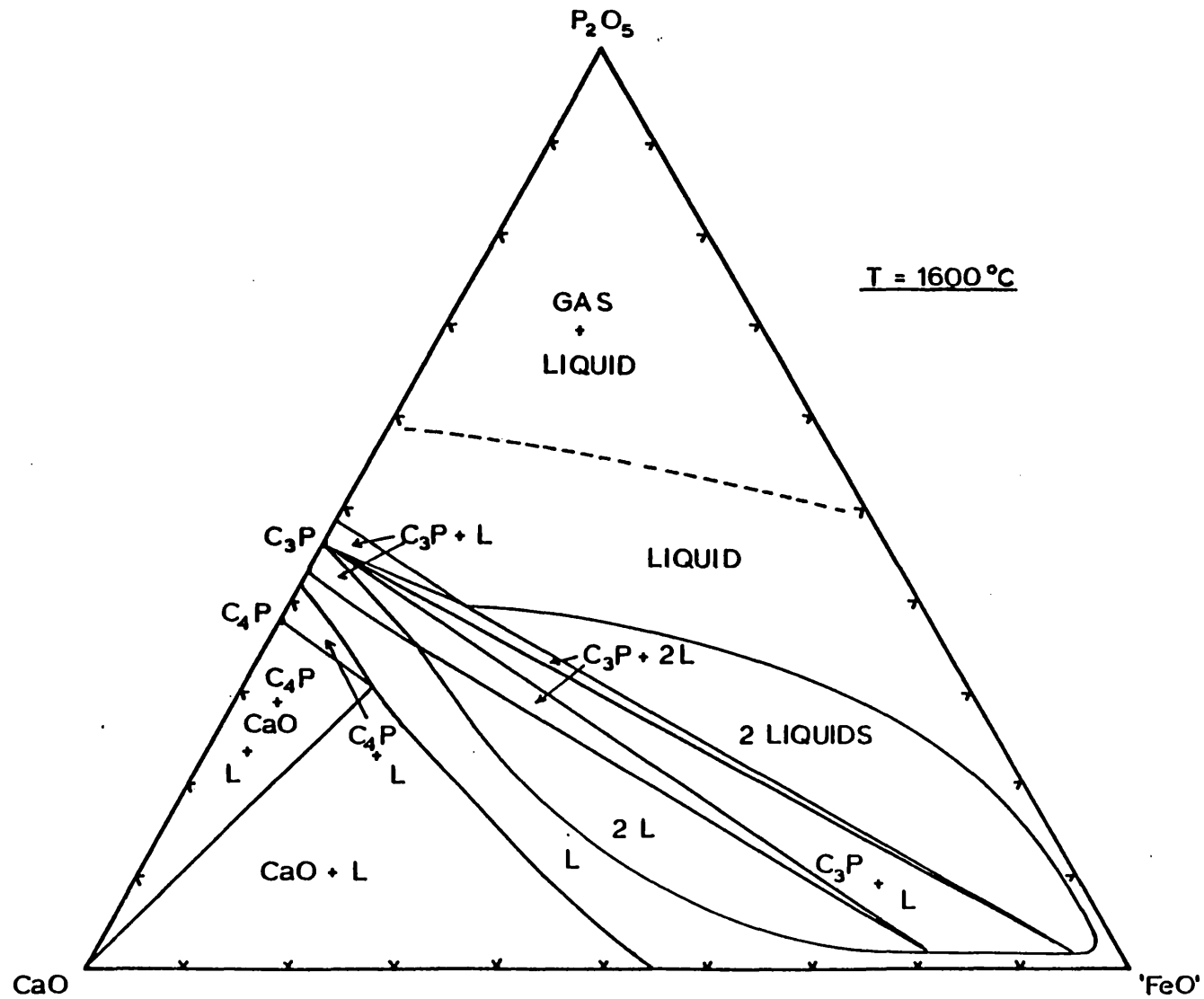


Figure 2.7 The $\text{CaO}-\text{P}_2\text{O}_5\text{'FeO'}$ Ternary Phase Diagram at 1600°C (96-99).

actual slags encountered in steelmaking practice or as a direct result of refractory contamination.

The earliest studies of the effect of silica additions on ternary phase relationships were conducted with reference to Thomas process slags. Attention was drawn to the predominant influence of silica additions in closing the ternary miscibility gap,^{95, 105-7} increasing the solubility of calcium oxide in the liquid at lime saturation,¹⁰¹⁻² and affecting phosphorus distribution in the region of both lime and dicalcium silicate saturated slags.^{96, 101-4}

The effect of magnesia on ternary phase relationships, the magnesia solubility in ternary slags and the influence of magnesia on slag-metal phosphorus distribution behavior were studied by Peter,¹⁰⁰ Oelsen,⁹⁵ Tromel,⁹⁹ Chipman¹⁰⁸ and Balajiva.¹⁰⁹ Tromel and co-workers reviewed previous work and compiled data on phase equilibria for the $\text{MgO-CaO-FeO-P}_2\text{O}_5$ pseudo-quaternary system and associated ternary systems.⁹⁹ A schematic diagram of the 1600°C isotherm is shown in Figure 2.8. As seen in this diagram, the solubility of magnesia is quite limited in both the liquid and refractory phosphate phases and addition of magnesia causes no significant changes in the phase fields of the ternary system. It is interesting to note that neither Peter¹⁰⁰ nor Tromel⁹⁹ were able to detect any change in phosphorus distribution behavior with limited magnesia additions to ternary slags.

3. Basic Silico-Phosphate Systems

Beyond evaluating the role of silica and its influence on phase relationships in Thomas-type slags, the development of detailed understanding of the role of silica in dephosphorization evolved rather slowly and many misconceptions persist within the literature. In this section, the $\text{CaO-P}_2\text{O}_5\text{-SiO}_2$ phase system is presented in Part A and the

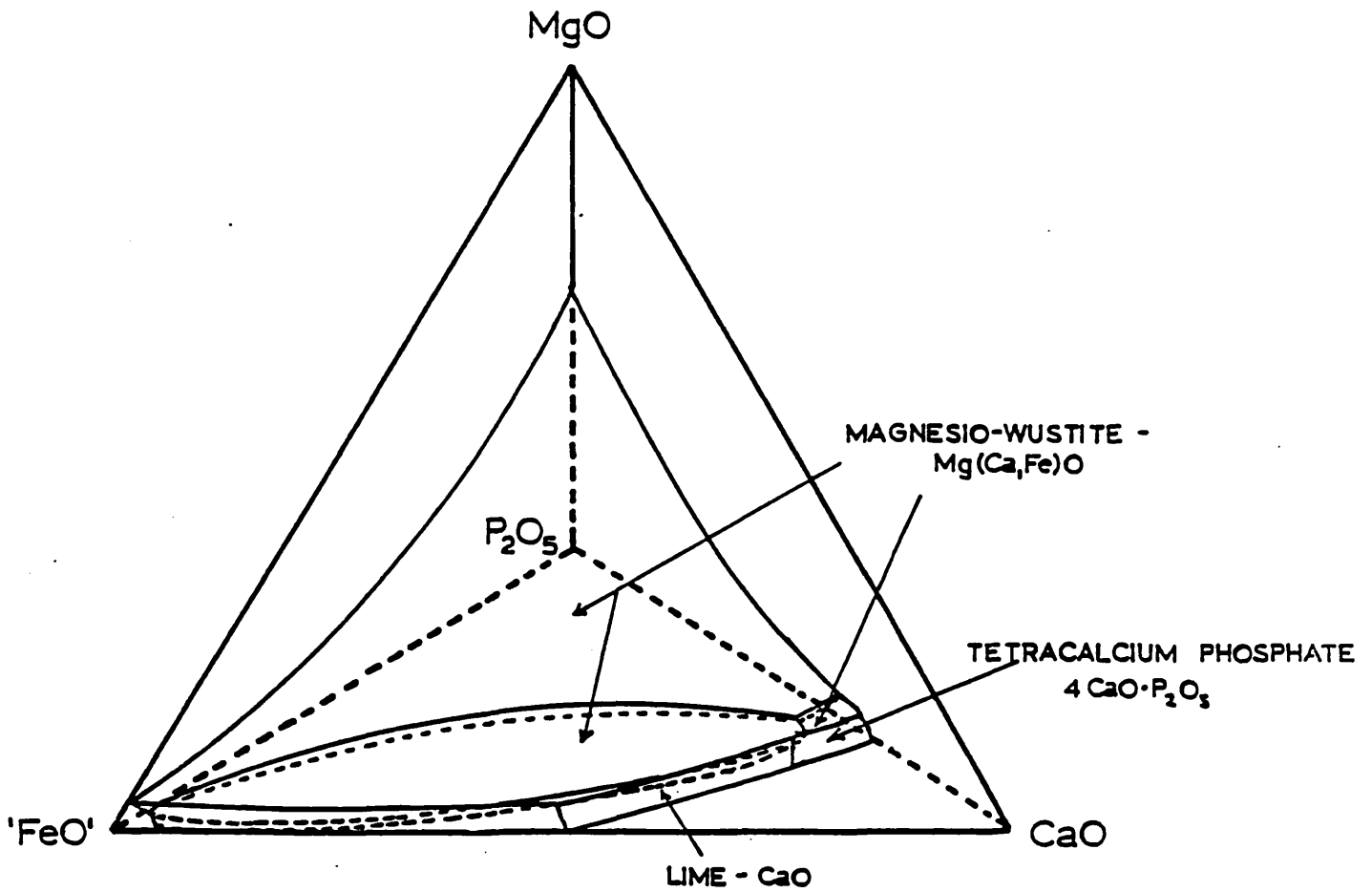


Figure 2.8 A Schematic of the $\text{MgO-CaO-}'\text{FeO}'\text{-P}_2\text{O}_5$ Pseudo-quaternary Phase Diagram at 1600°C (99).

critical importance of phase relationships in this system is discussed with respect to the very strong interactions which occur among the three components. In Part B, relevant multicomponent systems based on this ternary are reviewed and prominent features discussed with regard to their significance in slag refining behavior.

a. The $\text{CaO-P}_2\text{O}_5\text{-SiO}_2$ Ternary System

Early studies of this ternary system generated considerable confusion with regard to the presence and extent of the high temperature phase fields.¹¹⁰⁻¹¹³ Early workers considered the system as a quasibinary with a variety of solid solution phases lying between dicalcium silicate and tricalcium phosphate. Mineralogical studies¹¹³ of this system have confirmed the presence of two prominent mineral phases at low temperature, silico-carnotite ($5\text{CaO-P}_2\text{O}_5\text{-SiO}_2$) and nagelschmidtite ($7\text{CaO-P}_2\text{O}_5\text{-2SiO}_2$). Tromel¹¹⁰ proposed a phase diagram where three phase fields were located between dicalcium silicate and silico-carnotite at high temperatures, each of which possessed a limited range of solubility of tricalcium phosphate in dicalcium silicate. Barrett¹¹¹ proposed the presence of two phase fields within this region, each of which possessed different mutual solubility from Tromel's proposed phases. Bredig¹¹² proposed a single solid-solution phase region at high temperature having an α -hexagonal structure. He observed that this transforms upon quenching, via a solid state reaction, to either a metastable α' -hexagonal structure similar to nagelschmidtite or an orthogonal β -dicalcium silicate and silico-carnotite. This work agrees with transformations observed by Klement¹¹⁴ and was confirmed by the microstructural studies of Balajiva and co-workers.¹⁰⁹

In a later development, Bredig¹¹⁵ studied the various polymorphs of the α -hexagonal dicalcium silicate phase and the structural effect of additions of phosphorus pentoxide to the binary phase in forming ternary

solid solutions. Bredig argued that the transformations which occur upon quenching are suppressed by additions of phosphorus and certain cations. The high temperature α -hexagonal structure apparently possesses a higher coordination number for certain cations than lower temperature modifications and can readily accommodate and incorporate additional components into its structure. This explains much of the disagreement among early workers over phase regions and solubility limits in the ternary phase system. Recently Schurmann and co-workers¹¹⁶ have revitalized the controversy by postulating the existence of two high temperature modifications of the ternary solid-solution, an α -hexagonal dendritic structure having high solubility of silica and an α' -orthorhombic, equiaxed modification with lower silica solubility.

The currently accepted phase diagram for the ternary quasi-binary system is shown in Figure 2.9. This is taken from the work of Nurse¹¹⁷ and confirmed by Fix.¹¹⁸ In Nurse's study, high temperature hot-stage microscopy and high temperature x-ray diffraction were utilized in establishing the high temperature phase relationships. These workers found that suppression of low temperature transformations was impossible with conventional quenching techniques. By studying the system at temperature, they observed a continuous region of solid solution extending from dicalcium silicate to tricalcium phosphate. Liquidus temperatures were determined with high accuracy and, although solidus temperatures were more difficult to observe, the liquidus and solidus lines were shown to be virtually coincident. In agreement with Bredig's findings, Nurse found that tricalcium phosphate stabilizes the high temperature α -hexagonal structural modification.

In their high temperature x-ray diffraction study, Fix and co-workers¹¹⁸ found the results of Nurse to be fairly reproducible and the

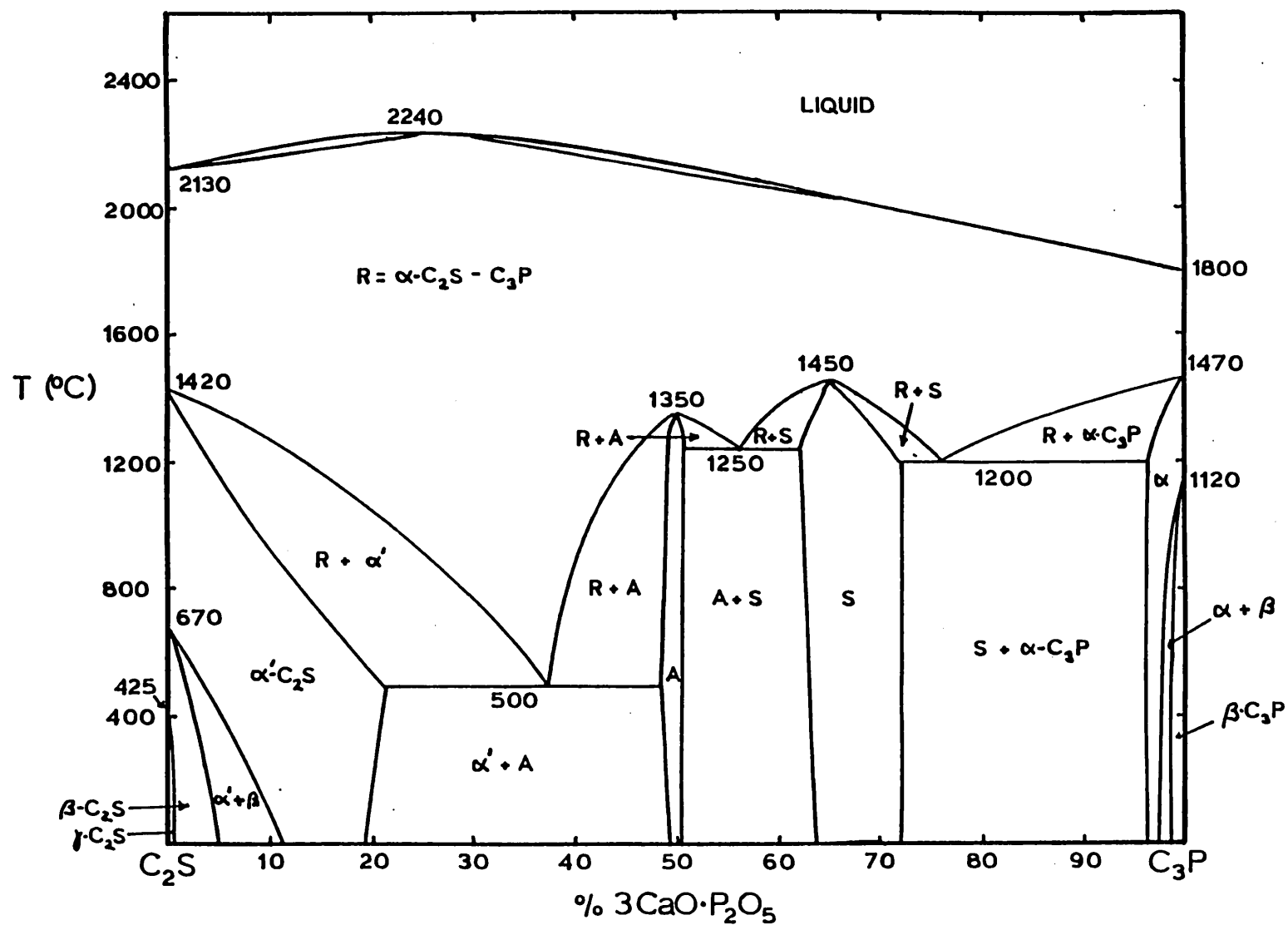


Figure 2.9 The $2 \text{CaO} \cdot \text{SiO}_2 - 3 \text{CaO} \cdot \text{P}_2\text{O}_5$ Quasibinary Phase Diagram (117, 118).

phase diagram proposed in their work was identical except for minor discrepancies within the low temperature phase regions where problems with metastability are significant and exceptionally long equilibration times are required for solid-state transformations to reach equilibrium. For this reason, these workers considered their high temperature data to be more reliable.

b. Silico-Phosphate Slag Systems

Although the presence of calcium silico-phosphate solid solutions were observed in early microstructural studies of industrial slags^{111, 119} and also in the synthetic slags of Balajiva and co-workers,^{109, 120} such phases have traditionally been assumed to be an artifact of quenching and solid-state transformations which occur during subsequent cooling.

In an early study, McCaughey¹¹¹ proposed that calcium silico-phosphates were present at temperature as a dephosphorization reaction product but, due to the lack of information of high temperature phase relationships in the ternary system, his theory was discounted by several workers. Mason¹¹⁹ found that in quenched open hearth slags some limited solubility of phosphorus was observed in calcium silicates. He proposed that some substitution of phosphate for silicate anion occurred in the slag silicate network and that no high temperature phases were present. Winkler and Chipman¹⁰⁸ argued that both Mason's work and the findings of Tromel¹¹⁰ and Bredig¹¹² disproved McCaughey's theory since no workers had observed a liquid phase in equilibrium with the calcium silico-phosphate solid solution. However, this argument was rather weak and they made no attempt to study slag microstructures in their experiments.

In their comprehensive laboratory equilibrium study, Balajiva and co-workers^{109, 120} observed a calcium silico-phosphate phase in both rapidly quenched and annealed slag samples. They postulated that this

phase was probably present at temperature since it is known to have high temperature stability. In their study, virtually the entire phosphorus content of the slag was found in an α -hexagonal solid solution of dicalcium silicate and tricalcium phosphate. With lower phosphorus contents, a solid-solution having the β -orthogonal dicalcium silicate structure was observed in slag microstructures. This was proposed to be a low temperature transformation of the high temperature α -hexagonal solid solution, as reported by Bredig.¹¹⁵ In quenched, high-phosphorus slags, silico-carnotite was found but this was thought to form as a result of a solid state transformation in accordance with Bredig's observations.

In their studies of the effect of silica additions on the $\text{CaO-P}_2\text{O}_5\text{-FeO}$ pseudo-ternary system, Tromel, Drewes, Fix and co-workers^{103-7, 121} clearly established the considerable stability of calcium silico-phosphate as a high temperature equilibrium phase in steelmaking slag systems. These workers confirmed the role of silica in closing the ternary miscibility gap and also brought attention to the dominant region of the silico-phosphate solid solution saturation surface within the pseudo-quaternary. They reviewed known phase equilibria data and provided schematic diagrams of the ternary and quaternary isotherms as shown in Figures 2.10 and 2.11.

Tromel, Fix and co-workers observed that the region of calcium silico-phosphate saturation extended from the lime-rich apex to the far region of the miscibility gap within the pseudo-quaternary phase system. This was confirmed by the work of Drewes and Olette¹⁰⁶ who studied the effects of oxygen potential and silica content on phase relationships in the pseudo-quaternary system. Schurmann and co-workers¹²² have claimed that there is no connection between the miscibility gap and the solid-solution saturation surface in technical slags at steelmaking

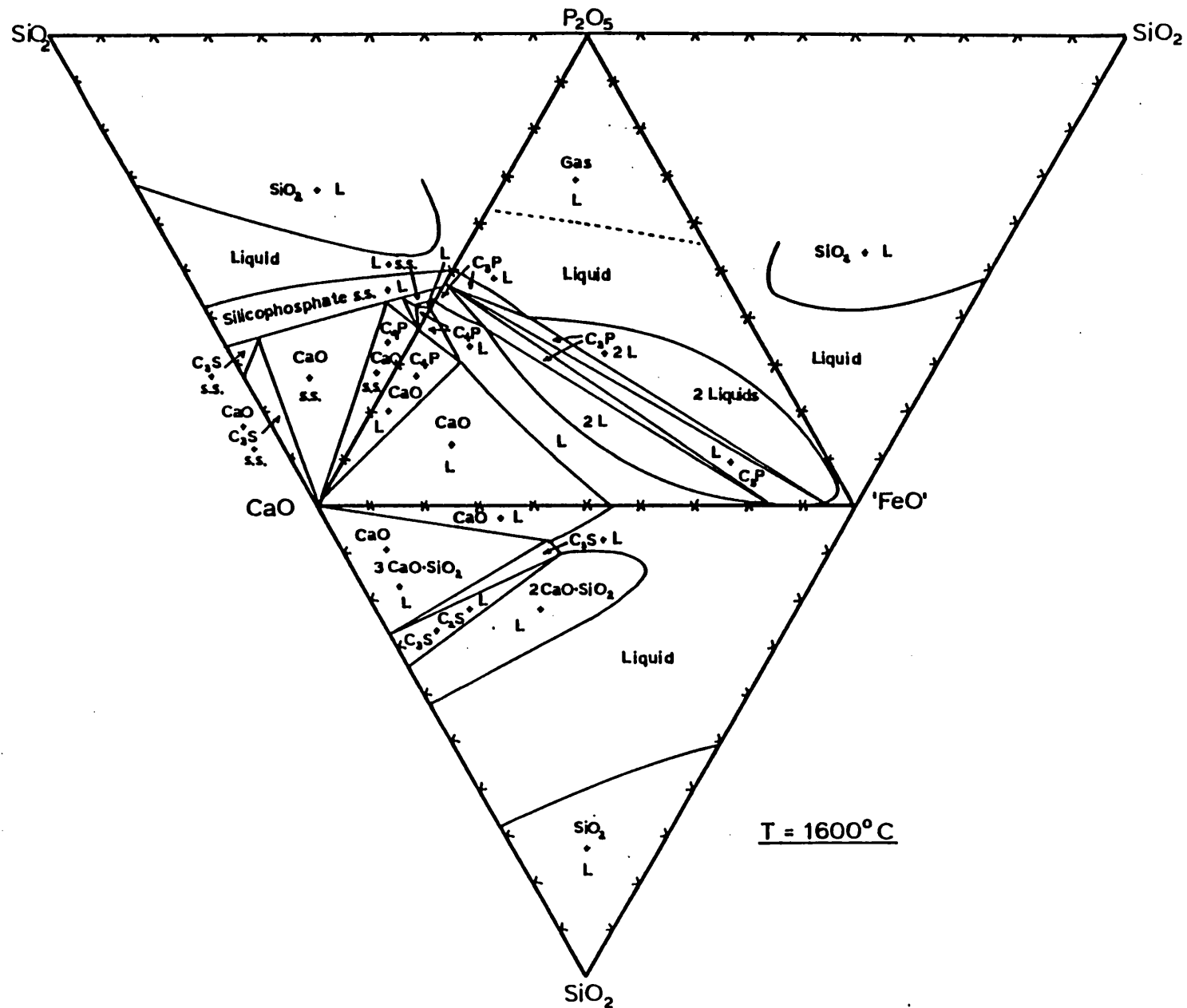


Figure 2.10 The Composite Ternary Isotherms for the $\text{CaO-P}_2\text{O}_5\text{'FeO'-SiO}_2$ Pseudo-quaternary System at 1600°C (103-7, 12).

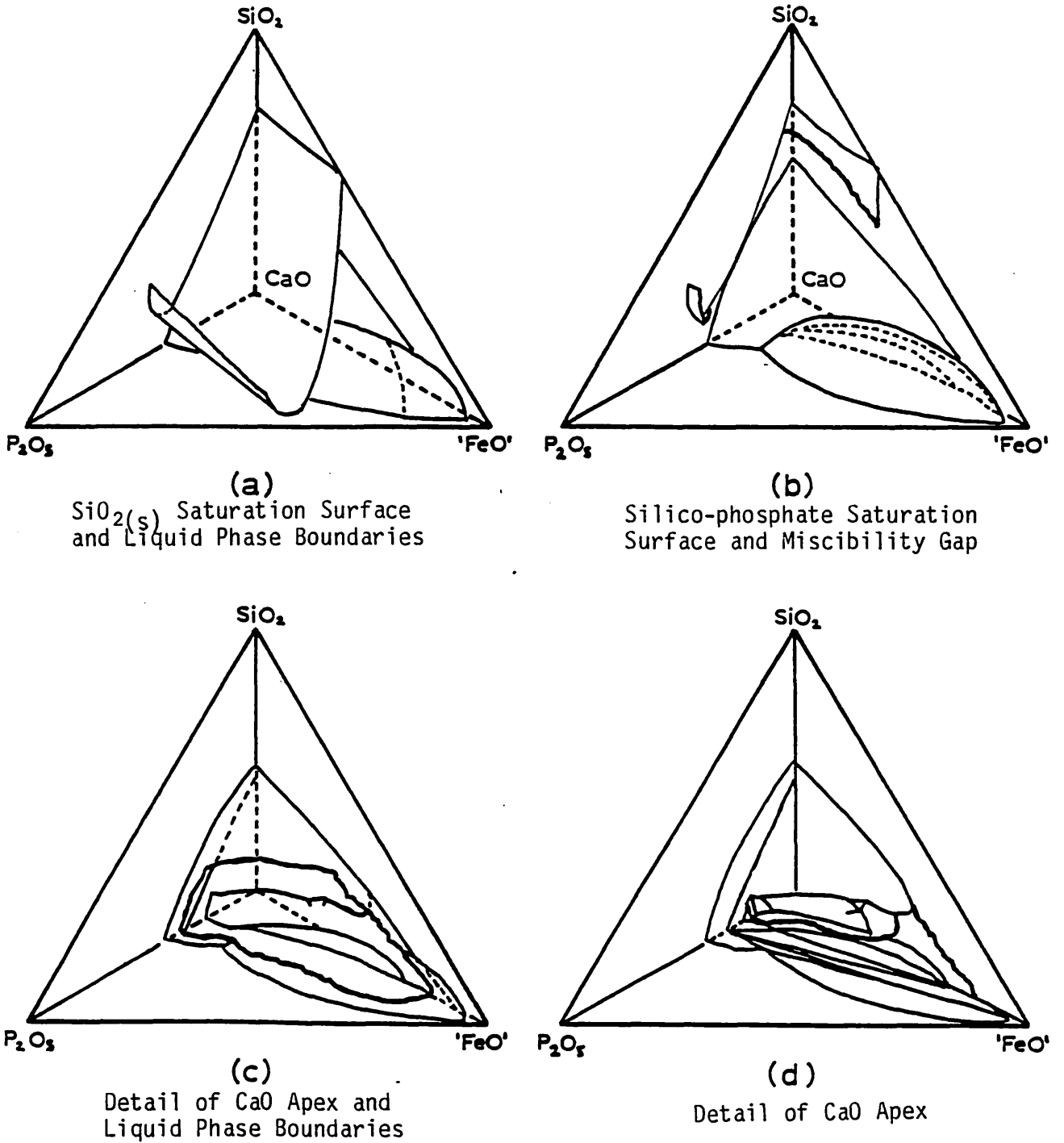


Figure 2.11 A Schematic of the $\text{CaO-P}_2\text{O}_5\text{'FeO'-SiO}_2$ Pseudo-quaternary Phase Fields at 1600°C (121).

temperatures. Additional components such as manganese, aluminum, magnesium and chromium oxide apparently restrict the region of stability of the calcium silico-phosphate phase.

Uncertainty over the region of silico-phosphate saturation in multicomponent phase systems and the high temperature stability of calcium silico-phosphate within liquid slag systems has been clarified in the recent work of Margo-Marette and Riboud.¹²³⁻¹²⁶ These workers studied liquidus temperatures in the $\text{CaO-P}_2\text{O}_5\text{-SiO}_2$ ternary and $\text{CaO-P}_2\text{O}_5\text{-SiO}_2\text{'FeO'}$ pseudo-quaternary systems over an extensive region of composition at oxygen potentials corresponding to relatively constant ratios of ferrous to ferric iron. As shown in Figure 2.12, where liquidus temperatures at selected iron oxide planes are presented, maximum liquidus temperatures fall within the silico-phosphate solid solution region and these temperatures lie well above steelmaking temperatures over extensive regions of the phase system. Addition of iron oxide causes a reduction in the region of solid solution stability but liquids are saturated with this phase over a wide range of compositions even at relatively high iron oxide content.

Riboud¹²⁴ has suggested that the optimum compositions for refining slags would lie in the region of the calcium oxide-calcium silico-phosphate eutectic trough where calcium oxide has a high activity, phosphorus pentoxide has a low activity, and the slag is reasonably fluid. These workers studied the effect of additional slag components on the eutectic line and proposed an analytical expression for optimum slag compositions based on these findings. For quaternary slags, the optimum lime content for charging was expressed as

$$\% \text{CaO} = 1.41 \% \text{P}_2\text{O}_5 + 2.61 \% \text{SiO}_2 + \% \text{'FeO'} - 0.005(\% \text{'FeO'})^2 .$$

For multicomponent slags, magnesia and manganese oxide were taken as lime equivalents and alumina and titania as phosphorus pentoxide equivalents.

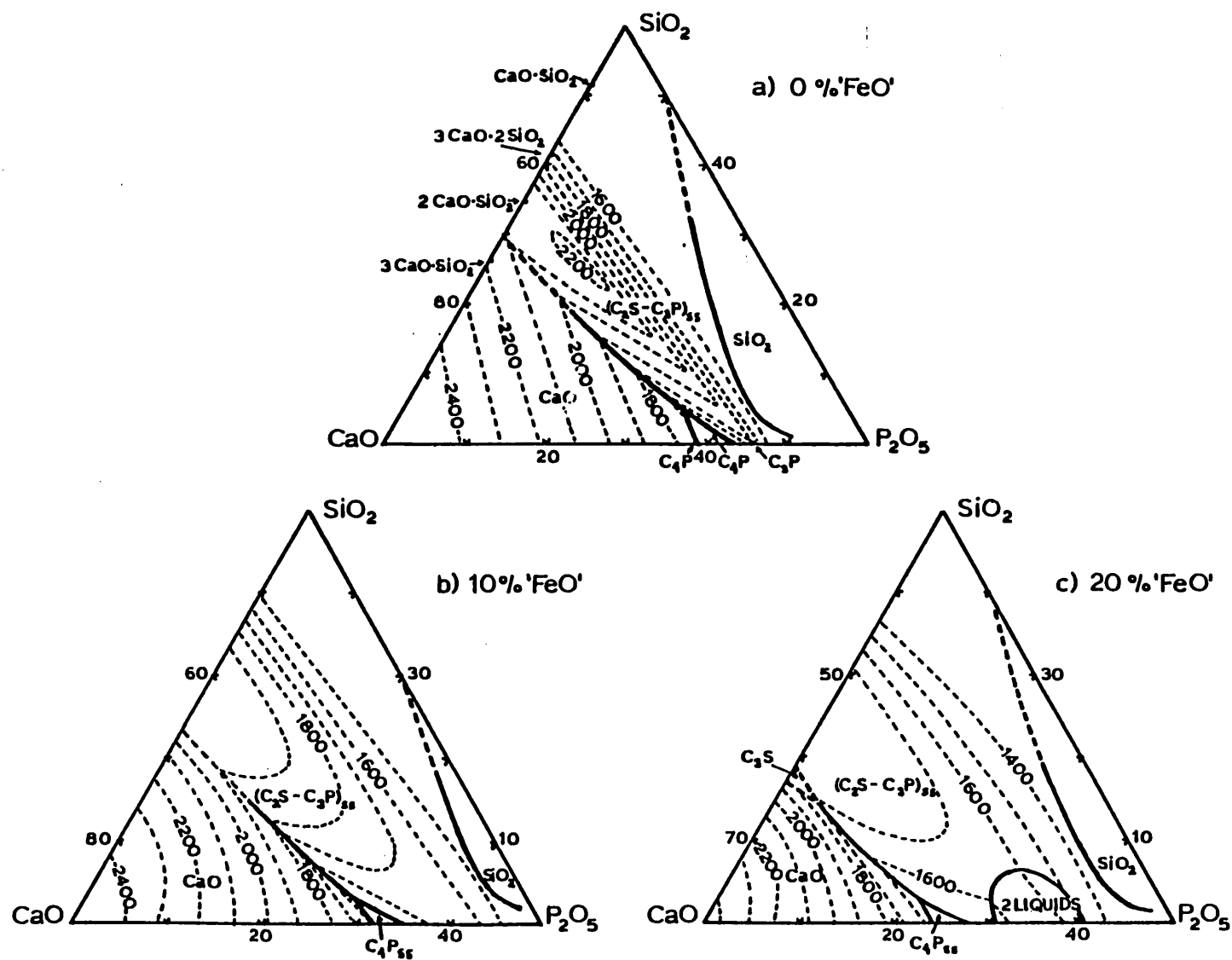


Figure 2.12 Liquidus Temperatures in the CaO-P₂O₅-'FeO'-SiO₂ Pseudo-quaternary Phase System at Various Iron Oxide Planes (123-126).

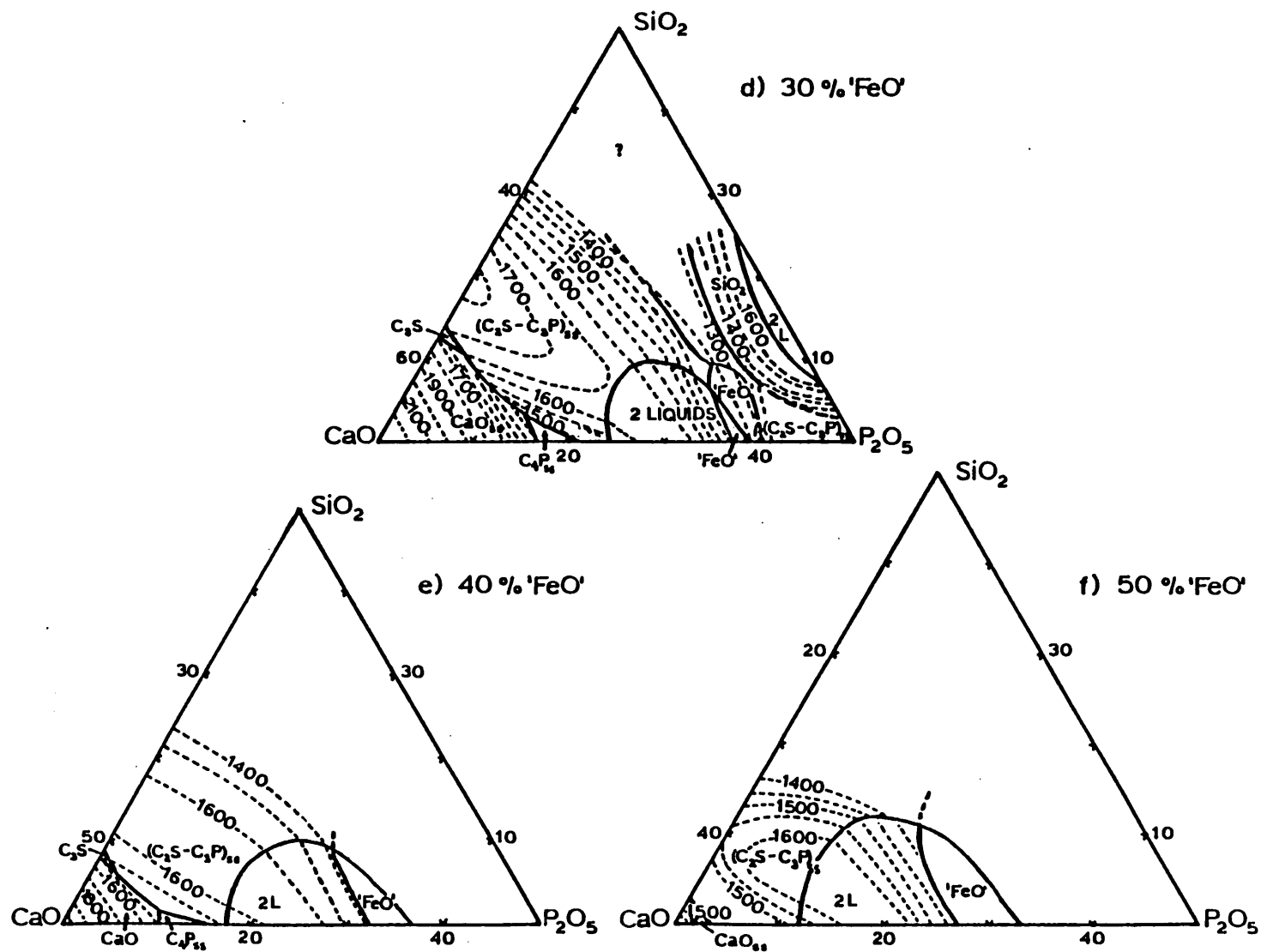


Figure 2.12 (Cont.) Liquidus Temperatures in the $\text{CaO}-\text{P}_2\text{O}_5$ - 'FeO' - SiO_2 Pseudo-quaternary Phase System at Various Iron Oxide Planes (123-126).

Since precipitation of solid phases from industrial slags causes significant operational problems with furnace emulsion formation, stabilization, foaming and slopping, some adjustment was made so that target compositions would lie above the liquidus temperature of the slag. In a later study, Riboud¹²⁶ utilized the data of Moncel¹²⁸ and developed analytical expressions for the compositional effects of magnesium, aluminum and manganese oxide on slag liquidus temperatures in the region of silico-phosphate saturation. These results demonstrated that while major additions of other components to the quaternary may significantly lower liquidus temperatures, the region of silico-phosphate saturation remains substantially intact at steelmaking temperatures.

Recent studies in Germany,²⁷²⁻³ France,⁵⁴ and Japan¹²⁹⁻¹³¹ have confirmed the presence of calcium silico-phosphate solid solution in quenched industrial slags. In mineralogical studies of both synthetic and industrial slags low in phosphorus, both Chavepeyr⁵⁴ and Suito and co-workers¹²⁹ observed that phosphorus was found only in a dicalcium silicate solid solution with both quenched and slow-cooled samples. With high phosphorus slags, silico-carnotite was found in slow-cooled samples. These observations agree with those of Bredig¹¹⁵ and Balajiva.¹⁰⁹ In a related structural study of quenched industrial slags, Masson and co-workers¹²⁷ found that the phosphorus was primarily present as a complex silico-phosphate anion, with only a limited fraction occurring as an orthophosphate.

Ono and co-workers¹³⁰ have attempted to take advantage of the unique features of calcium silico-phosphate phase relationships for selective recovery of phosphates and recycling of converter slag. Due to the relative densities of the solid solution and liquid slags, differential floatation and segregation of the phosphate-rich silico-phosphate phase is

possible when slag compositions lie below the liquidus temperature. In a related study, Ito¹³¹ measured the distribution of phosphorus between dicalcium silicate solid solution and liquid slag at steelmaking temperatures and found that over 80% of the phosphorus was present in the solid solution. No significant temperature effect was observed below slag liquidus temperatures and phosphorus distribution tended to increase significantly with increasing iron oxide content.

4. Fluoride Containing Slags

Fluoride is often encountered in steelmaking practice as a lime fluxing agent and is generally a minor, though significant, component in slags due to its pronounced effect on slag thermodynamic properties and physical behavior.

Mills¹³² has recently reviewed the physicochemical properties of fluoride-based slags and the reader is referred to this work for an extensive discussion of phase relationships and thermodynamic properties. Hawkins and Davies¹³³ and Mitchell and co-workers¹³⁴ measured the effects of calcium fluoride on iron oxide activities in binary, ternary and higher order melts relevant to steelmaking practice and found that fluoride additions dramatically increase the activity of iron oxide and produce major structural rearrangement of the liquid as observed in the extensive miscibility gaps found in these phase systems.

While the exact nature of fluoride-phosphorus interactions in slags is not well characterized, the presence of fluorapatite ($\text{CaF}_2 \cdot 9\text{CaO} \cdot 3\text{P}_2\text{O}_5$) has been observed in the microstructures of slow-cooled basic slags containing as little as 5% calcium fluoride.^{129, 135, 136} Turkdogan and Pearson¹³⁷ demonstrated that the presence of fluoride in open-hearth slags decreases the activity of phosphorus pentoxide. Herasymenko and Speight,¹³⁸ using Winkler and Chipman's data,¹⁰⁸ have shown that fluoride increases

slag-metal equilibrium phosphorus distribution. In recent laboratory studies both Kor¹³⁹ and Suito¹⁴⁰ claim improved dephosphorization in the presence of fluoride due to strong interactions between calcium oxide, calcium fluoride and phosphorus pentoxide and subsequent lowering of phosphorus pentoxide activity in the slag. Such observations have been made in steelmaking practice¹⁴¹ but the role of fluoride has traditionally been considered as a lime fluxing agent and silicate depolymerization agent.

While previous studies would indicate the presence of significant interactions between phosphorus and fluoride in liquid slags, the addition of fluoride to silico-phosphate saturated slags appears to increase the solubility of phosphorus in the liquid and reduces the stability of the silico-phosphate solid solution. These findings were confirmed by the results of Ito¹³¹ when studying phosphorus distributions between calcium silico-phosphate and liquid slags. Suito¹²⁹ observed that in slow-cooled dicalcium silicate saturated slags containing small amounts of fluoride, phosphorus was found within a fluorapatite phase rather than the α -hexagonal dicalcium silicate solid solution. This would imply that phosphorus was soluble in the liquid slag at temperature and precipitated in the secondary phase upon cooling. These observations are in agreement with the phase diagram study of Gutt and Osborne¹⁴² where addition of calcium fluoride significantly increases the liquid solubility and decreases the region of stability of dicalcium silicate in ternary slag systems. These results are confirmed by structural studies of quenched glasses.¹⁴³ It is interesting to note that similar observations have been made in the $\text{CaO-P}_2\text{O}_5\text{-CaF}_2$ ternary and $\text{CaO-P}_2\text{O}_5\text{-CaF}_2\text{'FeO'}$ pseudo-quaternary system where small additions of calcium fluoride significantly restrict the region of stability of the refractory basic phosphates and increase the

solubility of phosphorus in liquid slag.^{90, 144}

C. Slag-Metal Equilibrium Distribution Studies and Dephosphorization

Correlation Development

Traditionally, slag-metal steelmaking reactions have been assumed to operate close to equilibrium and an equilibrium approach to the dephosphorization reaction has been adopted by the majority of previous workers. As in any reaction study, it is desirable to establish a formal criterion for comparison of equilibrium phosphorus distribution behavior as a function of experimental variables. By proper choice of the slag-metal reaction and determination of the value of the reaction equilibrium constant, a relationship between activities or concentrations of reactants and products is established. This relationship enables one to estimate the equilibrium distribution of phosphorus and correlate dephosphorization behavior with slag composition. Unfortunately our current knowledge of activity-composition relationships in complex liquids is very limited and assumptions must be made as to the structure and behavior of components in the melt in order to determine such relationships. In this section some general thermodynamic concepts are introduced in Part 1 to provide a basis for further discussion of slag-metal dephosphorization equilibrium studies which are presented and critically reviewed in Part 2.

1. Thermodynamic Considerations

a. Equilibrium Phase Relationships and the Phase Rule

According to the phase rule, an N component system may have as many as N+1 phases in equilibrium at a univariant equilibrium point. For the multicomponent systems relevant to slag-metal phosphorus equilibrium in steelmaking, this means that as many as six phases may be present at temperature. As seen in the previous section, the slag phase relationships are rather complex and in many cases several phases coexist at temperature.

This factor introduces complications in evaluating slag-metal equilibrium relationships due to the heterogeneous nature of the reaction system. Thus, attempts to formulate the phosphorus equilibrium reaction must account for the possible formation of refractory type phases which initially saturate the liquid as well as the precipitation of solid phases from the liquid slag during the course of equilibration with the metal phase. Ignorance or avoidance of such complications has caused and continues to cause much confusion in studies of slag-metal dephosphorization behavior and is a primary reason for disagreement in data and current misunderstandings which persist in the literature.

b. Theoretical Approaches to Slag Structure and Solution Modeling

i. Molecular Theory of Slags

In the absence of reliable thermodynamic data, early concepts of slag structure proposed the existence of complex molecules which were inherently stable and unreactive, such as aluminates, silicates and phosphates, and reactive "free" oxides which were those excess basic oxides remaining after having accounted for complex molecule formation with acidic oxides. This approach was pioneered by Whitely¹⁴⁵ in early treatments of open-hearth data. While Whitely assumed the chemical equivalence of basic oxides, a modified approach developed by Colclough¹⁴⁶ attempted to account for non-equivalence of bases and their varying degrees of interactions with slag constituents. Schenk¹⁴⁷ proposed a further revision of molecular theory in postulating that some dissociation of complex slag molecules occurs in solution. By analyzing open-hearth data, Schenck was able to estimate values for these dissociation constants and was able to explain slag reactivity at compositions more acidic than the orthosilicate by dissociation of compounds to form "free" basic oxides. Utilizing knowledge of molecular combinations found in the solid state, Chipman^{68, 108}

developed a useful physicochemical model of slag behavior involving ideal solutions of molecular compounds. In a later development of this approach, Richardson¹⁴⁸ demonstrated that some basic silicate systems can be thermodynamically modeled by assuming ideal mixing of ortho and metasilicate compounds.

In recent years, much controversy has developed over this molecular approach to slag chemistry and, with present understanding of melt structure, it is extremely unlikely that such complex molecules are present in molten slags at high temperatures. However without adequate activity data, such an approach does account for the considerable degree of interaction that occurs in these liquids and helps to explain the non-ideal behavior of slag constituents.

ii. Ionic Theory of Slags

Experimental evidence has provided significant indirect proof of the ionic nature of molten slag systems. High temperature x-ray diffraction studies have provided structural evidence and measurement of radial distribution functions. Cryoscopic measurements, diffusivity and viscosity measurements, and measurements of solution mixing properties have indicated that slag systems possess similar behavior to molten salt systems. More recent theoretical treatments of molten slags have tried to incorporate these ionic structural considerations in formal solution models.

Herasymenko¹⁴⁹ first proposed an ionic treatment of slag-metal equilibria though his assumptions of random mixing of anions and cations was fundamentally incorrect. Temkin's treatment¹⁵⁰ is generally regarded as providing the foundation for later development of ionic theory by postulating separate lattice or network sites for cations and anions where random mixing occurred. Temkin defined ideal activity for an ion where the activity of an ion is equal to its ion fraction. For ionic compounds, the

activity is given as the product of its constituent ion fractions where

$$a_{MO} = X'_M{}^{+2} \cdot X'_O{}^{-2} = \frac{N_M{}^{+2}}{\sum N_{\text{Cations}}} \cdot \frac{N_O{}^{-2}}{\sum N_{\text{Anions}}}$$

Herasymenko and Speight¹³⁸ observed that correlations of slag-metal equilibria by use of ionic equilibrium constants often showed compositional dependence. They attributed this to non-ideal behavior and modified Temkin's treatment through the introduction of activity coefficients. Later quasi-chemical approaches provided formal solution models to account for non-ideal behavior.¹⁵¹⁻²

Flood and Grjotheim¹⁵³ interpreted slag-metal reaction equilibria in terms of a cyclic reversible reaction process of reciprocal salts and demonstrated that, for slag-metal exchange reactions, the overall anionic equilibrium is solely a function of slag cation composition and vice versa. Using expressions for electrically equivalent ion fractions, which account for differences in ion charges, the ionic equilibrium constant for a salt mixture is expressed as a weighted summation of ionic equilibrium quotients for the pure component systems where

$$\log K'_{\text{Anionic}} = \sum N'_i \text{Cation} \cdot \log K'_i \text{Anionic}$$

and

$$\log K'_{\text{Cationic}} = \sum N'_i \text{Anion} \cdot \log K'_i \text{Cationic}$$

Elliott⁹⁴ has modified Flood's treatment to include ionic activity coefficients which account for non-ideal behavior in the melt. However this derivation encounters conceptual difficulties in defining standard states for single ions and utilizing single ion activity coefficients.

As with the molecular treatment of slags where conceptual problems are created by introducing the concepts of discrete molecules and "free" bases, problems arise in the ionic treatment due to the necessity of assuming discreet ions and theoretical treatment of compositions more acidic than

the orthosilicate when the oxygen ion fraction becomes undefined. In addition, evidence indicates that considerable polymerization occurs at compositions close to the orthosilicate and Masson and others¹⁵⁴⁻⁷ have tried to account for anion chain formation using polymer theory developed by Flory.¹⁵⁸ Such approaches have met with limited success except for simple binary systems. Additional problems arise in attempting to account for the strong interactions of ionic constituents and non-ideal behavior of solutions. Corrections must be introduced through the use of activity coefficients. This development leads to theoretical difficulties in defining standard states for single ions, measurement of ion activities and conversion of activity data from more conventional standard states to hypothetical ionic standard states.

2. Slag-Metal Equilibrium Studies

In this section, previous slag-metal equilibrium studies and dephosphorization correlation development are critically reviewed in order to provide a historical perspective for the present study. A summary of the more prominent laboratory equilibrium studies is given in Table 2.5. The most frequently cited slag-metal equilibrium correlations, which have been derived from this work, are listed in Table 2.6. In the literature review which follows, early plant and laboratory studies are presented in Part A. More recent studies are presented in Part B, classified as either molecular or ionic treatments. In Part C, phase diagram related distribution studies are presented.

a. Early Equilibrium Studies

Most of the early correlations of slag-metal dephosphorization behavior were developed for particular applications in open-hearth or Bessemer-type operations and were rather limited to narrow composition ranges where activity effects could be neglected as a first approximation.

Table 2.5: Summary of Previous Slag-Metal
Laboratory Equilibrium Studies

Study-Ref	Temperature Range (°C)	Equilibration Time (Min)	Alloy Phospho- rus Content (%)	% P ₂ O ₅	% 'FeO'	% CaO	% SiO ₂	Other Slag Components	Slag Saturation Surfaces*
Balajiva (109,120, 168)	1550-1635	8-40	0.02-0.18	4-12	5-30	30-60	8-20	MgO, Al ₂ O ₃ MnO	M,S
Chipman (108)	1530-1700	30	0.005-0.18	0-20	5-60	10-46	3-30	MnO, Al ₂ O ₃ MgO	M,S
Fischer (169)	1530-1680	-	0.004-1.0	1-40	5-50	30-55	1-11	-	C, C ₄ P
Peter (100)	1590-1680	15	0.015-0.30	12-33	4-36	49-69	-	MgO, MnO	C, C ₄ P, C ₃ P, M
Tromel (97,98, 103)	1550-1675	30-60	0.006-21	1-46	3-93	3-56	0-7	MgO, MnO	C, S, C ₄ P, C ₃ P
Knuppel (101,102)	1550-1700	60	0.003-1.9	0-40	0-60	36-60	0-8	MnO	C, C ₄ P, C ₃ P, M
Kor (139)	1550	40-60	0.005-0.36	3-13	5-35	31-49	12-32	MgO, CaF ₂ , B ₂ O ₃ , TiO ₂ , Al ₂ O ₃	M,S

Table 2.5: (Cont.)

Study-Ref	Temperature Range (°C)	Equilibration Time (Min)	Alloy Phosphorus Content (%)	% P ₂ O ₅	% 'FeO'	% CaO	% SiO ₂	Other Slag Components	Slag Saturation Surfaces*
Suito (172)	1550-1650	3-5.5 hrs	0.002-0.16	.12-1.14	15-90	0-42	0-32	MgO	M,S
Suito (140)	1550-1700	3-5.5 hrs	0.002-0.08	0-3	15-87	1-36	0-33	MgO, CaF ₂	M,S

*Key to Slag Saturation Surfaces:

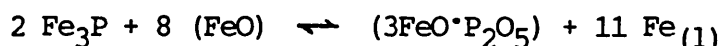
M: Mg(Fe,Ca)O; S: α - 2 CaO.SiO₂ - 3 CaO.P₂O₅; (ss) C: CaO; C₄P: 4 CaO.P₂O₅; C₃P: 3 CaO.P₂O₅; C₃S: 3 CaO.SiO₂

Table 2.6: Frequently Cited Slag-Metal Equilibrium
Dephosphorization Correlations

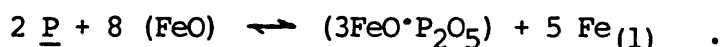
Study (Ref.)	Proposed Reaction and Equilibrium Quotient
Balajiva (109, 120 168)	$2 \underline{P}_{(1w/o)} + 5 (FeO) \rightleftharpoons (P_2O_5) + 5 Fe_{(l)}$ $K_p = (\%P_2O_5) / (\%P)^2 (\%FeO')^5$ $\log K = 10.78 \log (\%CaO) - 0.894T - 6.254$
Turkdogan (137, 170)	$2 \underline{P}_{(1w/o)} + 5 \underline{O}_{(1w/o)} \rightleftharpoons (P_2O_5)$ $K_p = \gamma_{P_2O_5} \cdot N_{P_2O_5} / (\%P)^2 (\%O)^5$ $\log K_p = 36850T^{-1} - 29.07 \text{ and}$ $\log \gamma_{P_2O_5} = 23.58 - 1.12 \sum A_i N_i - 42000T^{-1}$ where $\sum A_i N_i = 22X_{CaO} + 15X_{MgO} + 13X_{MnO} + 12X_{FeO} - 2X_{SiO}$
Healy (171)	$2 \underline{P}_{(1w/o)} + 5 (FeO) + 4 (CaO) \rightleftharpoons (4 CaO \cdot P_2O_5) + 5 Fe_{(l)}$ $\log [(\%P)_{slag} / (\%P)_{metal}] = 22350/T + 0.08(\%CaO) + 2.5 \log(\%Fe_{tot}) - 16$
Present Work	$2 \underline{P}_{(1w/o)} + 5 (FeO) + 5 (CaO) + (SiO_2) \rightleftharpoons \alpha - 2 CaO \cdot SiO_2 - 3 CaO \cdot P_2O_5(ss) + 5 Fe_{(l)}$ $K_p = 1 / (\%P)^2 (\%FeO')^5 (\%CaO)^5 (SiO_2)$ $\ln K_p = 3.22 \times 10^4 / T - 44.55$

One of the earliest empirical correlations developed for open-hearth slags was that of Whiteley¹⁴⁵ who discovered a relation between a slag basicity index and phosphorus distribution. Whitely assumed an equivalence of basic oxides in his treatment and found that no dephosphorization occurs for basicity values of less than two. In a similar statistical treatment of plant data, McCance¹⁵⁹ demonstrated that virtually no dephosphorization occurred at calcium oxide contents below 32%.

Other studies of slag-metal phosphorus equilibrium were conducted by Schackmann and Krings,¹⁶⁰ von Samson-Himmelstjerna,¹⁶¹ Bischof and Maurer,^{162, 163} Diepslag and Schurmann¹⁶⁴ and Herty.¹⁶⁵ While experimental conditions were not uniform, the earliest formulations of the dephosphorization reaction attempted to account for the known stabilities of the iron phosphide and phosphate. For example, von Samson-Himmelstjerna proposed the reaction

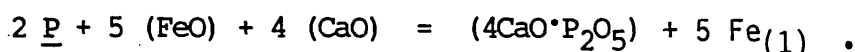


and Herty



Such early attempts to formulate a generalized equilibrium constant were unsuccessful for even the simplest binary and ternary slag systems and no correlation was developed which could apply to a range of compositions and data sets. These early studies have been critically reviewed by Zea,¹⁶⁶ Chipman,¹⁰⁸ and Balajiva¹⁰⁹ all of whom have commented on the general lack of agreement in formalistic approach and experimental results. Chipman considered that these studies were either too general and qualitative or, if quantitative, too restrictive and limited in scope to narrow composition ranges. He noted that none of these correlations was adequate if the implicit goal was to accurately predict residual phosphorus levels from slag compositions.

In considering more complex slag systems, some attempt was made to correlate slag composition with dephosphorization behavior by accounting for the relative stabilities of the various basic phosphates (see Table 2.4). Such an approach was taken by Schenck and Reiss,¹⁶⁷ based on the known thermodynamic stability of the calcium phosphates and Schenk's theory of molecular association in the liquid state.¹⁴⁷ These workers proposed the following reaction:



In this expression, "free" base concentrations are used for CaO and FeO and these were obtained from equilibrium diagrams developed from statistical analysis of plant data.¹⁶⁷ A quantitative formulation of the equilibrium constant was derived although it was necessary to introduce empirical correction factors. Zea¹⁶⁶ claimed that Schenck's correlation gave the best results in predicting residual alloy phosphorus levels in equilibrium with open-hearth slags.

Despite a lack of quantitative agreement in early slag-metal dephosphorization studies and lack of consensus in formulating the equilibrium reaction, several qualitative observations had been established:

- 1) Oxidizing conditions are required for adequate dephosphorization.
- 2) Calcium oxide is a basic requirement for phosphorus removal.
- 3) Residual alloy content is dependent on slag phosphorus content.
- 4) The dephosphorization reaction is temperature dependent and, as an exothermic reaction, is favored by lower temperatures.
- 5) The role of acidic oxides, such as silica and alumina, is viewed as being competitive with phosphorus over basic oxides due to the relative stabilities of basic phosphates, silicates and aluminates.
- 6) The role of basic oxides is considered beneficial in promoting dephosphorization by providing stable basic phosphate reaction products in the slag phase.

b. Post-War Equilibrium Studies

i. Molecular Treatments

While earlier studies relied heavily on statistical-empirical treatments, Winkler & Chipman¹⁰⁸ formulated an equilibrium constant based on a modification of Schenk's molecular treatment of slags. They proposed the reaction



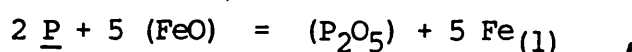
where the concentration of "free" lime was determined by assuming a molecular solution model based on the ideal mixing behavior of basic silicates, phosphates, ferrites and aluminates.

In this approach, Chipman recognized the importance of relatively strong interactions and non-ideal behavior of components in these slags while admitting that such molecular associations were not likely to occur at high temperature. The temperature dependence of this equilibrium was determined where

$$\log K = \frac{71667}{T} - 28.73$$

The effect of slag basicity and iron oxide content was shown to dominate both the "free" lime content and phosphorus distribution of slags. Based on these observations, Chipman assumed that all basic oxides would promote dephosphorization by increasing slag basicity and acidic oxides would inhibit dephosphorization by combining with "free" lime.

While the laboratory study of Balajiva and co-workers^{109, 120, 168} was primarily empirical in nature, it remains as perhaps the most systematic and thorough study to date and the correlation proposed by these workers is widely accepted as being truly indicative of the slag-metal equilibrium state. By considering the compositional dependence of the equilibrium quotient for the reaction



certain relationships involving slag basicity, lime and iron oxide content were identified with indisputable clarity. The equilibrium quotient was shown to be heavily dependent on the total lime content of the slag and slightly temperature dependent where

$$\log K_p = 10.78 \log (\%CaO) - 0.00894T - 6.245$$

In addition, slag-metal phosphorus distribution exhibited a maximum value dependent on slag basicity and iron oxide content. The significance of Balajiva's findings was that the effect of FeO and CaO were of overriding importance even in the presence of significant and varying levels of SiO₂, Al₂O₃, MgO, MnO and P₂O₅.

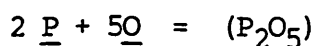
Fischer and von Ende¹⁶⁹ tried to formulate their own slag-metal equilibrium correlation by considering the dephosphorization reaction product to be tetracalcium phosphate. Since most of their slags were saturated with respect to either lime or the phosphate, these workers assumed dual saturation and expressed the slag-metal equilibrium as

$$K = \frac{1}{(\%P)^2 (\%O)^5}$$

where

$$\log K = \frac{53000}{T} - 19.4 \quad (T = 1530 - 1700^\circ C)$$

In their statistical treatment of laboratory and plant data, Turkdogan and Pearson¹⁷⁰ considered the simplest form of the slag-metal dephosphorization reaction and proposed the reaction



where

$$\Delta G_T^\circ = -168.6 + 0.133T \quad (KJ/mol)$$

These workers estimated the free energy change for this reaction where activities of phosphorus and oxygen in the alloy are defined relative to

the hypothetical 1 w/o standard state and pure P_2O_5 liquid is taken as the standard state for phosphorus in the slag. By making use of slag and metal analyses, activity coefficients of P_2O_5 were correlated with slag compositions and a generalized equation was developed from a statistical regression analysis of plant and laboratory data:

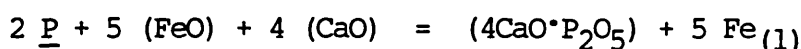
$$\log \gamma_{P_2O_5} = -1.12 \sum A_i N_i - \frac{42000}{T} + 23.58$$

where

$$\sum A_i N_i = 22N_{CaO} + 15N_{MgO} + 13N_{MnO} + 12N_{FeO} - 2N_{SiO} .$$

With this expression it is possible to predict the equilibrium phosphorus distribution based on slag composition. It should be emphasized, however, that there is no theoretical significance to be attributed to the coefficients of this equation as it is purely empirical in nature.

Although the correlation developed by Healy¹⁷¹ suffers from fundamental errors in its derivation, it remains primarily an empirical correlation and has enjoyed limited popularity in Japan. It is often cited as a dephosphorization criterion for basic slags saturated with lime. Healy proposed the reaction



and, as the result of a somewhat dubious theoretical treatment, arrived at the following empirical expression for phosphorus distribution between slag and metal

$$\log D_p^{(w/o)} = \frac{22350}{T} + 0.08 (\%CaO) + 2.5 \log (\%Fe_{TOT}) - 16.0 .$$

This correlation generally tends to predict lower residual phosphorus than is actually observed in steelmaking slags since it was derived from a statistical treatment of lime saturated slags.

In his study of slag-metal dephosphorization equilibria and the effect of flux addition on slag refining chemistry, Kor¹³⁹ proposed no new

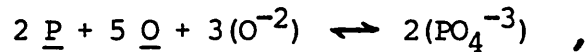
correlation but rather relied on Balajiva's correlation as a criterion of slag dephosphorization behavior. Since only data for fluorite containing slags fell above Balajiva's equilibrium line and resulted in higher values for the equilibrium quotient, Kor argued that CaF_2 was beneficial in promoting dephosphorization. Since Kor's study was not very systematic, direct comparison of the effect of various fluxes on dephosphorization is inconclusive. For CaF_2 slags, rather extreme variations in composition produced positive displacement of the Balajiva line due to very low FeO contents. If flux additions are evaluated at comparable P_2O_5 , FeO , SiO_2 or basicity ratios and compared to slag behavior where no flux was added, inconclusive results are observed. This study reveals one of the major weaknesses of Balajiva's correlation where the value of the equilibrium quotient is relatively insensitive to slag-metal phosphorus distribution or residual phosphorus levels in the alloy. This will be discussed in detail in a later section.

Suito and co-workers¹⁷² studied slag-metal dephosphorization behavior with basic oxygen steelmaking slags saturated with magnesia. In addition, they evaluated changes in refining behavior brought about by small additions of CaF_2 to these slags.¹⁴⁰ While these workers proposed no new correlation, they used the existing correlations of Balajiva, Turkdogan, Flood and Healy to evaluate their own data and critically reviewed the suitability of each of these correlations for modeling slag refining behavior. The correlations of Turkdogan and Flood agreed favorably with the results of this study with some modifications. In general, residual phosphorus levels calculated from Balajiva's correlation were found to be three to five times higher than observed values. Balajiva's correlation tended to overemphasize the dependence of dephosphorization on calcium oxide content when extrapolated to lower lime levels and the value of the

equilibrium quotient was underestimated with predictions of higher residual phosphorus than actually observed in the alloy phase. The role of CaF_2 was shown to be essentially equivalent to that of CaO using each of the correlations. By superposition of CaO-MgO-FeO-SiO_2 quaternary slag compositions on the CaO-FeO-SiO_2 ternary phase field, Suito plotted iso-distribution ratios for phosphorus and observed maximum values in regions of dual saturation with tricalcium silicate and magnesio-wustite. These results contradict the behavior observed by both Bardenheuer¹⁷³ and Koch¹⁷⁴ as well as the results of the present study where maximum phosphorus distribution coincides with the dicalcium silicate saturation surface "nose" and a pronounced decrease occurs at tricalcium silicate saturation.

ii. Ionic Treatments

Herasymenko and Speight¹³⁸ presented the first ionic treatment of dephosphorization with their analysis of open hearth plant data. By considering the following reaction,



they derived an empirical expression for an ionic equilibrium quotient using ion mole fractions

$$K = \frac{N_{\text{PO}_4^{-3}}^2}{(\% \underline{\text{P}})^2 (\% \underline{\text{O}})^5 N_{\text{O}^{-2}}^3}$$

where

$$\log K = 14 N_{\text{Ca}+2} + 2.7$$

and is strongly dependent on calcium oxide content.

As shown in a previous section, Flood and Grjotheim¹⁵³ derived a theoretical relationship between slag ionic composition and slag-metal exchange equilibria where

$$\log K'_p = \sum N'_i \text{ Cation } \log K_i \text{ Anionic } (\text{PO}_4^{-3}) .$$

By analyzing the data of Winkler and Chipman,¹⁰⁸ they developed a similar reaction model and derived an empirical expression based on equivalent ion fractions where

$$K'_p = \frac{N'^2_{PO4^{-3}}}{x_P^2 x_O^5 N'^3_O^{-2}}$$

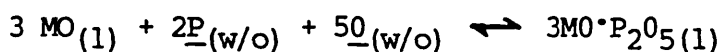
and

$$\log K'_p = 21 N'^{+2}_{Ca} + 18 N'^{+2}_{Mg} + 13 N'^{+2}_{Mn} + 12 N'^{+2}_{Fe}.$$

Flood noted that the coefficients for Mg^{+2} and Mn^{+2} were subject to considerable error due to limitations in extrapolating the data. The method for determining these coefficients by extrapolation to $N'_i = 1.0$ is not mathematically justified and a more sensible approach would be use of a regression analysis. Nevertheless, the significance of this approach was in demonstrating the critical influence of Ca^{+2} on phosphorus distribution and the primary influence of cation composition on anionic equilibria as predicted by ionic theory.

Since Flood had determined the individual cationic equilibrium quotients empirically from Winkler's data, they do not accurately reflect the equilibrium constants for the "pure" metal oxide-metal phosphate systems. More accurate data for the individual equilibrium quotients for the pure binary systems has become available from recent thermodynamic measurements on these systems.

Elliott⁹⁴ has provided estimates for the free energy change involving reactions of the pure binary oxide and phosphate liquids:



By utilizing these estimates, the theoretical values of the individual equilibrium quotients can be estimated and, for the generalized equation

$$\log K'_p = 9.2 N'^{+2}_{Ca} + 11.9 N'^{+2}_{Mg} - 2.2 N'^{+2}_{Fe} - 0.05 N'^{+2}_{Mn},$$

a rather surprising result is obtained. Based on theoretical predictions,

the dephosphorization ability of magnesia appears to exceed that of lime and the influence of iron oxide appears to be negative. Such predictions contradict empirical observations and can be explained on the basis of choosing the super-cooled liquid oxides and phosphates as standard states for lime and magnesia and extrapolation of low temperature data for iron phosphate beyond its region of application.

Recently Gaskell¹⁷⁵ has published a theoretical treatment of Suito's data based on Flood's ionic approach and a new slag basicity parameter proposed by Duffy and Ingram.¹⁷⁶ The "theoretical optical basicity" of a slag mixture is defined by these workers as

$$\Lambda = \sum f_{M_i}^{+Z} \cdot \Lambda_{M_i}^{+Z}$$

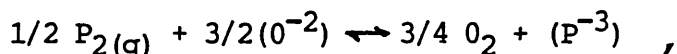
where $f_{M_i}^{+Z}$ is the fraction of charge on oxygen ions neutralized by M_i^{+Z} and $\Lambda_{M_i}^{+Z}$ is the "theoretical optical basicity" for the pure component oxide which is calculated from Pauling's electronegativity values

$$\Lambda_i = \frac{1}{1.36(E.N._i - 0.26)} .$$

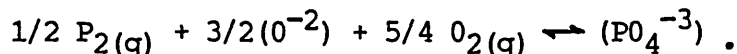
Gaskell demonstrated that the activity coefficient term resulting from Flood's treatment is linearly dependent on this slag composition parameter. Such an approach is virtually identical to Elliott's demonstration of the effect of oxygen ion fraction on ion activity coefficient ratios.⁹⁴ While Gaskell demonstrated that his approach is adequate in characterizing slag behavior, its predictive abilities are rather poor and it offers no additional refinement of our present understanding of slag refining chemistry.

In a recent publication, Sano¹⁷⁷ presented the results of a slag-metal dephosphorization study under very reducing conditions not normally encountered in steelmaking. Using alumina saturated calcium aluminate slag and Fe-P-Al alloys equilibrated with P_2 gas at 1550°C, these workers claim to have identified two distinct regions of dephosphorization. Under very

reducing conditions, they proposed the following reaction



and under relatively oxidizing conditions, the reaction



The immediate effect of these combined regions on dephosphorization behavior is to produce a minimum alloy phosphorus level at very low oxygen potentials of the order of 10^{-18} atmospheres. While experimental details were not provided and the results obtained must be subjected to critical review, this study does provide an interesting picture of slag chemistry quite similar to observed behavior for sulfur refining where regions of sulphide and sulphate stability have been identified. However such results are not likely to have any practical significance in refining practice since oxygen potentials of this order are unrealizable on an industrial scale. Furthermore, as will be shown later, there is no theoretical need nor justification for resorting to such exotic reaction models in order to explain hot metal refining behavior.

3. Distribution Studies Based on Phase Relationships

Oelsen and Maetz⁹⁵ provided the first attempt at understanding slag-metal dephosphorization behavior on the basis of slag phase relationships. In their investigations of alkali and alkaline earth metal oxide-based ternary systems with P_2O_5 and FeO they observed the considerable stability of the basic phosphates which were refractory in character and a pronounced tendency for immiscibility in the liquid state. Phase separation produced one liquid rich in basic phosphate and a highly oxidizing liquid, rich in FeO. They studied slag-metal phosphorus distribution behavior with basic oxide and basic phosphate saturated liquid and observed that slag dephosphorization ability was directly related to the stability of the basic phosphate reaction products, where sodium oxide

possessed superior refining characteristics to calcium oxide which was superior to magnesium oxide.

Later work by Tromel¹⁷⁸ and Schurmann¹⁷⁹ investigated the phosphorus distribution behavior in ternary liquid systems saturated with respect to magnesia, alumina^{178, 179} silica¹⁷⁸ and zirconia¹⁷⁹ and found these to be inferior to calcium oxide saturated liquids.

While Oelsen's work with phosphorus distribution behavior in the $\text{CaO-FeO-P}_2\text{O}_5$ ternary system was of an exploratory character, Tromel and co-workers^{180, 181} compiled extensive data on ternary phase relationships and slag-metal phosphorus distribution within various regions of the ternary phase fields. They studied distribution behavior at several temperatures with alloys in equilibrium with a variety of phases such as the two liquid miscibility gap region, mono and dual saturated liquids in equilibrium with calcium oxide or the calcium phosphates, and the single liquid phase field. These workers observed that the lowest residual phosphorus levels were produced with slags saturated with either calcium oxide or calcium oxide and tetracalcium phosphate while phosphate saturated liquids produced slightly higher phosphorus levels. Tromel noted that the dual saturated liquid composition were preferred from a practical point of view since these liquids produced the lowest residual oxygen levels in the alloy phase. An isothermal stability diagram, derived by these workers, is shown in Figure 2.13 where regions of ternary phase stability are shown as functions of phosphorus and oxygen potentials. It is interesting to note that these workers observed that phosphorus distribution behavior was not as strongly temperature dependent as predicted by actual steelmaking practice and they considered this to be due to non-equilibrium factors.

Both Peter¹⁰⁰ and Tromel⁹⁹ studied slag-metal phosphorus distribution behavior in magnesia saturated $\text{CaO-P}_2\text{O}_5\text{-FeO}$ liquids. Peter investigated

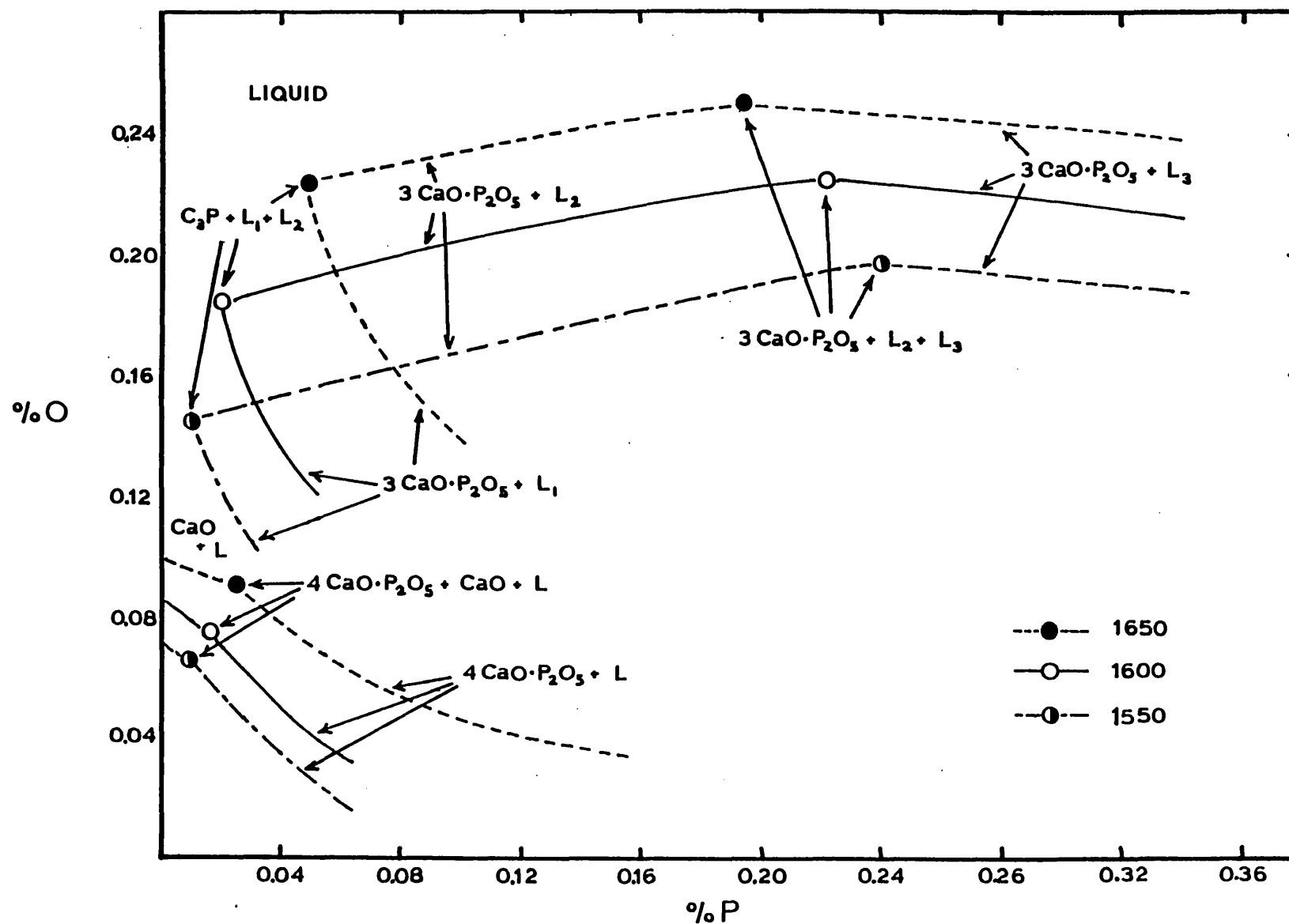
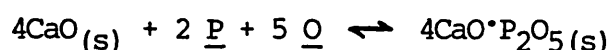


Figure 2.13 Oxygen and Phosphorus Isotherms and Saturation Surfaces in the CaO-P₂O₅-FeO Ternary System (180, 181).

liquids saturated with respect to both calcium oxide and magnesio-wustite and found that magnesia content had no influence on distribution behavior. Tromel, Fix and Kaup studied residual phosphorus levels in alloys in equilibrium with magnesia saturated liquids in the ternary miscibility gap and found no difference in behavior with magnesia additions.⁹⁹

As mentioned previously, Fischer and von Ende¹⁶⁹ provided an equilibrium formulation for ternary and multicomponent slags saturated with respect to calcium oxide and tetracalcium phosphate. Since they claimed that both oxide and phosphate activities approached unit activity at dual saturation, the slag-metal equilibrium was represented by the reaction



where

$$K = \frac{1}{(\%P)^2 (\%O)^5}$$

They determined the temperature dependence of this equilibrium quotient as

$$\log K = \frac{53000}{T} - 19.4$$

Since Thomas process slags were generally close to dual saturation with respect to calcium oxide and tetracalcium phosphate, this correlation was fairly representative of industrial slag refining behavior.

Knuppel and Oeters¹⁸² studied calcium oxide saturated ternary slags at various temperatures and based on somewhat restrictive assumptions they were able to estimate phosphate activity data and a temperature dependent equilibrium constant for the reaction



Based on several additional assumptions, they also estimated iso-activity lines for phosphorus within the single liquid phase region of the $\text{CaO-P}_2\text{O}_5\text{-FeO}$ ternary system.

Later studies by Bookey,⁶⁰ Banya and Matoba⁴² and Aratani and Sanbongi⁴³ focused on the equilibrium between calcium oxide and tetracalcium phosphate saturated iron-phosphorus alloy at controlled oxygen potentials. It should be emphasized that, according to Tromel's study of ternary phase relationships, dual saturation occurs at fixed oxygen and phosphorus potentials corresponding to 0.018 %P and 0.08 %O at 1600°C (See Figure 2.13). At this oxygen potential a slag phase would be present and the dual saturated slag-metal equilibrium would be an invariant point. At the phosphorus potentials utilized in these reaction studies, only tetracalcium phosphate saturation would be attained. At low phosphorus activities, only calcium oxide saturation is attained. These phase relationship features are rather significant in interpreting both dual saturated alloy equilibrium studies as well as the studies of Fischer and von Ende since in most of these experiments the system is saturated with respect to either calcium oxide or calcium phosphate, but not both phases. This raises some doubts as to the reliability of the thermodynamic data for calcium phosphate formation from calcium oxide.

The influence of silica on the $\text{CaO} \cdot \text{P}_2\text{O}_5 \cdot \text{FeO}$ ternary phase fields and slag-metal phosphorus distribution equilibria was studied by Oelsen,⁹⁵ Tromel and co-workers^{96-8, 103-4}, Knuppel,¹⁰¹⁻² and Peter.¹⁰⁰ While the majority of these workers studied the influence of silica additions at calcium oxide saturation and reported lower distribution ratios and higher residual phosphorus at equilibrium, only Tromel¹⁰³⁻⁵ reported improved dephosphorization at certain compositions enriched in silica. While he observed that silica additions inhibited dephosphorization at calcium oxide saturation, with silico-phosphate saturated slags, phosphorus distribution was increased and lower residual phosphorus levels were obtained. Such behavior was observed over a range of liquid compositions saturated with

respect to the silico-phosphate solid solution and the refining properties of these slags were similar to calcium oxide saturated slags, free of silica. Tromel postulated that precipitation of the silico-phosphate from the liquid lowered the effective phosphorus content of the slag which lowered, in turn, the equilibrium residual phosphorus content of the alloy phase. Tromel observed that at compositions which do not lie within the silico-phosphate saturation surface, at constant phosphorus pentoxide content, silica additions increase residual phosphorus levels.

With current industrial slag compositions used in basic oxygen steelmaking practice, both Koch¹⁷⁴ and Bardenheuer¹⁷³ observed maximum slag-metal phosphorus distribution ratios at the dicalcium silicate saturation "nose". Bardenheuer noticed a shift in this maximum with increasing temperature toward lower FeO contents. He also observed that phosphorus distribution values were lower at tricalcium silicate saturation regions. Ito¹³¹ observed that the distribution of phosphorus between the calcium silico-phosphate solid solution and liquid slag also exhibited a maximum at the dicalcium silicate "nose" and that the distribution coefficient increased with increasing iron oxide content.

In a soon-to-be published monograph on metallurgical slags, Turkdogan¹⁸³ has developed a new statistical-empirical correlation involving functional relationships and phosphorus distribution where

$$D_p = \phi [\% \text{'FeO'}, \% \text{SiO}_2, \text{Basicity Ratio}] .$$

By consideration of the phase rule at equilibrium, he proposes that the analytical expression for phosphorus distribution will take on a variety of compositional dependencies and formats depending on how many phases coexist at equilibrium. Thus at constant temperature, D_p will be a function of $((N+1)-P)$ variables. For example, the following assumed format is adopted for two-phase equilibrium involving slag and metal:

$$K_{ps} = D_p(1+\%SiO_2) = \phi [\%FeO, \text{Basicity}] .$$

For double saturated slag and metal, this formalism reduces to

$$D_p = \phi [\%FeO] .$$

By a graphical analysis of the data from previous workers,^{101-2, 108, 120, 139, 168-9, 172} Turkdogan demonstrates the validity of such an approach and underscores the necessity of considering phase relationships when analyzing slag-metal equilibrium refining behavior.

III. OUTLINE OF WORK AND EXPERIMENTAL APPROACH

As reviewed in the previous section, prior studies of slag-metal dephosphorization equilibria have emphasized the primary dependence of refining behavior on calcium oxide, iron oxide and silica content of slags. Since a major purpose in undertaking the present study was to characterize the role of magnesia in slag refining chemistry and determine what benefits might accrue from magnesia substitution practice, the first task was to scrutinize existing data bases for possible evidence which would clarify our understanding of the influence of magnesia on the slag-metal phosphorus equilibrium.

Once a critical review of previous equilibrium studies was completed, it became clear that insufficient information was available for evaluation of the role of magnesia on the phosphorus reaction and it became necessary to generate new data in order to establish a refined picture of slag chemistry. Initially, simple magnesia and calcia based binary and ternary slag systems were studied in order to develop understanding of the relative refining behavior of the two basic oxides. The effect of additions of both silica and fluoride on these simple slag systems was next evaluated since previous studies had indicated the significant influence of these two components in either inhibiting or promoting dephosphorization refining.

By developing understanding of slag component interactions in simple slag systems and moving on to more complex melts, it was possible to establish a detailed realistic picture of dephosphorization refining chemistry, more indicative of the complex multicomponent systems encountered in actual steelmaking practice.

For the equilibrium data generated in the present study, the levitation melting technique was utilized. The advantage of this technique lies with the rapid approach to equilibrium attainable under turbulent

stirring conditions and freedom from operating within the confines of liquid saturation surfaces in the phase systems studied. This eliminates refractory containment and contamination problems. An additional benefit is obtained since slag compositions are not forced to lie on liquid saturation surfaces where compositions are not independently variable but fixed by the requirements of liquid-solid equilibrium phase relationships. This feature was particularly critical in studying the role of magnesia in phosphorus refining since magnesia solubilities are severely restricted by the nature of the slag phase relationships, as shown in the previous section.

The unique advantage of the present study lies in this freedom from compositional restrictions imposed by system phase relationships. This is particularly true with regard to basic oxygen steelmaking slags where such restrictions have plagued previous studies. Thus CaO , MgO , FeO , SiO_2 and P_2O_5 content could be treated as truly independent variables within the pseudo-quinary phase system. Refining behavior and component interactions could be evaluated within both the single liquid phase volume as well as with slags saturated with respect to several phases. Such freedom enabled a realistic assessment of compositional dependence of refining behavior and slag component interactions within the homogeneous liquid region. It also clarified the relative significance of the various high temperature phases and liquid saturation surfaces and their influence on slag chemistry.

Having generated a new data base with systematic and independent variation of experimental parameters and composition variables, previously derived correlations were critically evaluated in regard to their ability to predict slag-metal phosphorus distribution and residual phosphorus levels on the basis of slag composition variables. The inadequacies of existing correlations was demonstrated and a new correlation was derived in

an attempt to integrate the results of previous studies and the present study in light of known phase relationships.

IV. EXPERIMENTAL DETAILS

In this section, some general background information on the levitation melting technique is provided in Part A. The levitation apparatus and gas delivery system used for slag-metal equilibrations is described in Part B. Experimental technique involving alloy and slag synthesis and sample preparation as well as experimental procedures in levitation experiments are described in Part C. In addition, post-levitation sample treatment and procedures for chemical analysis are described in detail.

A. The Levitation Melting Technique

While a detailed review of the principles of levitation melting is beyond the scope of this work, some general description of the technique is perhaps appropriate for understanding the particular experimental design used in this study.

When a conductor is placed in a non-uniform, rapidly alternating electromagnetic field, eddy currents are induced and forces acting between the induced currents and applied field support the conductor and tend to displace it to a weaker, more divergent part of the field. At the same time, induction heating of the conductor occurs and, depending on the charge material, coolant gas flow, coil design and power input, with proper control over variables, melting proceeds and steady-state temperatures can be maintained with the liquid droplet in suspension.

The stability of the drop is a critical requirement for conducting reaction studies and this is generally a function of the sample properties, coil geometry and matching of coil with the output impedance of the high frequency generator. Temperature control is brought about by proper choice of coolant gases, sample mass, coil design characteristics and the dynamic balance of power input and coolant gas flow rate and pressure.

The advantage of levitation melting as an experimental technique is

that it provides great versatility in the study of high temperature reactions, free from contamination by containment materials. The technique is particularly suitable for slag-metal reactions as non-conductive oxide phases may be levitated in association with a metal specimen when the liquid oxide wets the metal and adheres to the metallic drop due to surface tension forces. In addition, reactive gases can be introduced in the coolant gas and brought into contact with the suspended sample for the purpose of studying gas-metal reaction kinetics, or, in some limited cases, gas-metal equilibrium. The technique provides for both rapid equilibrations, due to the turbulent contact conditions produced, and a rapid sample quenching technique, where samples can be either drop-quenched at selective stages of reaction in kinetic studies or rapidly quenched for representative sampling of the high temperature phases during equilibrations. In addition, the geometry of the reaction system is relatively well defined and the sample can be unobstructively viewed from virtually any angle during the course of a reaction.

The principle disadvantages of the levitation technique are in temperature control and measurement, sample stability during reaction, limitations in sample size and tedious preparation and analysis of samples.

While Distin¹⁸⁴ developed a cumbersome calorimetric technique for measuring levitated sample temperatures, experimental technique generally requires use of radiation pyrometry methods for temperature measurement of the specimen surface. Problems arise since high frequency induction heating of these samples is from the surface skin inwards and a gradient may be present between the sample surface and the bulk sample. This surface heating effect is additionally complicated by the surface cooling effect of gas flow over the sample. Thus, relying on the surface emissivity for temperature measurement may not be entirely reliable.

Additional problems are encountered with heterogeneous samples, since temperature gradients are established between the inductively heated alloy and non-inductive and insulating slag layer. Thus, the slag-metal interface is inductively heated, insulated and not exposed to coolant gases. On the other hand, the slag-gas interface is heated by way of conduction and radiation within the slag, and is cooled by radiation and convection at the gas interface. Complex temperature gradients may be established within the sample due to the unique heating characteristics of the contacting technique.

While temperature control is also problematic, with proper control over experimental conditions and coil design, stable temperatures can be readily attained. However, during the course of reaction, sample stability and temperature stabilization are sometimes jeopardized when strongly exothermic or endothermic reactions occur or when compositional changes bring about a change in sample physical properties such as emissivity, alloy fusion temperature or slag liquidus temperature. Often dynamic equilibrium is disrupted by a change in sample characteristics and levitation variables such as gas composition and flow rate and coil power have to be modified to maintain stable levitation.

Limitations as to sample size and slag-metal weight ratios are severely restrictive due to levitation geometry, heat transfer and lifting force requirements. While levitation of alloy samples of up to several hundred grams has been achieved,¹⁸⁵ with large samples experimental control over sample stability and temperature is rather poor. For this reason, small samples of no more than a few grams are recommended and for temperatures below 1800°C one gram samples are ideal. The amount of slag phase used is restricted by sample density, dimensional considerations and heat transfer limitations where a suitable conductor mass is required for

both levitating and heating the combined sample. Because it is non-inductive, slag fusion enthalpy requirements necessitate superheating of the alloy during levitation and the amount of slag is limited to what can be adequately fused during sample alloy melting. In addition, there is a physical limit on the amount of powdered slag that can be initially combined with the alloy charge due to density and volume limitations of the composite phases. Generally, with iron alloy-slag systems a metal to slag weight ratio restriction of ten to twenty is required with this technique.

Sample preparation is a major disadvantage in the levitation technique since this requires considerable care in alloy preparation in order to maintain homogeneity. Extensive cutting, machining and polishing of individual specimens and tedious handling and weighing procedures are required both prior to and after levitation. In addition, restrictions in sample mass make chemical analysis of the slag and metal phase exceptionally troublesome, particularly in the case of residual trace analysis of minor components such as phosphorus. While micro-analytical techniques are available, they are exceedingly tedious and exceptionally complicated especially when matrix interferences are present. For these reasons most studies of high temperature reactions have been limited to rather simple reaction systems involving gas phase oxidation and decarburization of iron alloys.

For a more detailed discussion of the theoretical principles of levitation and a review of prior experimental studies, the reader is referred to more comprehensive reviews.¹⁸⁶⁻⁸

B. Experimental Apparatus

The apparatus used in these experiments consisted of: a) a levitation coil and Radyne high frequency generator (250 kHz, 15 kW) equipped with a variable output transformer to match output impedance with individual

coils; b) a levitation chamber assembly providing an enclosed atmosphere and a six position turntable for multiple loading and quenching of samples; and c) a gas cleaning and delivery system with timer-controlled solenoid valves for directing coolant and reactant gases to the sample chamber. Each of these assemblies is described below in more detail.

1. The Levitation Coil

a. Coil Design

The reader is referred to other references for a general discussion of coil design considerations^{186, 189}. A drawing of the coil used in this study is shown in Figure 4.1. This coil design was originally used by Polonis¹⁹⁰, modified by Jenkins¹⁸⁶ and recently recommended by Jahanshahi¹⁹¹ for levitation of iron alloys.

The coil design consists of two distinct sections with five bottom turns connected in series with two top turns. The two lowest turns are wound coplanar while the next three form a helical cone, having a 30° semi-apex angle, with the inner lower turn. This bottom section provides a laterally stabilized lifting force. The upper coil consists of two turns connected in series to the lower coil and wound helically in reverse direction to the bottom section. This upper section provides a magnetic stopper for containment of the sample in a magnetic envelope or bottle. This type of arrangement has been shown to provide very stable levitation behavior at relatively low temperatures, enabling excellent temperature control at low flow rates of coolant gases.

b. Coil Fabrication

The coil was fabricated from a one meter length of 5/32" o.d. thin-walled, straight copper tubing. This was first pre-annealed to red heat and pickled in an acid mixture to remove oxide scale. It was then covered with a fiberglass insulation sleeve and filled with water prior to

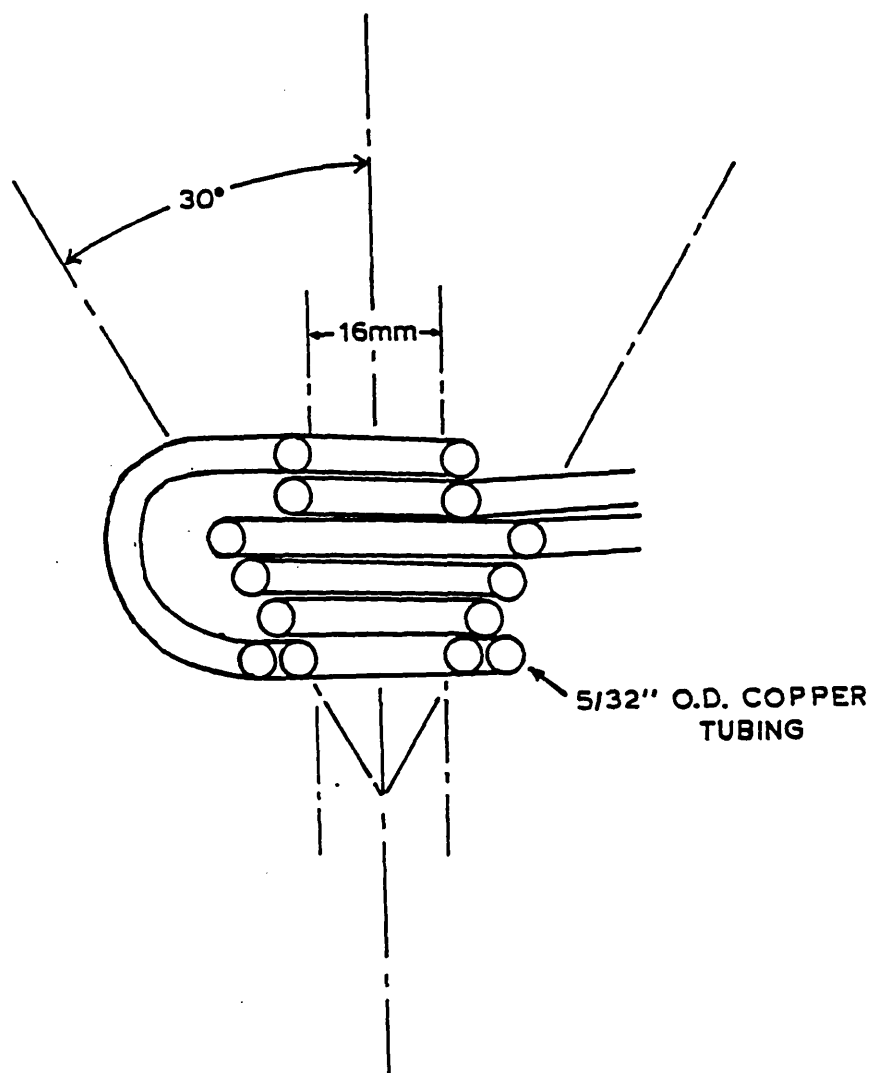


Figure 4.1 The Experimental Levitation Coil Design.

sealing the ends shut. This prevented crimping of the tube during subsequent shaping.

A contoured steel mandrel was used for bending the coil to a predetermined design specification. The mandrel consisted of a 16 mm o.d. shaft attached to a solid cone having a 60° apex angle. The shaft diameter approximately matched the outside diameter of the levitation chamber tube so that the coil could slide easily over the quartz tube when disassembling the chamber.

The coil was shaped as follows. First, at approximately ten inches from one end, the top two helical turns were wound using the shaft of the mandrel. Then, at a point approximately nine inches from these turns, the two coplanar bottom turns were wound from inside to outside using the mandrel shaft for the internal diameter. The opposite end of the tubing leading from the inside turn was then wound in a helical fashion for three turns using the conical portion of the mandrel. Finally, the length of tubing between the two coil sections was bent so that, with the top turn of the top section connected to the bottom turn of the bottom coil section, the top two turns were nested in the bottom cone. The two remaining tubing ends were arranged so that these protruded from approximately the same point on the finished coil. The coil was then fitted to the levitation chamber and the tubing ends were cut to appropriate lengths and brass tube fittings were silver-soldered to the ends for connection to the generator.

2. The Levitation Chamber Assembly

a. Functional Design Requirements

The design of a levitation cell must meet several functional requirements. It must provide for controlled atmospheres and direct the gas flow over the sample for cooling. It should provide some physical protection for the levitation coil either from accidental deformation or

shorting by sample contact since both actions will render the coil useless. It must provide for the simple loading and unloading of samples and provide means for rapidly quenching samples from high temperature. Finally, it should provide some flexibility for viewing the sample from either top or bottom for the purpose of observation, photography or pyrometry temperature measurement. All of these functional requirements were incorporated into the chamber design used in this study.

b. Description of Levitation Chamber

A drawing of the levitation chamber assembly is shown in Figure 4.2. It is basically the same arrangement used by Jahanshahi¹⁹¹ with some modifications.

The turntable assembly is supported on a small platform pedestal which allows access from the bottom and provides a rigid support and reproducible positioning of the coil. The turntable, which was machined from brass, consists of an inner rotating disk having six evenly spaced hollows for sample loading cups, a copper quench mold, and a viewing prism. This disk rests within an outer brass base and is supported by sealed roller bearings. It is manipulated via a stainless steel turn-key which protrudes through the bottom of the base. Holes are positioned in the base and in each of the hollows so as to provide for loading and removal of samples via a quartz push-rod. The outer base and its corresponding top completely seal the inner rotating turntable with o-ring protected seals and parts. The base top contains a support fitting for the quartz chamber tube and provides for a gas exit from the sample chamber. The quartz chamber tube is compression sealed with an o-ring fitting on the turntable base and also fitted with a seal-protected cap or chamber head which provides for gas entry into the chamber. This arrangement directs the gas flow over the levitated sample and provides for atmospheric control. In addition the

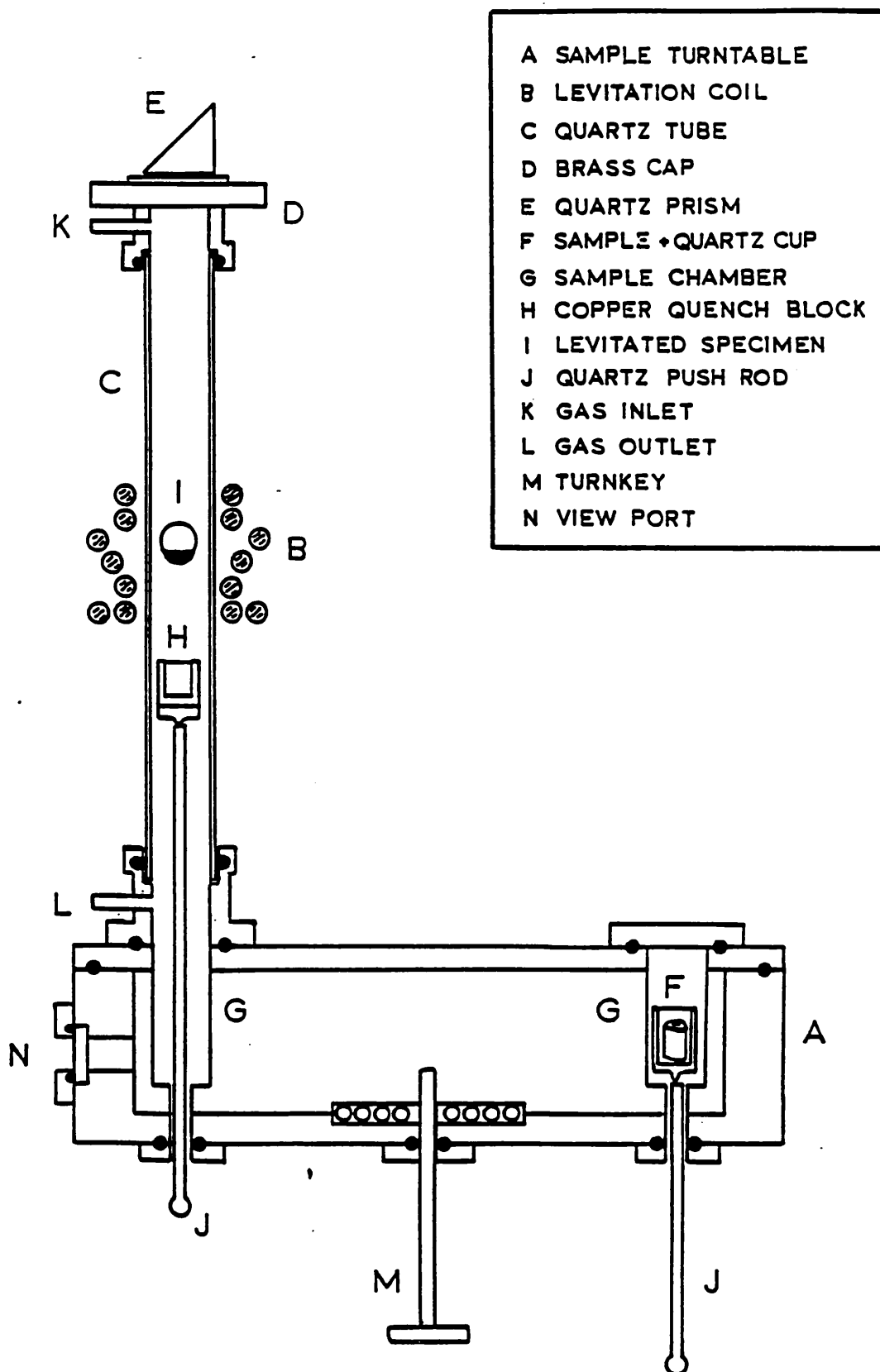


Figure 4.2 The Levitation Chamber Assembly.

quartz tube gives rigid support for the coil and protects it from the levitated sample. It also allows viewing of the sample from various angles. The chamber cap acts as a base for a prism arrangement which allows multiple features such as continuous temperature monitoring with a recording two-color radiation pyrometer, photographic recording of sample reactions and general viewing of the sample during levitation.

3. Gas Train Assembly

a. Functional Requirements

Since flow of coolant gases over the levitated sample is one of the primary means of temperature control, and the cooling effect of these gases depends on the physical and thermal properties of each gas as well as flow rate and pressure, it is necessary to provide means for introducing coolant gas to the levitation chamber at a range of flow rates, with some provision for blending of gases so as to obtain proper heat transfer characteristics and refined temperature control. Since fairly high flow rates are required and large volumes of gas are used, this necessitates efficient cleaning of coolant gases and removal of residual impurities which may react with levitated samples. In the present study, since the kinetics of in-situ slag formation and development rate and alloy oxidation behavior were of interest, it was desirable to provide a means of accurately metering oxidizing gas and directing it over the levitated sample for fixed exposure times. This required precise metering of oxidant gas and reproducible mixing of the high flow rate coolant gases with the low flow rate oxidant gas without encountering problems with mixing accuracy due to back pressure and venturi effects in the low flow rate line. It also was desirable to conserve coolant gas and provide the least amount of disruption to the sample when switching from coolant to oxidant gas and back.

b. Gas Train Description

A schematic diagram of the gas train used in this study is shown in Figure 4.3. For each gas utilized, separate cleaning columns and flow meters were used and mixing was provided downstream prior to gases entering the levitation chamber. For the helium and argon coolant gases it was necessary to permit a range of high volumetric flow rates yet maintain efficient cleaning and prevent excessive back pressure in the gas lines and cleaning columns. This was accomplished by using large diameter glass tubing (13mm) and fairly large cleaning columns (60mm o.d. x 500mm length) to increase the residence time of gases within the columns. The principle impurities of interest were O_2 , CO_2 and H_2O and thus molecular sieve was used for water adsorption, activated copper (at $150^\circ C$) was used for deoxidation and $CO-CO_2$ catalysis, and soda lime was used for CO_2 adsorption. The residual oxygen content of the gases after this treatment was measured with a calcia-stabilized zirconia probe and found to be too high for levitating iron samples. In order to prevent oxygen induced fuming of samples and limit excessive oxidation, further purification was necessary. This was particularly true for the grade of helium used and was often the case for the "High Purity" argon supplied since both of these gases routinely exceeded the limits of impurities claimed by the distributor, British Oxygen. Thus it was necessary to pass the gases over titanium sponge heated to $900^\circ C$ to bring the oxygen down to acceptable levels. Glass tubing was used throughout the system except for a short length of flexible vacuum tubing used to connect the gases to the magnetic gas valve.

Coolant gas flow rates were accurately metered with mercury-filled capillary flow meters and mercury blow-offs were used to maintain constant flow rates. The use of these flow meters permitted accurate measurement of

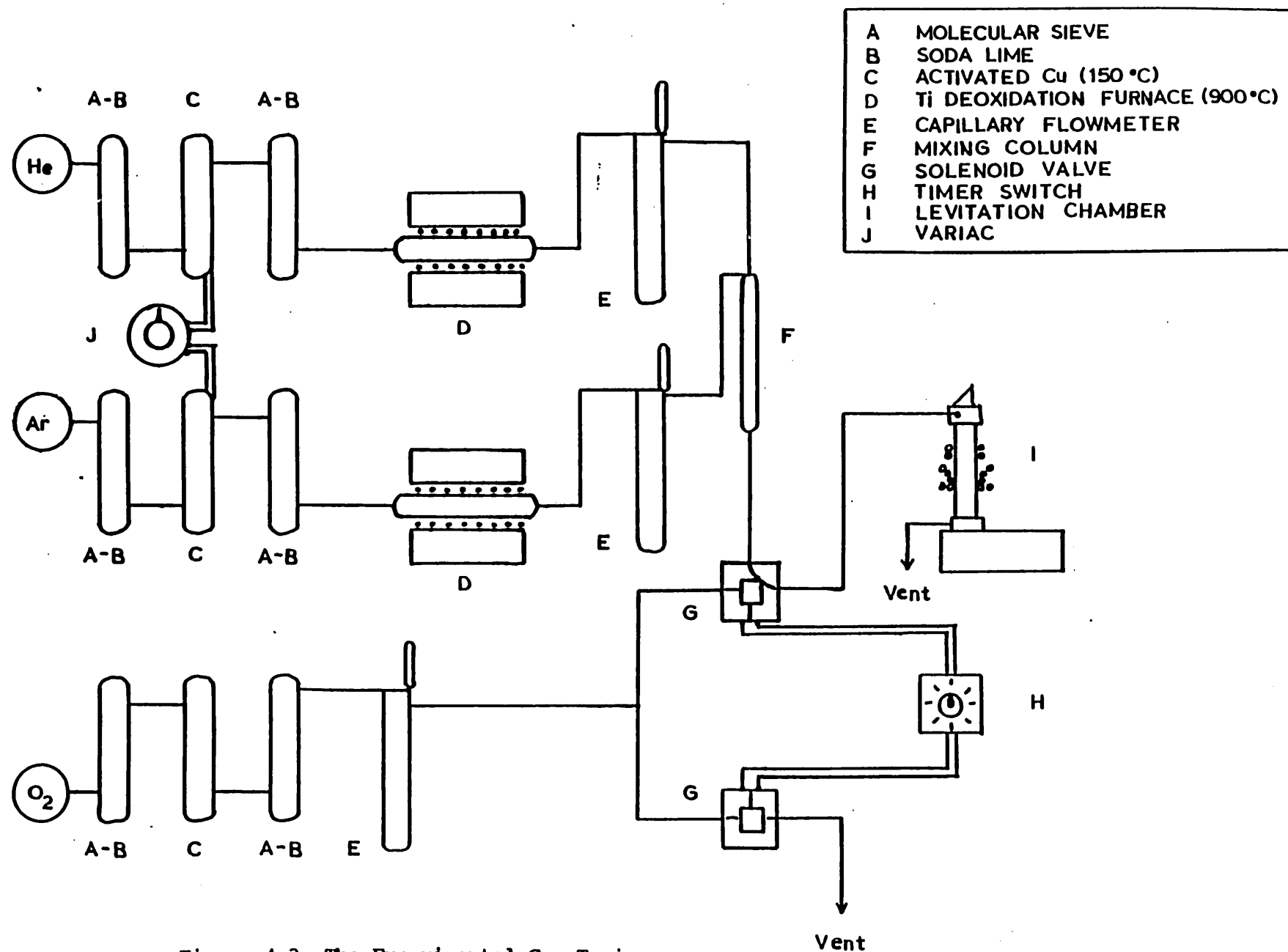


Figure 4.3 The Experimental Gas Train.

flow rates ranging from 0.5 to 10 liters per minute by merely changing capillaries. With such an arrangement the two gases could be reproducibly metered and mixed at predetermined ratios and flow rates suitable for maintaining constant temperature with a given generator setting and sample characteristics.

Since the oxidant gas flow rate was considerably lower and of the order of 0.1 to 0.5 liters per minute, conventionally sized 6mm glass tubing was used throughout this circuit and column sizes were considerably smaller (30mm o.d. x 250mm long). As with the coolant gas lines, molecular sieve was used to remove H_2O and soda lime was used for removal of CO_2 . Dibutyl thallate was used in both the capillary flow meter and the blow-off since much lower pressure drops were required at low flow rates. A short length of capillary tubing was placed downstream prior to the switching valve to prevent backmixing with the coolant gases during oxidation of the sample.

In order to provide accurate and reproducible oxidation of the levitated samples, it was necessary to introduce oxidant gas into the coolant gas for short exposure times with adequate mixing of the two streams and minimum disruption of gas flow during the changeover. To accomplish this, two timer-controlled magnetic valves were used. One of these permitted oxygen flow to a vent when closed and, with the timer engaged, it diverted the flow to the second valve associated with the coolant gases. This second valve permitted continuous flow of coolant gases to the levitation chamber and when the timer was engaged the valve opened, thus permitting mixing with the oxidant gas which was diverted by the first valve. Since the system was designed so that there was no detectable back pressure downstream of the flow meters, the flow rates of all three gas lines could be initially fixed and were thus essentially

unaffected by downstream mixing and diverting of flow. This permitted very accurate setting of the flows and reproducible timed oxidation of levitated samples.

C. Experimental Procedure

In this section, details of alloy and slag synthesis and levitation sample preparation are presented in Part 1. In Part 2, the procedures and technique used in levitation experiments are described. Finally, in Part 3, post-levitation sample treatment and analytical procedures are presented.

1. Sample Preparation

a. Alloy Preparation

Iron alloys were prepared from either iron carbonyl or electrolytic iron. While the carbonyl iron was of high metallic purity, preliminary vacuum degassing was necessary for removal of dissolved oxygen, hydrogen, nitrogen and carbon and this proved to be too inconvenient so that the majority of alloys were prepared from the less pure electrolytic grade.

Iron-phosphorus alloys were prepared in 200 gram batches by weighing out appropriate amounts of iron phosphide and electrolytic iron, placing in a 200 ml recrystallized alumina crucible with cover, and induction heating the alloy to approximately 1600°C under a high purity argon protective atmosphere. The alloy was bubble-stirred with argon gas and, after approximately one-half hour at temperature, suction samples were taken with 5mm i.d. quartz tubing. These were rapidly quenched in water to prevent segregation upon solidification. Sample rods prepared in this manner were easily removed from the quartz tubing since no adherence occurred.

Rods prepared from the alloy synthesis were subsequently cut into small cylinders and drilled so as to accommodate a powdered slag charge. Sample and hole dimensions were chosen so as to provide approximately one

gram of alloy and accommodate 50 mg of slag. Small cylinders (6mm long) were cut with a silicon carbide slitting wheel and holes (2.5mm O.D. x 4mm deep) were drilled with carbide spade drills to accommodate the slag powder. Prior to charging the slag, alloy samples were ground and polished to remove burrs and surface oxidation and then stored under methanol.

b. Slag Preparation

Raw materials used in slag synthesis were generally of Analar grade except for optical grade CaF_2 and high purity Angolan quartz. Magnesium and calcium carbonates were precalcined at 1000°C for one hour prior to use. Ferrous oxalate was precalcined in a covered iron crucible at 800°C for one hour and water quenched.

Appropriate amounts of reagents were preweighed and intimately mixed prior to charging to a given crucible. For iron-free slags a Pt / 5 %Au alloy crucible was used, and for iron-based slags an iron crucible machined from Swedish iron was utilized. Slags were fused in a muffle furnace at 1400 to 1550°C and water quenched after one hour at temperature. The solidified slag was crushed in a Tema mill and fused again. This procedure was repeated twice to obtain homogeneity. Powdered slag was milled to pass through a 150 mesh sieve size and stored in a desiccator with soda lime prior to use. Slags which had been stored for extended periods were calcined at 1000°C prior to use in order to drive off adsorbed water and CO_2 .

c. Sample Preparation

Individual alloy samples were weighed and slag was charged by tamping powder into the sample hole and weighing periodically until the appropriate amount had been added. The combined slag and alloy sample was then weighed to obtain the weight of each phase. While there was some variation in sample mass, an attempt was made to keep sample weights within an

approximate range of 50 mg of slag and one gram of alloy. Generally, the weight ratios of the two phases were kept relatively constant so as to insure comparable phosphorus levels in the slag phase within sample groups.

2. Levitation Procedure

Preweighed samples were put in quartz sample cups and placed in position with the levitation turntable. The oxygen and argon-helium coolant gas flows were set to predetermined flow rates and the timer switch was preset. The generator was turned on and adjusted to a predetermined power setting while the sample cup was pushed into the activated levitation coil with a quartz rod. The sample cup and rod were removed and the sample levitated and melted. As the fusion point was reached an adjustment in power was required due to the change in properties created by the solid-liquid transition. The sample temperature was continuously monitored via the top prism arrangement using a focused two-color radiation pyrometer with associated chart recorder. Fine control over temperature could be achieved by adjusting either the helium-argon flow ratio or the variable output transformer on the generator.

Once stable levitation and constant temperature had been achieved, several experimental options were available with regard to sample reaction, equilibration, and quenching depending on whether gas phase or slag phase oxidation was selected.

If gas phase oxidation was utilized, the timer switch was activated and a flow of helium-argon-5 % oxygen was passed through the levitation chamber for preset exposure times, corresponding to various slag oxidation potentials. This oxygen gas mixture was selected since it minimizes fuming losses during oxidation and produces a manageable rise in sample temperature. In this manner, both slag development rate and slag-metal reaction behavior during oxidation could be studied with in-situ slag

formation. The sample could then be either immediately dropped from the coil for rapid quenching or allowed to equilibrate with the oxygen which was introduced prior to quenching. The first approach is somewhat problematic since spinels may form during oxidation and refractory phases may also be initially present. In such cases, the solid oxide-liquid slag dissolution mechanism may be slow, taking up to several minutes to equilibrate, and thus a metastable situation is created in the slag and the slag-metal reaction may be retarded due to slag development kinetics. The second option proposed enables the slag to come to equilibrium with any metastable refractory phases present and provides a means of following the slag-metal reaction and correlating slag development during oxidation with slag reactivity.

If a prefused, oxidizing slag is initially charged, no oxidation is required via the gas phase and the slag and metal can be readily equilibrated and quenched. This offers the advantage of both faster equilibration and avoidance of metastable slag formation from excessive oxidation or inhibited oxide dissolution mechanisms. In addition, no fuming losses are produced with this type of charge. When slag-metal reaction was promoted with oxidizing slag, slag-metal equilibration was achieved in seconds and no difference in the phosphorus equilibrium was observed, even when samples were equilibrated for long times.

Several sample quenching variations were possible in this study and this provided some degree of freedom in sampling slag or metal. Samples could be drop-quenched into a copper quench mold by shutting off the coil power. This produced rapidly quenched samples which were difficult to separate because of entrainment and adherence to the quenching mold. This caused problems in sample analysis and led to an inaccurate sample mass balance. An alternative technique was to gas quench the sample in

suspension by either increasing the helium flow or increasing the generator power. While this type of quench was not as rapid as the drop quench, solidification of the alloy occurred readily and very little time was available for a shift in slag-metal equilibrium. Excellent separation was achieved and a good mass balance was possible. For these reasons this was the preferred method. A final variation was sampling the slag at temperature with an alumina rod and drop quenching the alloy. This produced a good slag sample, providing the slag was homogeneous. For heterogeneous samples this method was unsuitable because the sample was not representative and a shift in slag-metal equilibrium could result from a disproportionate sampling of the slag phase. Also, slag and metal entrainment, resulting from drop quenching the alloy, produces problems with the sample mass balance and analysis.

3. Sample Treatment and Analysis

The final weight of each sample was determined and where losses of more than 1 % were observed the sample was discarded. The slag and metal phase were separated with gentle percussion milling and the two phases were weighed individually and placed in separate containers.

The metal phase was cleaned with a sandblaster and polished to remove all traces of slag. A small section from 0.1 to 0.2 gms was cut and weighed for phosphorus determination. The remainder was saved for repeat analysis.

Slag samples were either weighed on a microbalance and dissolved in an HCl-HF mixture (3 and 5 ml per sample, respectively) for wet chemical analysis, or prepared as thin sections for microprobe wavelength and EDX analysis as well as microstructural analysis. Occasional x-ray analysis was sometimes performed to identify crystalline phases present in samples.

For wet chemical analysis the following procedures were adapted for

the elements of interest:

Phosphorus. For metal alloys, samples were digested in an HCl-HNO₃ mixture and treated according to the standard phospho-vanadomolybdate method¹⁹² where phosphate is complexed and extracted in an isobutyl-methyl ketone and analyzed using spectrophotometry. For slag samples, after dissolution the phospho-vanadomolybdate method was used and found to give unreliable results apparently due to high silicon contents. For this reason, a modified molybdenum blue method¹⁹³ was used in silicate slags. However, this method proved to be troublesome when high iron contents were present. Thus a plasma photometry method was found¹⁹⁴ which enabled freedom from interferences but had somewhat lower sensitivity due to the high dilutions required for lowering the acid content of the sample solution.

Iron. Iron was not analyzed in alloys but it was desirable to compare analyzed iron in the slag with that predicted from a mass balance and slag weight change during oxidation. While a standard reliable method for total iron was available with atomic absorption, it was desirable to determine the oxidation state of iron in the slag and relative proportions of Fe⁺³ and Fe⁺² to see how this may correlate with phosphorus distribution. A very sensitive spectrophotometric method for Fe⁺² was found which enabled, with slight modification, analysis of total iron as well.^{195, 196} This permitted calculation of Fe⁺³ by difference. While use of this method was very reproducible, problems were identified in the samples themselves as variations in sample quenching produced irregular variation in the Fe⁺³/Fe⁺² ratios analyzed. Thus only total iron analysis was considered reliable and data was correlated assuming all iron was present as Fe⁺².

Calcium and Magnesium. Each were analyzed by atomic absorption according to standard methods and in the case of calcium, a lithium salt

was added to the solution in order to inhibit interferences.

Silicon. While silicon can be analyzed by atomic absorption, it is not a reliable method. The molybdenum blue method is generally reliable although both silicon and phosphorus form molybdenum blue complexes and interference is usually unavoidable. A modified molybdenum blue method was utilized¹⁹⁷ where color formation of the phosphorus complex is inhibited by high acidity. However, results varied somewhat depending on the relative ratio of phosphorus to silicon and matrix corrections were required. For this reason a preferred method was plasma photometry¹⁹⁴ where interferences were absent.

V. RESULTS

In this section the experimental equilibrium data are presented in graphical form for the various slag systems studied. In Figures 5.1 through 5.7, equilibrium residual phosphorus is plotted as a function of slag oxidation state. This type of plot is considered to be the most reliable indicator of the dephosphorization ability of a given slag system and offers the most straightforward comparison of various systems.

Data are grouped according to the essential characteristics of a given slag system or slag type such as, basic oxides, basic oxy-fluorides, basic silicates, basic fluoro-silicates and synthetic basic oxygen steelmaking slags. The order of presentation ranges from the most simple systems to increasingly complex melts. Since the study of idealized slag systems other than basic steelmaking slags was essentially of an exploratory nature, only the effect of slag oxidation state was evaluated while other composition variables were kept constant. The primary goal was to survey the behavior of components in relatively simple slags and evaluate the relative merits of magnesia as a lime substitute by way of comparing analogous slag systems. It was also necessary to clarify the behavior and considerable influence which silica and fluoride possess as additions to multicomponent slags.

In order to evaluate the refining behavior of basic oxygen steelmaking slags, more detailed information was required and a comprehensive systematic study of composition variables was undertaken. The primary reason for this approach was to clarify component interactions, identify solution thermodynamic factors, establish the critical role of system phase relationships in refining behavior, and identify optimum composition regions for phosphorus refining. By providing a comprehensive systematic variation in composition variables, compositional correlation of refining

behavior was facilitated and improved predictive capabilities were achieved in estimating residual phosphorus levels from knowledge of slag compositions. The matrix of experimental variables evaluated in the present study is shown in Table 5.1. Slag compositions and metal analyses are presented in tabular form in Appendix A. A critical discussion of the results obtained for each slag system studied and application of various slag-metal equilibrium correlations are presented in Section VI.

Table 5.1: Matrix of Experimental Variables for Synthetic Basic Oxygen Steelmaking Slag-Metal Equilibrations ($T = 1600^{\circ}\text{C}$).

Initial Phosphorus Content of Alloy (%P _{Fe})	Slag Basicity Index: (CaO+MgO)/SiO ₂	Lime Substitution Index: CaO/ (CaO+MgO)	Slag Oxidation Potential (%'FeO')
0.1 and 0.2	4.0	1.0 0.8 0.6	10-70
0.1, 0.2 and 0.4	2.33	1.0 0.8 0.6	10-70
0.1 and 0.2	1.5	1.0 0.8 0.6	10-70
0.1	1.0	1.0 0.9 0.8 0.7 0.6	10-70

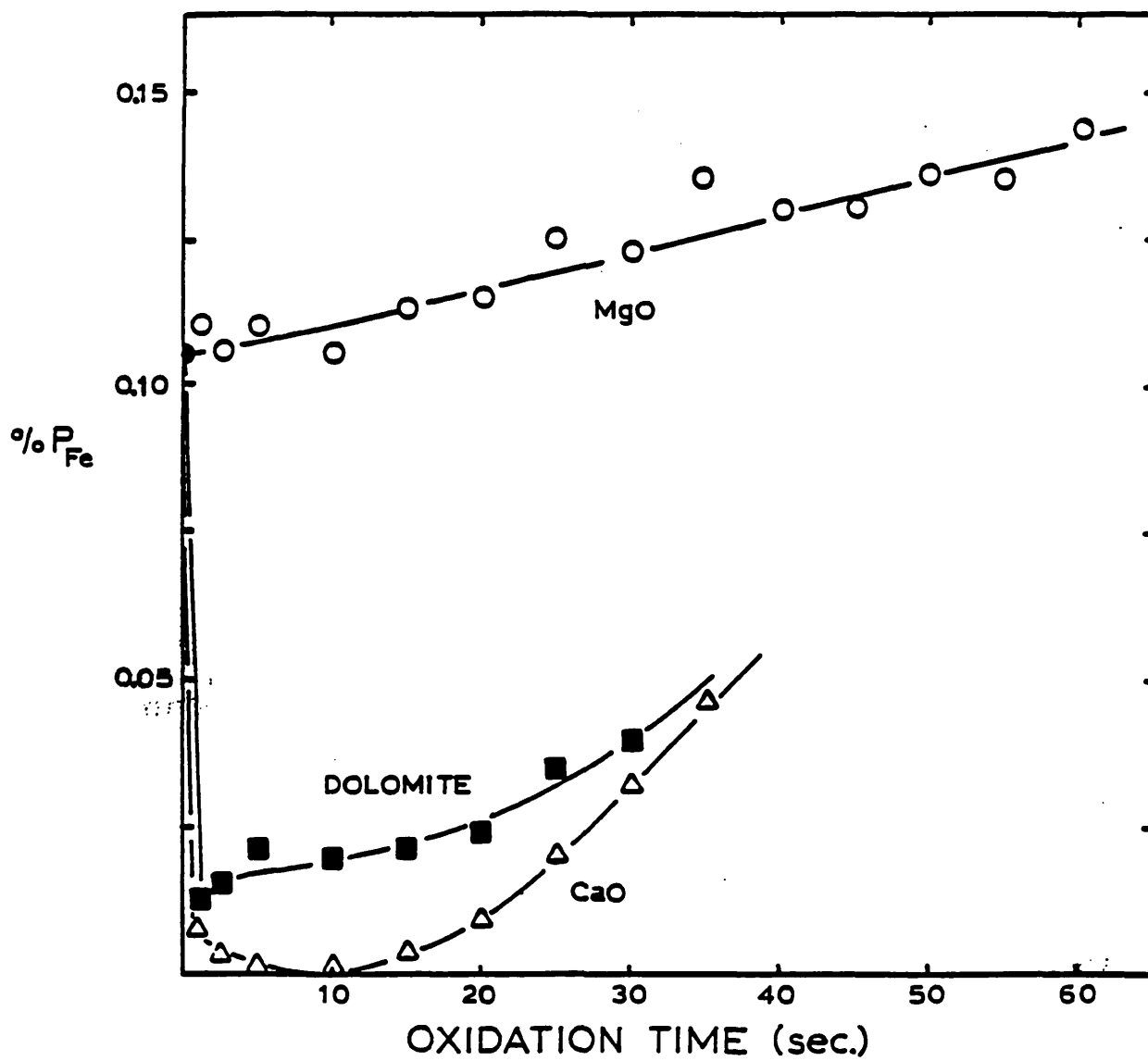


Figure 5.1 Residual Phosphorus Levels in Basic Oxide Slag Systems.

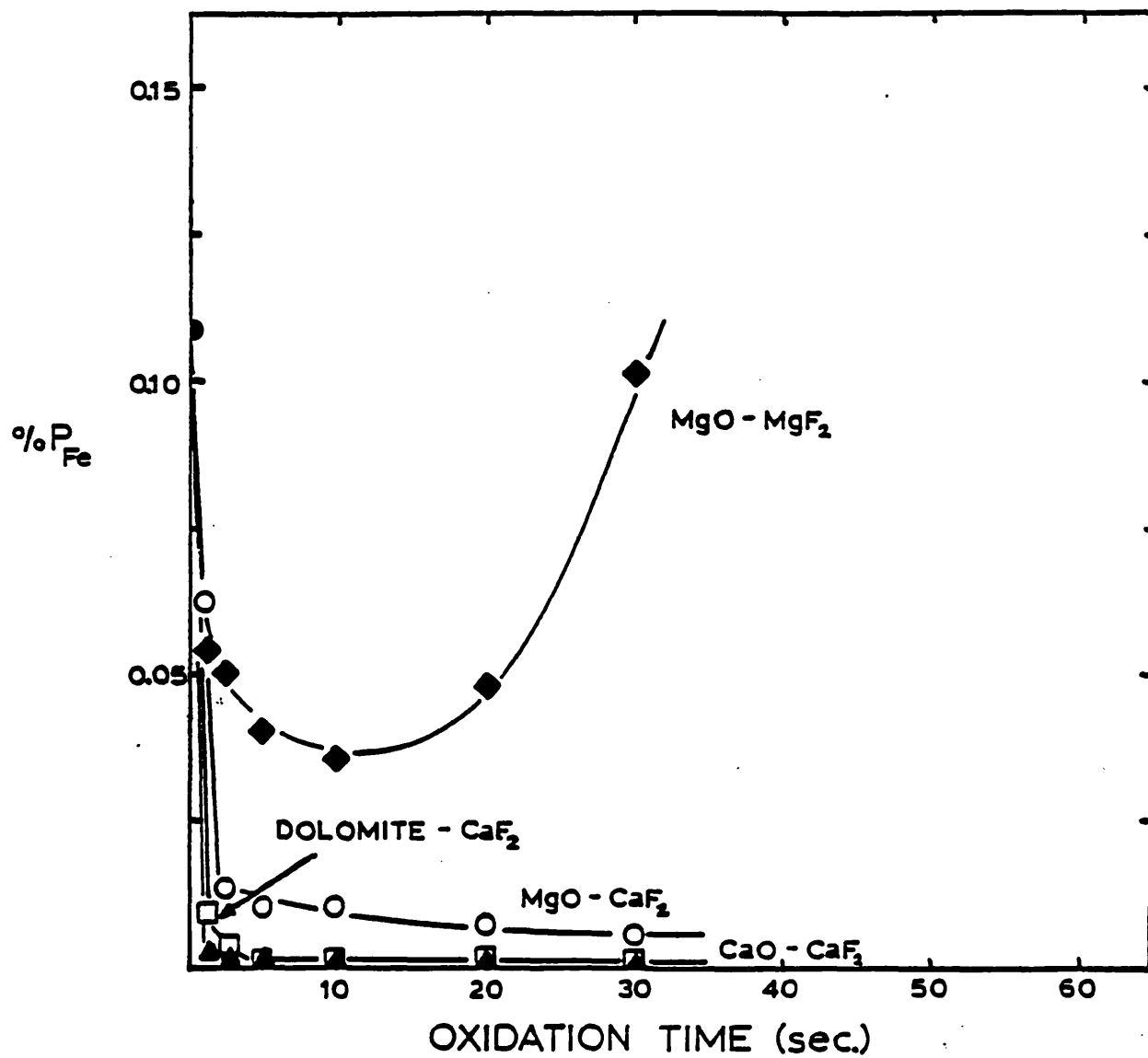


Figure 5.2 Residual Phosphorus Levels in Basic Oxy-fluoride Slag Systems.

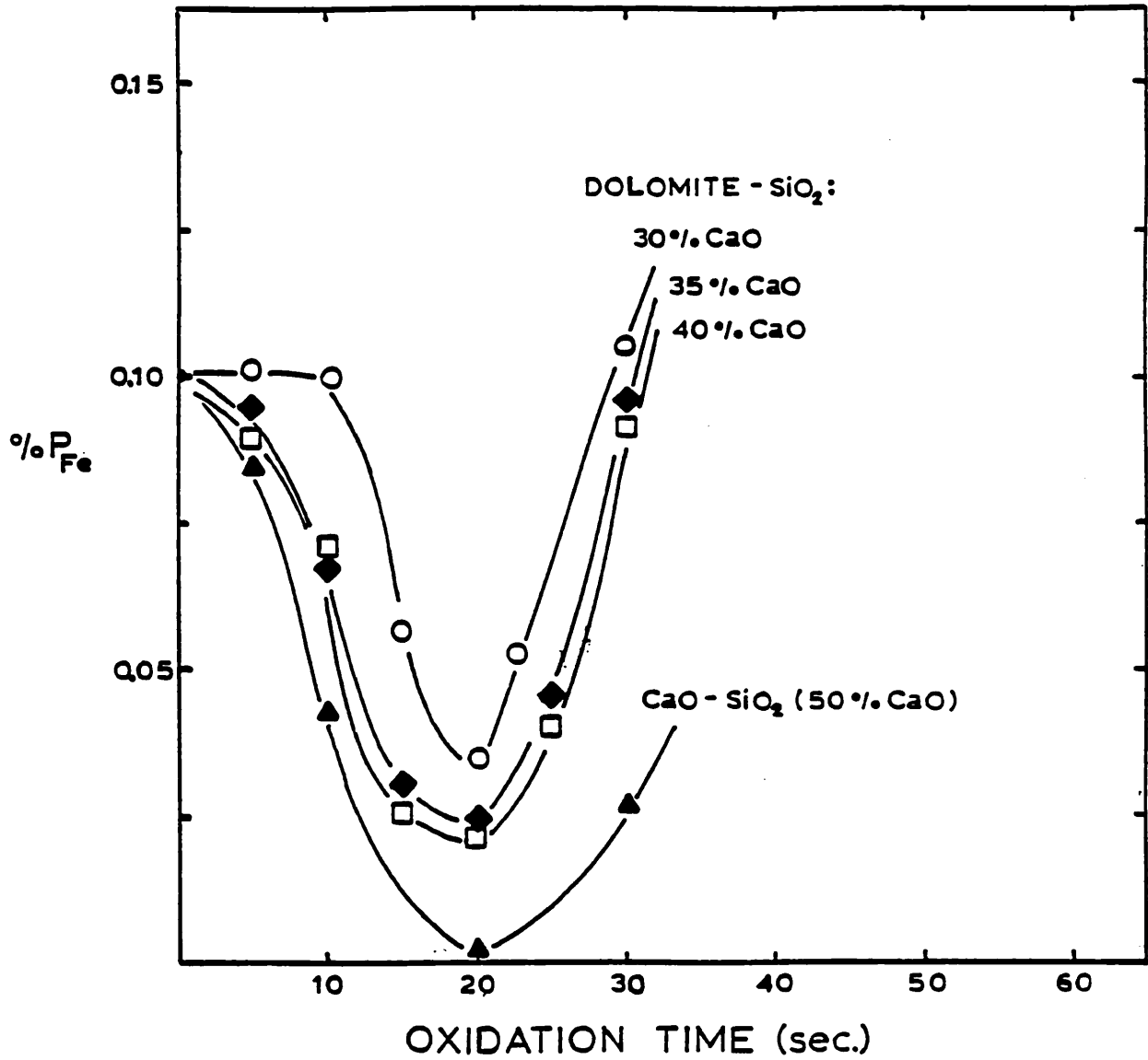


Figure 5.3 Residual Phosphorus Levels in Basic Silicate Slag Systems.

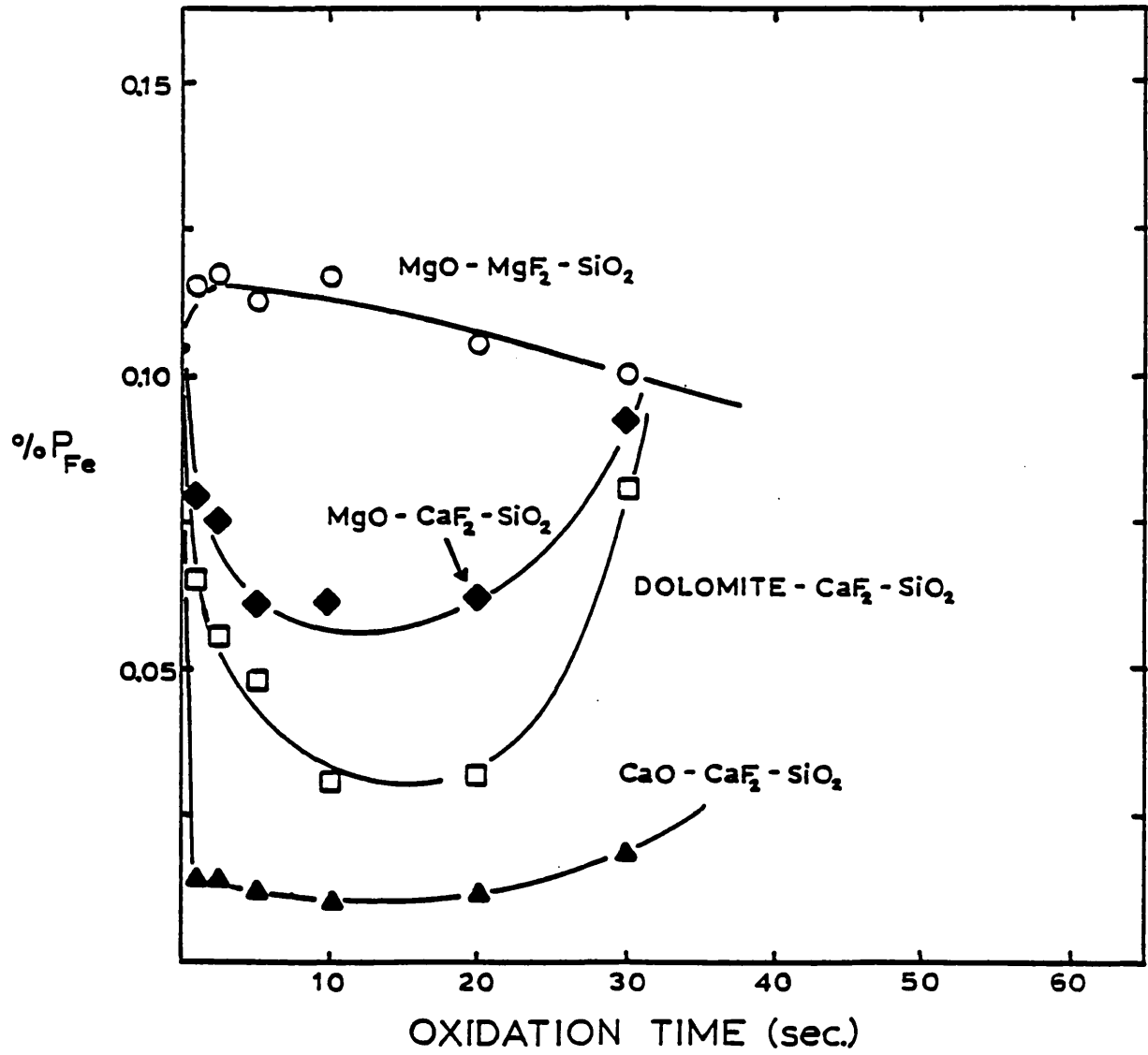


Figure 5.4 Residual Phosphorus Levels in Basic Silico-oxy-fluoride Slag Systems.

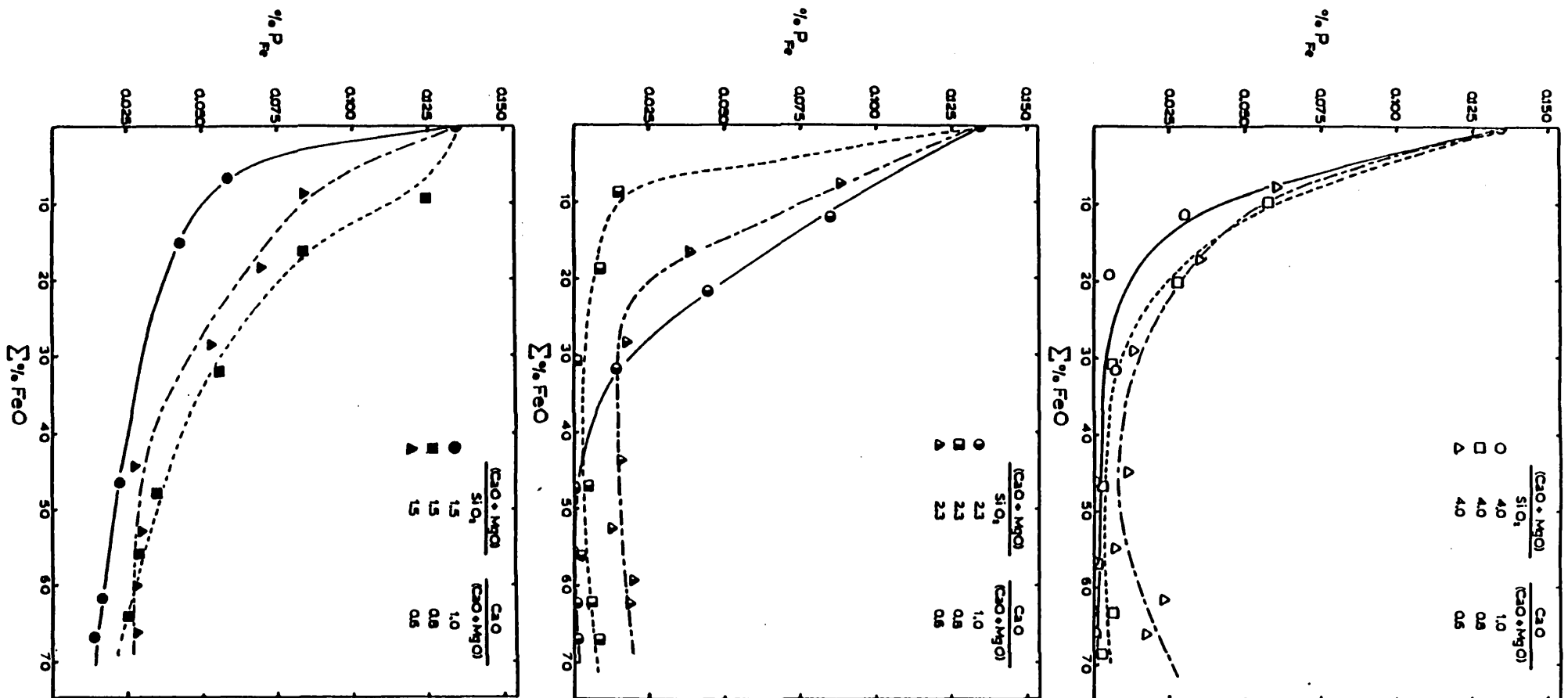


Figure 5.5 Residual Phosphorus Levels in Synthetic Steelmaking Slags (Low Phosphorus Alloy)

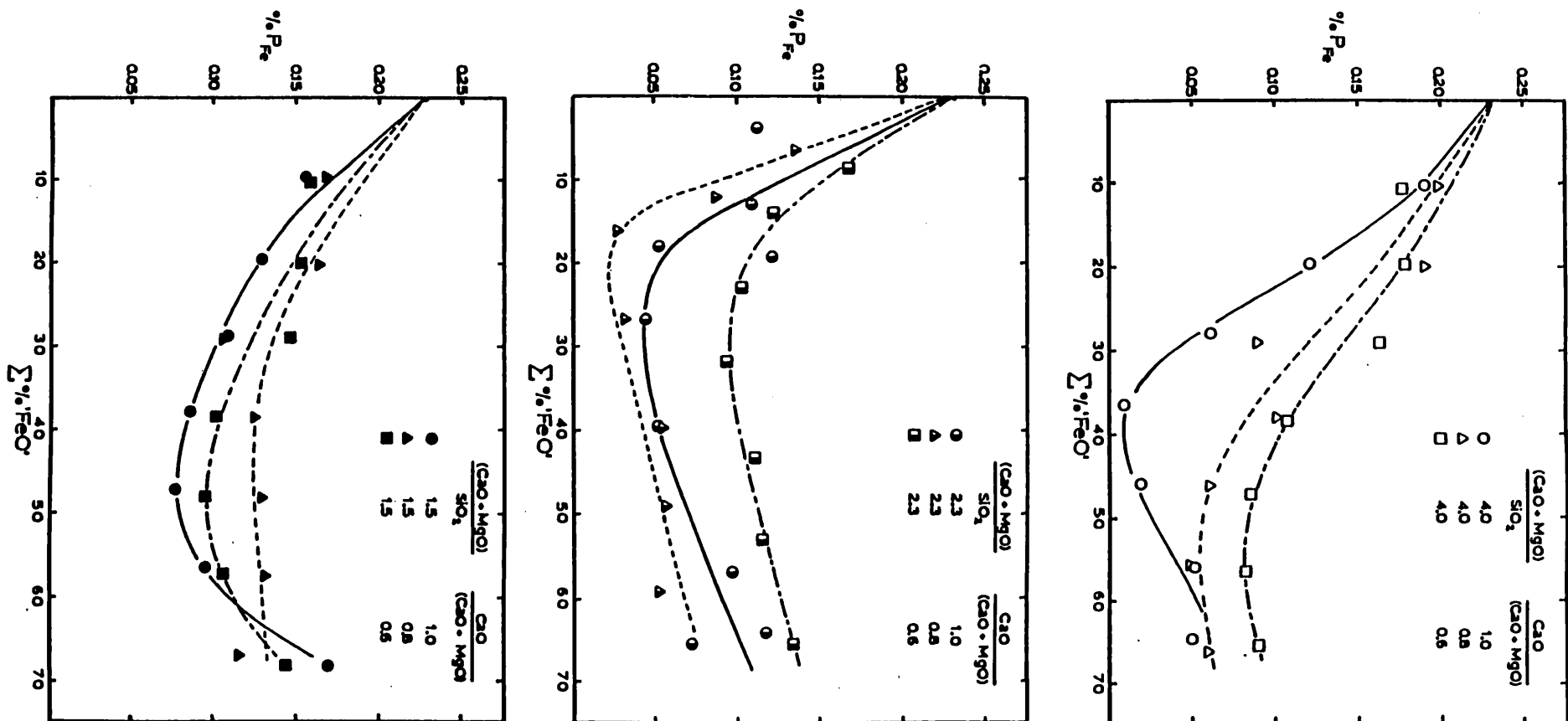


Figure 5.6 Residual Phosphorus Levels in Synthetic Steelmaking Slags (Intermediate Phosphorus Alloy).

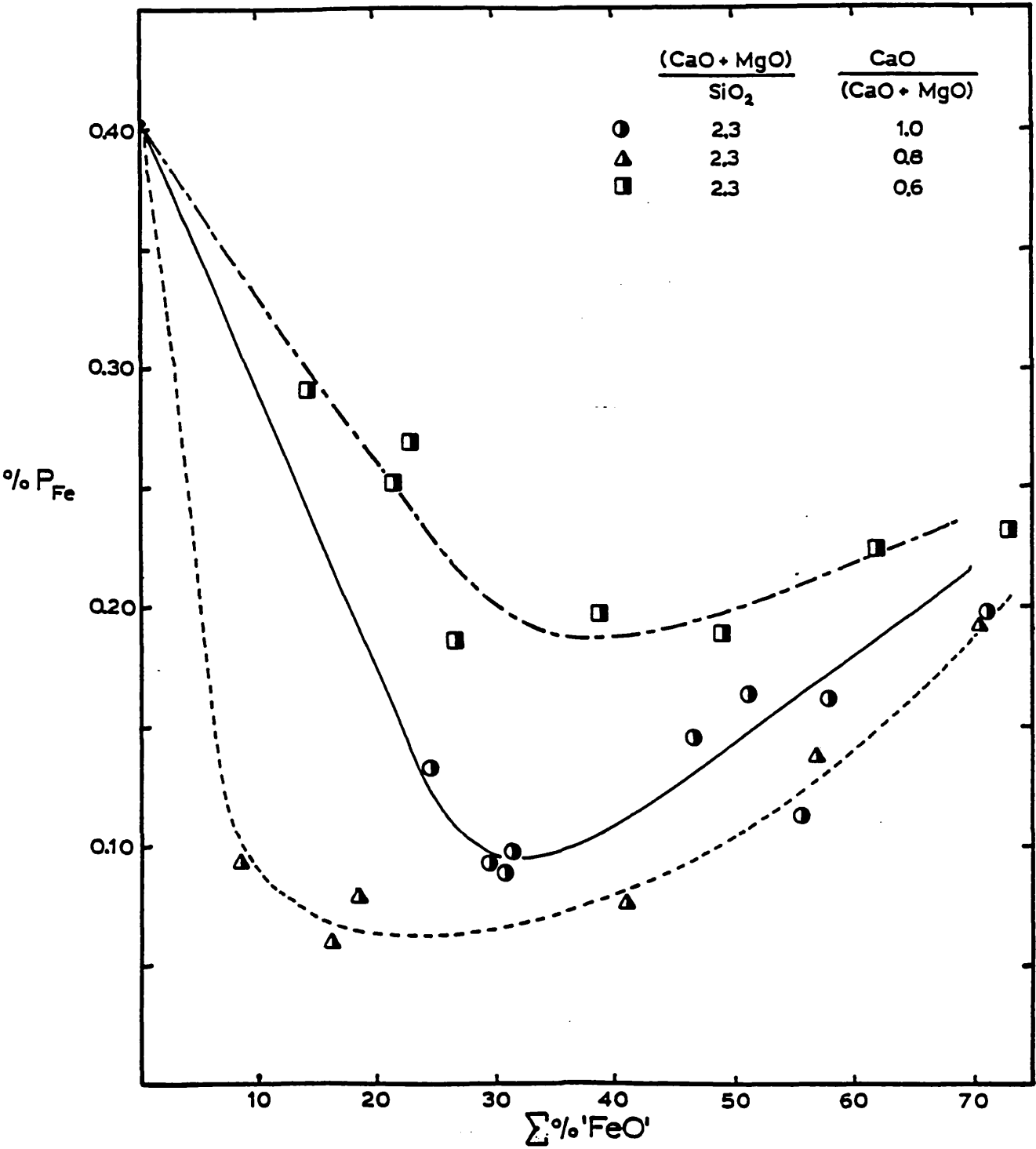


Figure 5.7 Residual Phosphorus Levels in Synthetic Steelmaking Slags (High Phosphorus Alloy).

VI. DISCUSSION OF RESULTS

In this section a detailed discussion of the results obtained with individual slag systems is presented with reference to phase relationships and thermodynamic factors in Part A. The discussion proceeds from simple basic oxide slag systems to basic fluoride and basic silicate slags, in order to develop a progressive understanding of slag component interactions, the relative merits of MgO and CaO additions, and primary as well as secondary effects of oxide, fluoride and silica additions. In Part B, existing correlations are compared and criticized as to their suitability and predictive capabilities in light of the present results. In Part C, a new correlation is presented based on present knowledge of the complex slag phase relationships and proposed phosphorus reaction product. The advantage of this new approach is discussed by way of comparing its predictive capabilities with existing correlations. In Part D, the implications of the present approach to previous laboratory results and steelmaking practice are discussed with reference to the relative importance of equilibrium and kinetic factors and slag development paths. Optimum composition regimes are proposed for phosphorus refining and the relative merits of current plant practices are discussed.

A. Behavior of Individual Slag Systems

1. Basic Oxide Slags

Traditional approaches to understanding slag-metal dephosphorization behavior and correlation development emphasize the role of basic oxides and the stability of basic phosphates and the results of the present study confirm the validity of this approach for simple basic oxide slags. While Oelsen and Maetz,⁹⁵ Tromel¹⁷⁸ and Schurmann¹⁷⁹ all observed dephosphorization with magnesia saturated $\text{MgO-P}_2\text{O}_5\text{-FeO}$ slags, the compositions studied were relevant only to high phosphorus, Thomas-type steelmaking

slags. With modern day basic oxygen steelmaking operations, relatively low P_2O_5 slags are produced due to low initial phosphorus levels in the alloy. The results of the present study shown in Figure 5.1 demonstrate clearly that magnesia slags are unable to dephosphorize at the low levels of phosphorus encountered in modern practice. Comparison of results with lime-based slags demonstrates the superior refining characteristics of calcia. Dolomite slags follow an intermediate behavior based essentially on the amount of CaO which is present in the slag.

Presumably, at $1600^{\circ}C$ magnesia is a relatively poor dephosphorizer at low alloy phosphorus activity because its basic phosphates are unstable. This behavior is comparable to observations with the iron phosphates at lower temperatures. Both Tromel⁹³ and Yavoiskii¹⁹⁸ observed significant dephosphorization at low temperatures and high phosphorus activity with iron phosphate formation. At higher temperatures no dephosphorization is observed. The calcium phosphates, on the other hand, possess high temperature stability which surpasses that of magnesium and iron phosphates.

As Tromel observed,⁹⁹ MgO has very little influence on the lime ternary dephosphorization behavior since it has such low solubilities in lime-based liquids. While MgO has been shown to raise iron oxide activity in silicates^{69, 70, 87, 199} and basic oxide slags,⁷¹ this effect is of minor significance relative to the strong attractions between calcium ions and phosphate anions, which produce a very stable liquid or solid dephosphorization reaction product. In such simple slags, magnesia substitution is most likely detrimental to refining from an equilibrium point of view.

2. Basic Oxy-Fluoride Slags

Fluorides have traditionally been used as a fluxing agent in

steelmaking slags due to the pronounced effect small additions have on slag development. They are particularly effective in lowering slag liquidus temperatures and in increasing the solubility of lime and magnesia in basic steelmaking slags. Fluoride is also known to form stable fluorapatite compounds with phosphorus and is thus generally considered to be beneficial for dephosphorization.

The residual phosphorus levels obtained with oxy-fluoride slags are shown in Figure 5.2. With calcium oxy-fluorides, a significant benefit is obtained by fluorite addition as no reversion of phosphorus is observed with highly oxidized slags, in contrast to simple basic oxide slag behavior. This is due to the nature of the $\text{CaO-CaF}_2\text{-FeO}$ ternary phase relationships where a two-liquid miscibility gap is traversed. A highly oxidized, calcium-rich liquid is formed which provides excellent dephosphorization characteristics and varies only slightly in composition within the two phase region. An iron oxide-rich liquid is also present within this slag composition region and the effect of increasing oxidation merely varies the ratio of the two phases while maintaining the optimum refining characteristics of the lime-rich liquid.

Comparison of results with the magnesium oxy-fluoride system demonstrates the dramatic influence of fluoride on magnesia-based slag. In the absence of fluoride, no dephosphorization was observed with simple magnesium oxide slags, whereas, with fluoride additions, significant dephosphorization was observed, although not to the extent of calcium oxy-fluoride slag. Presumably this behavior is due to formation of a stable reaction product within the slag phase due to the presence of fluoride. While x-ray patterns of synthetic slags rich in phosphorus show the presence of magnesium-fluorophosphates, the trace amounts of phosphorus present in experimental slags do not provide sufficient material for an

identifiable pattern. The rather pronounced reversion which occurs with highly oxidized magnesium oxy-fluoride slags may be due to either slag phase relationships or solution behavior or is possibly an artifact of technique caused by extensive fuming losses during oxidation.

Since basic oxy-fluoride slags can be treated theoretically and structurally as reciprocal salts, mixtures of magnesium and calcium oxides and their fluorides are reciprocal salt mixtures and it makes little difference whether the cations are added as oxides or fluorides since the melt is completely ionized. Thus the behavior of dolomite slags and various mixtures of magnesium and calcium salts is fairly similar. However, it is rather significant that, in the presence of fluoride, magnesium-calcium oxy-fluoride mixtures clearly demonstrate equivalent refining behavior to calcium oxy-fluoride slags. This provides additional evidence to support the claim that fluoride is able to "activate" the refining ability of magnesia since observed refining behavior is not critically dependent on slag calcium oxide content.

3. Simple Basic Silicate Slags

Silica is present in slags due to oxidation of silicon during hot metal conversion. Traditionally, the presence of silica in slags is regarded as being detrimental to dephosphorization due to competitive interaction with basic oxide components. Such interactions are a result of the strong attraction between alkali earth cations and silicate anions as demonstrated by the refractory character and thermodynamic stability of basic silicates. While basic phosphates possess similar characteristics, they are not as stable as the silicates and thus silica tends to dominate the slag chemistry. This is particularly true when there is a deficiency of basic oxides at compositions more acidic than the orthosilicate.

Due to the protrusion of the dicalcium silicate saturation phase field

into the $\text{CaO-SiO}_2\text{-FeO}$ liquid region, ternary slags are generally saturated with calcium silicate. Initially, slag compositions were chosen outside of this heterogeneous region so as to evaluate component interactions within the region of the homogeneous liquid. This required the choice of rather acidic compositions which would normally be of no interest to steelmaking processes although the behavior of such slags would be of academic interest.

In Figure 5.3, the dramatic effect of silica addition is observed with a general suppression of refining behavior over extensive regions of composition. A peculiar feature of these slags was the pronounced residual phosphorus minimum present with highly oxidized slags. Since these slags are within the homogeneous liquid phase field, this behavior must be related to either liquid solution properties or structural effects, both of which are interdependent. Generally, significant dephosphorization would not be expected in this composition region. In order to explain these observations, several possible interpretations are available. From an equilibrium point of view, the activities of CaO , SiO_2 and FeO can be estimated from the thermodynamic treatment of ternary slags provided by Elliott⁸¹ and activity-composition data compared with the observed minima in residual phosphorus. This approach is shown in Figure 6.1 where the phosphorus minimum coincides with the calcium oxide activity maximum. Apparently there is a minimum calcia activity which is required for initiation of dephosphorization. An alternative, non-equilibrium or kinetic explanation would be based on the slow dissolution kinetics of the basic silicate in iron oxide-rich liquid. As oxidation proceeds, both the FeO content and temperature of the slag increases and these promote dissolution and homogenization of the basic silicate. This increases the effective CaO content of the liquid and promotes dephosphorization.

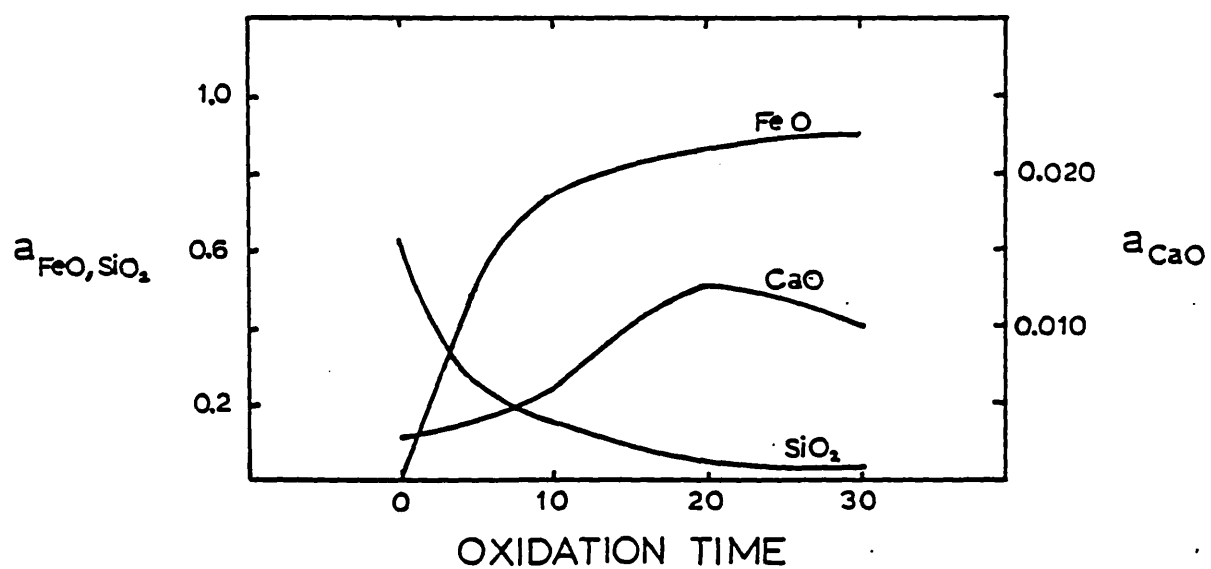


Figure 6.1 Ternary Slag Component Activities at Successive Stages of Oxidation.

Continued oxidation merely causes dilution of the CaO content of the liquid and produces a characteristic phosphorus minimum due to the dynamic nature of slag development and CaO dissolution.

Substitution of CaO with MgO in these acidic composition regions does not produce significant changes in refining behavior although there is some shift in the residual phosphorus minimum and generally higher residual phosphorus levels. Such behavior can be explained, as above, with either equilibrium or kinetic arguments. General observation of substitutional effects indicates that a dilution effect predominates. This effect is countered by the strong interactions which occur between magnesia and silica and the possible formation of a refractory olivine phase which possesses high temperature stability. Presumably, the presence of magnesia should reduce the dominant interaction between calcia and silica, thus raising the activity of calcium oxide and freeing lime for dephosphorization. However, since refining behavior is somewhat reduced by substitution with MgO, the predominant factor appears to be one of dilution.

4. Basic Silicate Slags with Fluoride Additions

In basic silicate slags, fluoride has traditionally been considered as a major network modifier. Because of the strength of the silicon-fluoride bond, it causes extensive depolymerization of silicate anions and considerable disruption of the silicate network, forming more fluid slags. It also increases the solubility of calcium oxide in liquid slags, acting primarily as a fluxing agent for the calcium silicates and decreasing the regions of liquid saturation with these phases. In evaluating the relative interactions of silica and fluoride in multicomponent slags, it is desirable to determine their predominant influence on phosphorus refining. Two methods of evaluation are available, either in establishing what

influence fluoride has at constant silica content, or establishing what influence fluoride has at constant lime content in $\text{CaO-CaF}_2\text{-FeO-SiO}_2$ slags.

The results of the present study are shown in Figure 5.4. Based on the residual phosphorus levels produced by these slags, the addition of fluoride is shown to be of little benefit at high basicities. At low basicities fluoride addition may be beneficial, although the overriding effect of high silica content appears to dominate refining behavior.

In more conventional type steelmaking slags, the presence of fluorapatite, observed with small additions of fluoride, may be superficially indicative of the stabilizing influence of fluoride on phosphorus solution in liquid slags. However, this phase has only been observed in slow-cooled slags and is probably not a primary phase but rather forms upon cooling from high temperature. There is evidence to suggest that fluoride additions may be undesirable in the region of dicalcium silicate saturation. Both Ito¹³¹ and Suito¹²⁹ observed that small additions of fluoride significantly lower the high temperature stability of the α -hexagonal silico-phosphate solid solution and decreases the distribution ratio of phosphorus between the solid solution and liquid slag.

Such statements presumably contradict previous observations of refining behavior with fluoride containing slags. From a statistical analysis of plant data, both Bardenhauer¹⁴¹ and Turkdogan¹³⁷ claim that fluoride containing steelmaking slags produce lower residual phosphorus levels than encountered in normal slags. The laboratory studies of Kor¹³⁹ and Suito¹⁴⁰ and the data treatment of Herasymenko and Speight¹³⁸ also claim improved refining behavior with fluoride containing slags based on their interpretation and use of existing equilibrium correlations. Chipman¹⁰⁸ claimed that fluoride slags showed no apparent benefit in

dephosphorization and were not harmful from a metallurgical point of view. Elliott and co-workers⁹⁴ claimed that fluoride additions inhibit dephosphorization based on their ionic treatment of equilibrium data.

To understand these discrepancies and conflicting views of the role of fluoride addition in slag refining, one must clarify the criteria used in making such evaluations and distinguish the relative importance of equilibrium and kinetic factors in slag-metal reaction behavior and slag development.

Any statistical evaluation of actual plant data is subject to considerable uncertainty when attempting to apply meaningful interpretations to slag-metal equilibrium behavior. This is particularly true when attempting to evaluate the influence of fluoride on slag refining behavior. Fluoride is added initially as a fluxing agent and, as such, it enhances rapid development of a basic refining slag which has good refining properties. This kinetic factor of slag development is a dominant refining feature in basic oxygen steelmaking and the problem with an equilibrium approach is that it fails to take into account the non-equilibrium, dynamic state of slag development. The kinetics of slag development is more important in actual furnace operations than attainment of slag-metal equilibrium and this makes evaluation of flux refining behavior very difficult.

Kor¹³⁹ attempted to evaluate the relative effects of various fluxes on slag-metal equilibrium refining behavior. Using Balajiva's correlation as a criterion, he claimed improved dephosphorization with fluorite additions. However, a critical review of his data proves that such claims are bogus based on the residual phosphorus levels obtained with various fluxes. In Suito's¹⁴⁰ laboratory study, no dramatic claims of improved dephosphorization were made although Suito's treatment demonstrated the essential

equivalence of CaO and CaF_2 in dephosphorization. This would be expected in a reciprocal salt mixture where the source of cations is irrelevant.

As magnesia is substituted for lime in fluoride containing basic silicates, dephosphorization tends to progressively deteriorate, presumably due to the reduced stability of magnesia fluorapatite compounds. When no calcium is present, dephosphorization is essentially suppressed in magnesium fluoro-silicates. This is probably due to the formation of a series of stable high temperature compounds with silica, magnesium oxide and fluoride which are competitive with phosphorus fluorapatite compounds.⁵³ It is significant to note that such compounds are not present in the $\text{CaO-CaF}_2\text{-SiO}_2$ ternary system.

In summary, the role of fluoride in slags is multi-dimensional and depends on the slag matrix. In basic slags, CaO and CaF_2 are essentially equivalent due to the reciprocal salt characteristics of the slag. In such slags, little refining benefit is obtained at high basicities and low silica. In the region of α -hexagonal solid solution saturation, although fluoride increases the solubility of calcium silicate and calcium oxide, fluoride additions may be counterproductive in reducing the stability of the silico-phosphate solid solution. In acidic slags, high in silica content, fluoride addition may be of major benefit in both providing a source of calcium ions and in depolymerizing the silicate anion network. Additional benefits are obtained in highly basic slags containing low silica where fluoride appears to activate magnesia so that it participates in phosphorus refining. Although fluoride is known to raise the activity of FeO in slags, this effect is considered to be minor in regard to dephosphorization refining behavior. Apatite formation in slags is generally observed to occur upon slow cooling and the presence of phosphorus fluorapatite at temperature is considered to be highly

improbable. The observed presence of apatite in silicate slags is considered undesirable as it is indicative of the reduced stability of the silico-phosphate solid solution.

5. Synthetic Basic Oxygen Steelmaking Slags

The traditional approach to refining with basic oxygen steelmaking slags has been one of putting as much lime as possible into solution and saturating the slag with calcium oxide. This manner of dealing with refining chemistry evolved as a result of formulating the slag-metal dephosphorization equilibrium as a reaction between phosphorus and basic oxide in forming basic phosphates. By saturating the slag with lime, the thermodynamic driving force for this reaction was optimized and, thus, dephosphorization should be optimized. Many studies of steelmaking slags have thus been concerned with lime dissolution mechanisms and lime solubilities. As a direct result, considerable interest has developed in the effect of lime fluxing agents on equilibrium refining behavior. The relative effects of CaF_2 , TiO_2 , B_2O_3 , MnO and MgO have been evaluated by several workers.^{108, 139, 140, 200-4}

Although no general consensus exists, the substitution of magnesia for lime in steelmaking slags has traditionally been considered beneficial for three reasons: 1) magnesia fluxes lime and enhances the dissolution process in fayalite slags, 2) as a basic oxide, magnesia is an active refining agent in dephosphorization, and 3) magnesia addition to the slag reduces slag attack on magnesia linings. Of these three claims only the latter has substantial validity. In the present study, magnesia was shown to have no refining ability on its own due to the relative instability of its basic phosphate at high temperatures. As a fluxing agent, small additions of magnesia do produce a eutectic liquid but significant additions raise the slag liquidus. In addition, refractory magnesium

silicate phases tend to form on the magnesia surface during dissolution in similar fashion to lime dissolution and slag attack is retarded.

The role of silica in steelmaking slags has been viewed as somewhat predatory of lime by competitively dominating slag refining chemistry due to the strength of lime-silica interactions. Most studies have attempted to deal with the propensity for dicalcium silicate formation in slags and how to circumvent this barrier to lime dissolution. As such, silica has been traditionally regarded as an undesirable though necessary constituent of slags and its content has been restricted to minimum levels, fixed primarily by slag-metal weight ratio requirements and hot metal compositions.

The presence of iron oxide in slags is the direct result of oxidation during refining and it is a necessary constituent for oxidation of phosphorus during refining. The only ultimate restrictions placed on FeO content in slags are due to iron losses to the slag as well as prevention of excessive slopping during blowing.

In the present work, the refining characteristics of synthetic basic oxygen steelmaking slags was studied over an extended range of compositions in order to provide a detailed understanding of slag component interactions, identify optimum refining regions and evaluate the significant role of slag phase relationships in refining behavior and dephosphorization correlation development. The distinct advantage of the levitation technique was fully realized in this study by providing truly independent slag composition variables. The study was not restricted by refractory containment requirements and liquid saturation surfaces so that component interactions could be independently evaluated.

The results for synthetic steelmaking slags are presented in Figures 5.5, 5.6 and 5.7 where residual phosphorus is plotted as a function of slag

oxidation state and composition for three different levels of phosphorus in the slag-metal system. Generally, lower residual phosphorus is produced by high basicity compositions and high lime content. Magnesia substitutions generally weaken the refining behavior of a slag at a fixed basicity and oxidation state. While low silica slags can refine alloys to the same extent as silica-free slags, high silica additions to slags increase the residual phosphorus beyond levels achieved with basic oxide slags. As seen in comparing these three figures, slag refining power is heavily dependent on slag phosphorus content and only low phosphorus slags can effectively refine alloys to acceptable low residual phosphorus levels. This would imply a possible saturation effect at higher P_2O_5 levels in the slag which results in correspondingly higher phosphorus activities in the alloy phase.

A remarkable feature of the present results is the optimum substitution level of magnesia observed at basicity ratio 2.3, where fifty percent substitution of dolomite for lime results in significantly lower residual phosphorus at low slag oxidation states. Improved refining behavior is observed, independent of the phosphorus content of the slag. The implication of this discovery is that magnesia substitution is of major benefit in this composition region, providing superior refining behavior at lower slag FeO content than with an all lime charging practice. In order to explain this surprising behavior, it is necessary to consider the slag path followed in the quaternary phase system and the phase relationships encountered within these composition regions.

The liquid phase volume and corresponding saturation surfaces for the $CaO-MgO-SiO_2-FeO$ quaternary system are shown in Figure 2.2. As magnesia additions are made to the $CaO-SiO_2-FeO$ ternary system in the region of tricalcium silicate saturation and dual saturation with dicalcium and tricalcium silicate, which corresponds to a slag basicity ratio of 2.3,

slag compositions fall outside of the region of stability of tricalcium silicate and the slag is saturated with both dicalcium silicate and magnesio-wustite at low to moderate FeO contents.

Due to structural considerations, phosphorus pentoxide cannot be incorporated into the tricalcium silicate structure although it readily forms an α -hexagonal solid-solution with dicalcium silicate. Magnesia is known to stabilize this high temperature α -hexagonal structure and may promote formation of the structure and incorporation of phosphorus into the solid solution.¹¹⁵ Because of these considerations, limited magnesia addition would be of obvious benefit within this narrow region of compositions in the quaternary system. However, at these basicity ratios excessive substitution would be of no benefit as compositions would fall outside of the dicalcium silicate saturation region and slags would be saturated solely with magnesio-wustite. The results of the present study tend to confirm this analysis.

Generally, basic oxygen steelmaking slags are never saturated with respect to lime but rather tend to lie within the dicalcium silicate saturation field. The incorporation of phosphorus into a refractory α -hexagonal solid solution with dicalcium silicate appears to be a major factor in the refining chemistry of these slags and slag component behavior should ideally be interpreted with this in mind. Observed basicity effects in slags are more correctly related to the phase relationships and the region of stability and extension of the dicalcium silicate "nose". Substitution effects must be evaluated on the basis of how components effect the structure or phase stability of the α -hexagonal solid solution. The influence of slag oxidation state on refining behavior should be interpreted relative to slag phase relationships, melt structure and physical properties of these liquid-solid emulsions. Of primary

importance in formulating any slag-metal equilibrium relationship is the role of the silico-phosphate solid solution, the solubility of the solid solution in slags, and the true, as opposed to apparent, solubility of phosphorus in slags which is actually a measure of the relative stability of the silico-phosphate solid solution in contact with liquid slag. Clarification of these factors and the role of the silico-phosphate in refining chemistry is presented in a later section.

B. Slag-Metal Dephosphorization Correlation Comparison

Several popular dephosphorization correlations are frequently referred to in the literature as established standards and used by way of comparison with data sets as indicators of the slag-metal equilibrium state. However, the weakness of these correlations lies in their inability to predict observed phosphorus distributions and residual phosphorus levels with acceptable accuracy. All existing correlations were developed for application to rather limited composition regions and as such they are essentially exercises in "curve fitting".

The Balajiva correlation is the most widely accepted measure of slag-metal dephosphorization equilibrium because many data sets fall within the Balajiva "equilibrium" line. Initially, the results of the present study were analyzed by the use of this correlation but it became quite obvious that the value of Balajiva's approach was quite limited, if not entirely misleading. If the experimental results obtained for simple basic oxide, fluoride and silicate slags are compared using both the equilibrium residual phosphorus levels (Figures 5.1 through 5.4) and Balajiva's equilibrium correlation, there is a definite contradiction in any attempt at evaluating slag refining behavior. Basic oxide slag compositions produce lower residual phosphorus levels than silica containing slags although comparison of the two slag groupings using Balajiva's expression

(Figure 6.2) would indicate that silicate slags possess superior refining properties since data for these slags lie above data for basic oxide slags. Yet slag-metal phosphorus distribution and residual phosphorus levels are obviously superior with basic oxide slags containing no silica. Similar discrepancies were observed in analysis of the results for synthetic steelmaking slags.

The reason for these anomalies lies with the inherent weakness of Balajiva's equilibrium expression. This correlation is relatively insensitive to both phosphorus distribution ratios and residual phosphorus levels and tends to overemphasize the slag oxidation state dependence due to a fifth power relationship. In addition, the use of a log-log plot is really too strong of a correction factor for evaluating dephosphorization compositional dependence and this is why data comply so well and why the correlation is relatively insensitive to subtle variations in dephosphorization behavior with slag composition.

While the ionic approach to slag-metal dephosphorization makes some attempt to account for the realities of melt structure, it remains primarily a coordinate transformation of the molecular approach. Flood's treatment¹⁵³ demonstrated important theoretical features of ionic exchange reactions and equilibria but, due to his reliance on empirical determination of ion fraction coefficients, his approach had to resort to "curve fitting" to account for refining behavior over narrow composition regions. Elliott's later development⁹⁴ provided a means of predicting the refining behavior of slags from estimates of theoretical equilibrium quotients but these predictions are subject to considerable error. Both approaches fail to account for anion polymerization and complex ion formation in the melt. In addition, they implicitly assume that the dephosphorization reaction product is a basic phosphate. As mentioned

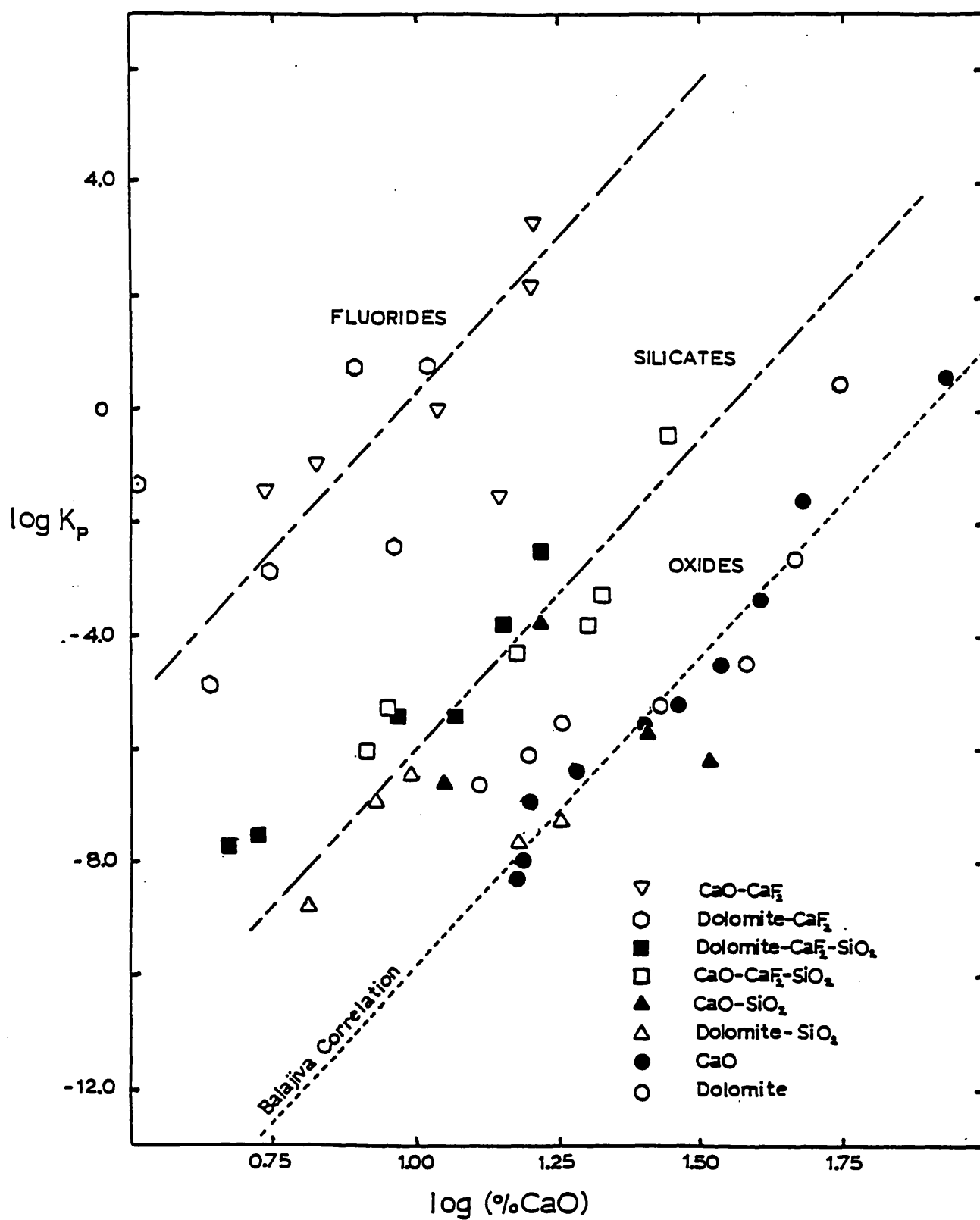


Figure 6.2 Comparison of Some Simple Slag Systems Using the Balajiva Equilibrium Correlation.

previously, this assumption is generally invalid, particularly for silicate slags.

Both Turkdogan¹⁷⁰ and Healy¹⁷¹ resorted to statistical-empirical treatment of plant and laboratory data in developing their respective correlations, but this approach was only of interest to steelmakers as crude predictions of refining behavior from statistical analysis of a large number of compositions in rather narrow composition ranges. Such approaches are data fitting exercises which tend to muddle compositional effects and provide no real insight into refining chemistry.

In summary, the limitations of existing correlations are numerous. They implicitly assume that the dephosphorization reaction product is a basic phosphate although this assumption is generally not valid, particularly in the case of silicate slags. They fail to incorporate the considerable amount of information on slag phase relationships and relate this to slag refining behavior. As composition correlations, they often lead to meaningless and inadequate analysis of data since slag-metal equilibrium studies are generally conducted at slag saturation surfaces and thus compositions are not really independent variables but must follow the restrictions imposed by equilibrium phase relationships. As curve fitting exercises, they are relatively insensitive to subtle compositional effects due to excessive damping of the data and are generally too insensitive for accurate prediction of residual phosphorus levels or equilibrium phosphorus distribution. In general, they do not adequately reflect the refining behavior of slags and because of this they are of nominal value when comparing the relative behavior of slag systems from an equilibrium point of view.

C. Proposed Dephosphorization Equilibrium Correlation

The existence of a stable, high temperature, α -hexagonal solid

solution of dicalcium silicate and tricalcium phosphate has been well established in the literature and observations of this phase in slag microstructures have been made by several independent investigators.^{109, 111, 116, 119, 120, 122, 123, 129-131} Studies of slag liquidus temperatures have demonstrated that the solid solution is a primary phase and coexists with liquid slag at high temperatures over a broad region of composition.¹²³⁻¹²⁶ Both Suito and Ito^{129, 130} observed that phosphorus in slags is primarily found to be incorporated in this phase and has very low true solubility in liquid slags. The distribution ratio of phosphorus between slag and metal has been shown to reach a maximum value in the region of the dicalcium silicate nose^{173, 174} and slag compositions within this region possess excellent refining properties, essentially equivalent to silica-free slags. Bookey⁶⁰ observed that the calcium silico-phosphate possessed higher thermodynamic stability than the basic calcium phosphates and produced lower residual phosphorus in alloys equilibrated at a fixed oxygen potential.

Since previously derived dephosphorization correlations fail to account for the presence and significance of the silico-phosphate solid solution, an attempt was made to incorporate knowledge of this phase and general slag phase relationships with observed slag refining behavior in basic steelmaking slags.

While Balajiva's attempt to correlate slag-metal refining behavior suffers from major inadequacies, the empirical observations made in this study are of fundamental significance. His systematic choice of composition variables enabled the establishment of several interesting empirical correlations. When slag-metal phosphorus distribution ratios were plotted as a function of slag FeO content and basicity, a pronounced distribution maximum was found in the vicinity of 18 % FeO. This maximum

happened to coincide with observed slag refining behavior in open-hearth steelmaking practice since Balajiva's synthetic slags approximated actual steelmaking compositions. Balajiva explained this behavior by referring to the well-characterized dependence of phosphorus refining on iron oxide and calcium oxide content. He argued that maximum refining power is obtained by increased FeO and CaO additions up to that point where further addition of FeO dilutes slag lime content and weakens the refining character of a given slag. In reviewing Balajiva's data, a serious flaw in this argument was observed. If Balajiva was correct, and a dilution effect was responsible for observed behavior, a pronounced maximum should exist in slags having a low lime content whereas a weak maximum should be observed in slags rich in lime. His data apparently contradict this explanation as the maxima become more pronounced at high basicities.

While Balajiva's explanation of his results was incorrect, the observed optimum refining behavior and interrelationship of slag basicity, oxidation state and phosphorus distribution was clear. The results of the present study were plotted in similar manner and are shown in Figure 6.3, together with Balajiva's data. While the present results follow similar behavior, and a pronounced maximum in phosphorus distribution is observed, several major discrepancies exist between the two data sets. The phosphorus distribution ratios observed in this study are two to three times greater than that observed by Balajiva. Also, the distribution maxima are dramatically shifted to higher FeO contents, centered approximately at 45% FeO.

While the difference in magnitude of the distribution ratios is indicative of the difference in slag phosphorus content, and the major influence slag phosphorus content has on refining behavior, the relative location of the distribution maxima was perplexing. At first this was

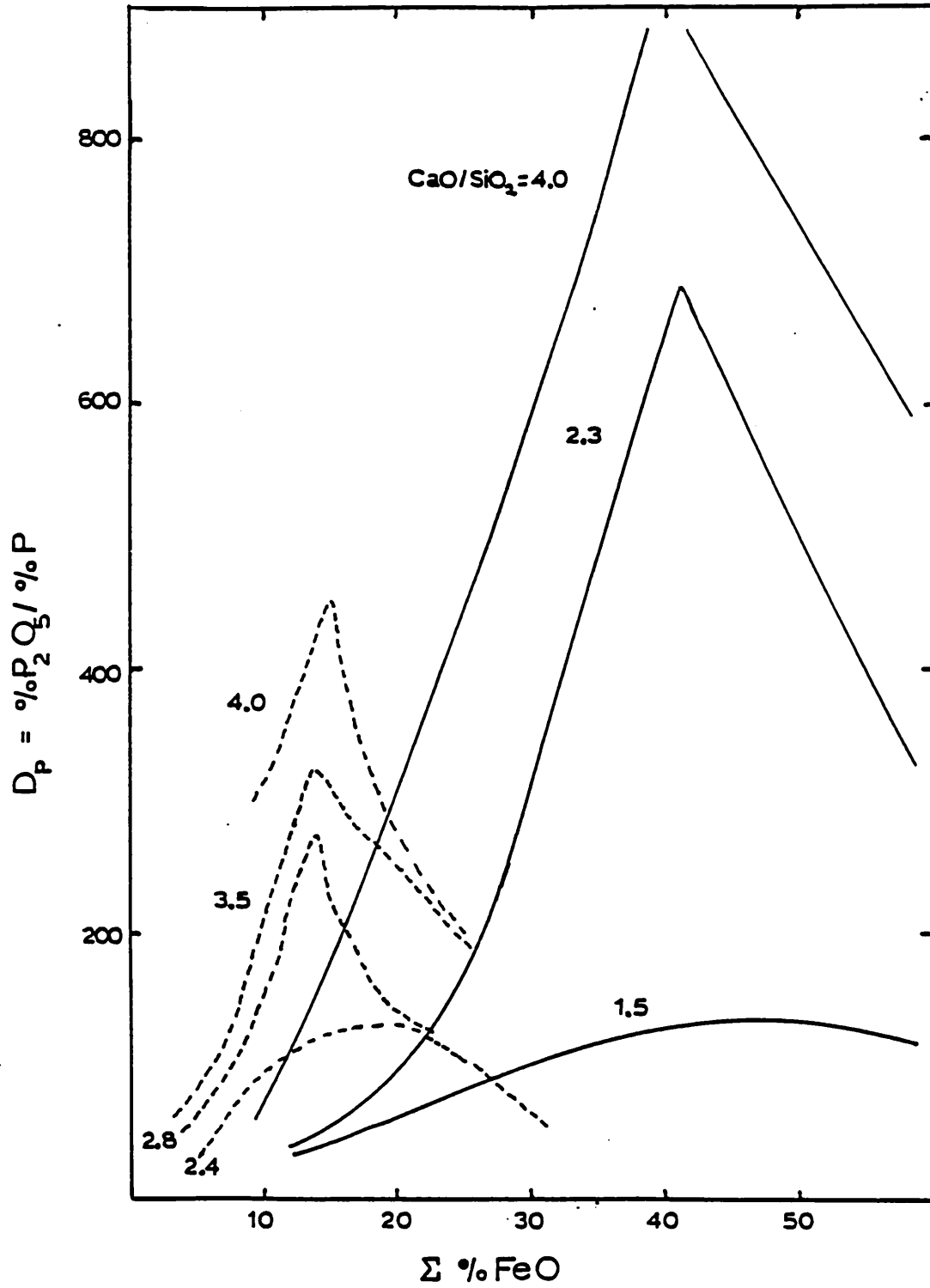


Figure 6.3 The Compositional Dependence of Slag-Metal Phosphorus Distribution.

thought to be an artifact of poor experimental technique but such a pronounced difference could not be accounted for on the basis of experimental error or uncertainty.

Previous workers have reported a distribution maximum in steelmaking slags in the vicinity of the dicalcium silicate "nose"^{173, 174} and the presently observed maximum was thought to be related somehow to the slag phase relationships and dicalcium silicate saturation surface. Since Riboud and co-workers¹²³⁻⁶ demonstrated the significant influence of FeO content on both slag liquidus temperatures and the extent of the phase stability of the calcium silico-phosphate solid solution, the results of their study were evaluated and their experimentally determined slag liquidus temperatures were plotted at constant basicity and phosphorus content as a function of FeO content. From these diagrams, an initial estimate of slag liquidus temperatures was obtained for the synthetic slags used in this study. An identical approach was taken for estimating slag liquidus temperatures in Balajiva's study. Since Riboud's study focused on the pure $\text{CaO-P}_2\text{O}_5\text{-SiO}_2\text{'FeO'}$ quaternary system, this required some correction in the initial estimate of liquidus temperatures. Fortunately, in a later study, these workers evaluated the effect of other additions on depression of liquidus temperatures and described a method for correcting data obtained from the pure quaternary system.¹²⁶

When the results of the present study and Balajiva's study are replotted, as shown in Figure 6.4, a direct correlation is found between slag liquidus temperatures and phosphorus distribution maxima and the maximum observed distribution ratios for the two studies become coincident with liquidus temperatures approximately equal to, though slightly lower than, the experimental temperature for each study.

Presumably, with slags having lower liquidus temperatures, the

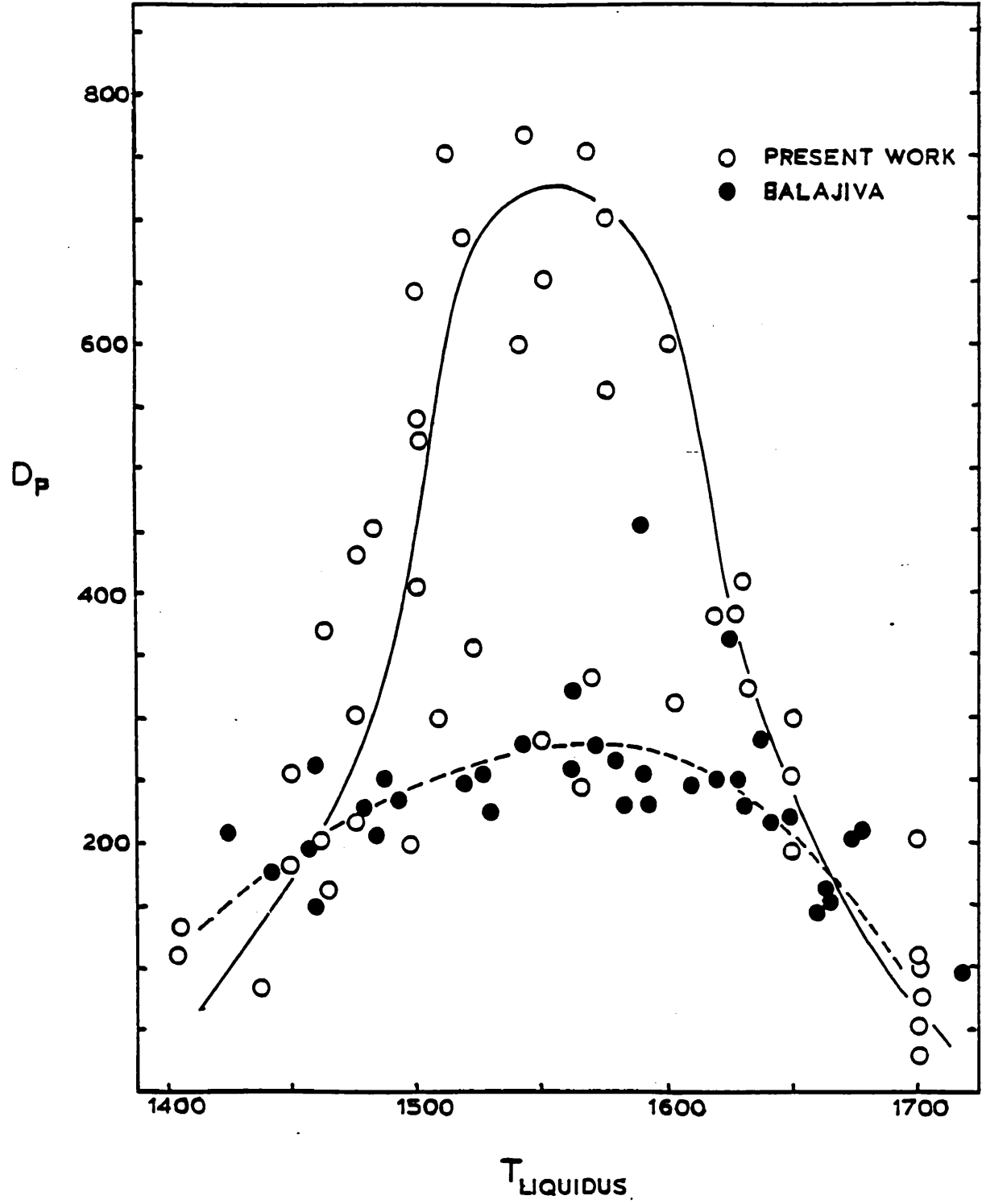


Figure 6.4 The Influence of Slag Liquidus Temperature on Slag-Metal Phosphorus Distribution.

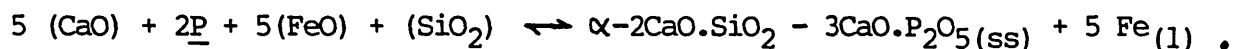
silico-phosphate solid solution is not stable at temperature and does not saturate the liquid or precipitate from solution within these composition regions. At higher slag liquidus temperatures, a fairly viscous liquid, saturated with the solid solution, is present and solid-state transport limiting mechanisms would very likely inhibit incorporation of phosphorus into the solid solution. This would explain the observed maxima in phosphorus distribution and the optimum situation obtained when liquidus temperatures are slightly lower than experimental temperatures. At these temperatures the solid solution is stable in contact with the liquid slag and incorporation or precipitation of phosphorus as a silico-phosphate is possible. In addition, the slag remains sufficiently fluid to promote slag-metal exchange reactions.

Additional supporting evidence tends to verify this explanation of observed behavior. Tromel¹⁰⁴ and Bardenheuer¹⁷³ noted that the dephosphorization reaction was only slightly temperature dependent at low to moderate temperature and strongly temperature dependent at high temperatures. Such behavior would not be consistent with reaction enthalpy considerations and is more likely related to slag liquidus temperature and high temperature instability of the silico-phosphate in contact with the liquid above slag liquidus temperatures. Other workers have observed optimum refining behavior at the dicalcium silicate "nose", giving rise to the traditional steelmaking operation requirements for refining slags having basicity values of at least two.

Assuming this approach is correct, then evaluation of the role of slag constituents becomes one of determining to what extent addition of components effects the phase relationships by depressing the silico-phosphate stability and slag liquidus temperatures. Additional considerations of the role of slag components in structurally modifying the

α -hexagonal solid-solution would also be an important factor. Such phenomena have been observed by Bredig¹¹⁵ and are discussed in a previous section with regard to the role of magnesia addition in the region of dicalcium silicate saturation.

Having developed a self-consistent explanation of observed slag refining behavior in the region of dicalcium silicate and calcium silico-phosphate saturation, a new formulation of the slag-metal dephosphorization is proposed, based on present knowledge of slag phase relationships and the predominance of the calcium silico-phosphate solid solution. If the slag-metal phosphorus exchange reaction is reformulated to account for silico-phosphate formation as a dephosphorization reaction product, then the following reaction is of major interest:



Since slags in the composition region of interest are generally saturated with respect to the solid solution, this phase is at unit activity and the equilibrium constant is expressed as follows

$$K = \frac{1}{a_{\text{CaO}}^5 \cdot a_{\text{P}}^2 \cdot a_{\text{FeO}}^5 \cdot a_{\text{SiO}}}$$

Phosphorus generally follows Henrian behavior and, if the hypothetical weight percent standard state is selected, its activity is equal to its weight percent. Since activity data are generally not available for complex slags, as a first approximation ideal solution behavior is assumed, and the equilibrium quotient is determined from slag composition and metal analysis. Refinement of this simple reaction model can be made through introduction of either a compositionally dependent activity coefficient term or a correction factor which accounts for compositional dependence of slag liquidus temperatures and, thus, silico-phosphate stability.

Using both present data and the results of previous laboratory

studies, values for the proposed equilibrium quotient were calculated by neglecting activity corrections and taking the average values obtained for each temperature and study in the vicinity of the dicalcium silicate saturation surface. The temperature dependence of this equilibrium expression was derived where data was available. The equilibrium quotient values obtained from each data set and the temperature dependence of the reaction are presented in Table 6.1.

Without resorting to regression analysis and incorporation of an activity coefficient correction term, the results of this approach are shown to be equal to or better than previous correlations based on its predictive accuracy in residual phosphorus estimation. Phosphorus levels estimated from slag compositions fall well within the uncertainty of chemical analysis without resorting to any correction factor. Since the proposed reaction model is based on known phase equilibria and provides a coherent explanation of slag refining behavior, it is preferred over previous correlation attempts. It must be emphasized, however, that this approach is only valid within the region of dicalcium silicate and calcium silico-phosphate saturation. Extension of this model beyond the immediate saturation phase fields is subject to considerable uncertainty.

D. Implications of the Present Study

Acceptance of the dephosphorization reaction model proposed in this study and consideration of the critical role which complex phase relationships play in slag refining behavior, have dramatic implications in interpreting both slag-metal equilibrium and kinetic behavior in either laboratory or plant environments.

The possible presence of a refractory-type dephosphorization reaction product dispersed within a heterogenous liquid-solid suspension brings into question virtually all previous studies of phosphorus refining behavior

Table 6.1: Calculated Values of the Proposed Dephosphorization Equilibrium Correlation Obtained from the Results of Various Studies

Study (Ref)	Temperature (°C)	K	Temperature Dependence
Balajiva (109,120,168)	1550 1585 1635	1.77×10^{-13} 1.14×10^{-13} 3.55×10^{-14}	$\ln K = \frac{55270}{T} - 59.63$
Chipman (108)	1550 1600 1650	3.95×10^{-13} 2.12×10^{-13} 1.18×10^{-13}	$\ln K = \frac{53491}{T} - 58.63$
Suito (172)	1550 1600 1650	1.94×10^{-12} 1.28×10^{-12} 7.73×10^{-13}	$\ln K = \frac{32150}{T} - 44.53$
Kor (139)	1550	2.49×10^{-13}	-
Present Work	1600	1.30×10^{-12}	-

with basic steelmaking slags. Solid-liquid segregation, slag and sampling inhomogeneity, impeded solid-state reaction mechanisms, choice of direction of approach to equilibrium, uncertainty as to the thermodynamic equilibrium state and inadequacy of equilibration times are very serious technical difficulties which must be overcome, if not considered. Major problems exist in interpreting and comparing data from previous studies due to the predominance of kinetic rather than equilibrium factors brought about by poor experimental technique and the unique physicochemical features of the reaction system. Previous reaction models are inadequate and compositional correlations suffer from the inhomogeneity of the slag phase where a distinction must be made between true and apparent solubilities, particularly in the case of phosphorus. Observed temperature and compositional dependence may not be directly related to thermodynamic reaction equilibria, but rather dependent on solid solution phase stability and slag liquidus temperatures. Due to the presence of solid solution reaction products and slow, solid-state reaction processes the possible attainment of non-equilibrium, metastable contacting situations makes equilibrium interpretation of reaction behavior unsuitable and direct comparisons of previous studies virtually impossible. The exact mechanism of phosphorus incorporation into the silico-phosphate solid solution remains as a primary reaction feature having major implication to observed slag refining behavior and underlines the considerable importance of slag development path and slag-metal contacting conditions on dephosphorization.

VII. SUMMARY & CONCLUSIONS

Several interesting observations of the role of various slag components and their relative interactions have been established as a direct result of the present study utilizing both timed oxidation experiments and slag-metal equilibrations.

Magnesia has been shown to be incapable of dephosphorizing low phosphorus alloys on its own and slag lime was shown to be entirely responsible for slag reactivity in phosphorus refining.

Fluoride additions are able to activate slag magnesia so that it becomes an active refining agent in basic slags, producing adequate refining behavior at lower lime levels than calcium based slag systems. In basic slags, in the absence of silica, fluoride additions apparently prevent phosphorus reversion under highly oxidizing conditions.

In simple basic silicates having high silica contents, slags are generally unreactive and dephosphorization is essentially suppressed. However, maximum refining behavior was observed within the homogeneous liquid region at high iron oxide contents (65 % FeO). Similar behavior occurs in both substituted slags and pure lime silicates although a dilution effect is observed with increasing substitution of lime with magnesia. It is not clear whether this behavior is due to kinetic features of slag dissolution and homogenization or to solution thermodynamic factors.

While fluoride additions to basic silicate slags apparently counteract the inhibiting effect of silica on dephosphorization, silica content tends to dominate slag refining behavior. Fluoride produces little benefit at low silica content and high basicity and major benefit at high silica where it provides both a calcium source and acts as a silicate depolymerizing agent. In basic steelmaking slags, fluoride additions may be favorable

from a kinetic point of view in promoting early basic slag development. However, such additions are considered undesirable from an equilibrium point of view as fluoride lowers the high temperature stability of calcium silico-phosphate and increases the true solubility of phosphorus in liquid slags.

In conventional basic oxygen steelmaking slags, refining behavior is generally dominated by slag basicity values and optimum refining behavior occurs within the region of dicalcium silicate saturation and the so-called dicalcium silicate "nose". This behavior is explained on the basis of formation of a stable calcium silico-phosphate solid solution in equilibrium with a highly oxidizing and fluid FeO-rich slag. Optimum conditions for magnesia substitution are observed within this phase region. Small additions of magnesia to the calcium based ternary system place compositions beyond the region of tricalcium silicate and dual, tricalcium and dicalcium silicate, saturation and liquids are saturated solely with dicalcium silicate. Small magnesia additions also tend to stabilize the high temperature, α -hexagonal, calcium silico-phosphate solid solution which has been identified as the dephosphorization reaction product in these slags. Excessive additions of magnesia are considered undesirable since such compositions generally lie beyond the dicalcium silicate saturation region and slags are saturated with respect to either magnesio-wustite or olivine phases which play no role in the refining reaction.

The proper choice of the dephosphorization reaction product in basic oxygen steelmaking slags has been identified on the basis of known phase equilibria and microstructural observations and has been established as a high temperature, α -hexagonal solid solution of tricalcium phosphate and dicalcium silicate.

Compositional correlation of slag-metal equilibrium data was developed by postulating the formation of a calcium silico-phosphate solid solution dephosphorization reaction product. Observed phosphorus distribution maxima were correlated with the high temperature stability and saturation surface of the silico-phosphate. By considering such factors, interpretation of the role of CaO , SiO_2 , FeO , MgO and CaF_2 in refining behavior was related to the effect of these components on silico-phosphate formation and phase stability.

The relative importance of kinetic and equilibrium factors was discussed in evaluating the importance of slag development paths and direction of approach to equilibrium in slag refining behavior. Implications of the results of the present study were made with respect to previous laboratory and plant studies.

Part B. DEPHOSPHORIZATION KINETICS

I. INTRODUCTION

During the course of this study, it became evident that slag-metal dephosphorization refining behavior could not be adequately characterized without some fundamental understanding of those kinetic features which determine the relative reaction rate and mechanism during refining. As seen in Part A, the system reaction behavior cannot be explained solely on the basis of slag-metal equilibrium considerations due to the complex heterogeneous nature of the reaction system and presence of solid-state reaction products having considerable high temperature stability. For this reason, a critical review of previous kinetic studies of the dephosphorization reaction was made in light of the present understanding of equilibrium phase relationships and likelihood of attaining metastable reaction contact conditions and pseudo-equilibrium states between slag and metal.

Previous kinetic studies of the dephosphorization reaction in steel refining have generally suffered from an unsystematic approach and lack of methodical experimental design. As a direct result, most of these studies are of rather poor quality and are misleading in their conclusions. For example, considerable confusion has been generated in careless and casual usage of the terms "chemical rate constants" and "mass transfer coefficients". Lack of experimental control over reaction geometry, contact conditions and initiation, and side reactions with crucibles and gas phases are commonly observed. In addition, failure to consider the establishment of comparable hydrodynamic conditions in comparing the reaction behavior of various slag systems has made direct comparison of previous studies virtually meaningless.

Discussions of process reaction behavior during converter refining have

taken a thermodynamic approach in attempting to explain the observed refining sequence. In general, they fail to take into account the dynamic nature of slag development, blowing practice, and emulsion formation, and their importance to relative reaction rates of solute elements during oxidation. This equilibrium bias persists in the current literature on hot metal dephosphorization where attempts are made to explain unusual observations in refining behavior with thermodynamic arguments.

It is the purpose of this short addendum to clarify some of these misconceptions and misunderstandings and to underscore the relative importance of thermodynamic and kinetic factors in dephosphorization refining. In order to achieve this purpose, it was necessary to briefly review previous literature on the kinetics of dephosphorization to provide an up-to-date perspective on what is currently known regarding the reaction. In the course of this review, and in light of knowledge gained from the study of equilibrium slag-metal behavior presented in Part A, key features of the reaction emerged as being suitable topics for further study.

A series of kinetic experiments was planned to clarify and substantiate some basic concepts which evolved during the course of this work. Unfortunately, not all of these experiments could be completed within the context of this study due to restrictions of funding and time. However, the results of those studies which have been completed are discussed with regard to their immediate implications in clarifying observed refining behavior of existing steelmaking processes, as well as in demystifying external refining treatments of hot metal.

II. LITERATURE REVIEW

A brief review of previous work on dephosphorization kinetics is presented with the intent of clarifying misunderstandings which persist in the literature and providing a basis for elucidating the complex observed reaction behavior. These studies are grouped according to generic reaction types and reviewed in the following order: process reaction kinetics, gas-metal-solid reactions, slag-metal reactions and external phosphorus refining studies.

A. Process Reaction Kinetics

General reviews of phosphorus refining behavior in specific basic oxygen steelmaking processes have been published by McBride,²⁶³ Messin,²⁶⁴ Coheur,²⁶⁵ Kalling,²⁶⁶ and Savard.²⁶⁷ Studies of the refining sequence of solute elements during oxidation in a variety of converter types have shown that the sequence of removal generally follows thermodynamic predictions based on the oxidation potential of the metal bath during refining. Figure 2.1 provides a schematic picture of refining behavior observed in basic Bessemer or Thomas processes, top blown or LD processes, the Kaldo process and bottom blown or Q-BOP type processes.^{219, 263-7, 276} In general, silicon is oxidized preferentially, followed by carbon, manganese, iron and phosphorus with some variation in degree of removal or onset of oxidation depending on the particular practice followed.

Relying solely on a thermodynamic approach in explaining the refining sequence during conversion is a remnant of the equilibrium bias established in earlier studies of open hearth reactions and the rather slow approach to equilibrium during the refining period of these processes. The refining behavior in modern basic oxygen steelmaking converters is exceptionally more complex due to the dynamic nature of the reaction system and operation of processes far from chemical and thermal equilibrium.

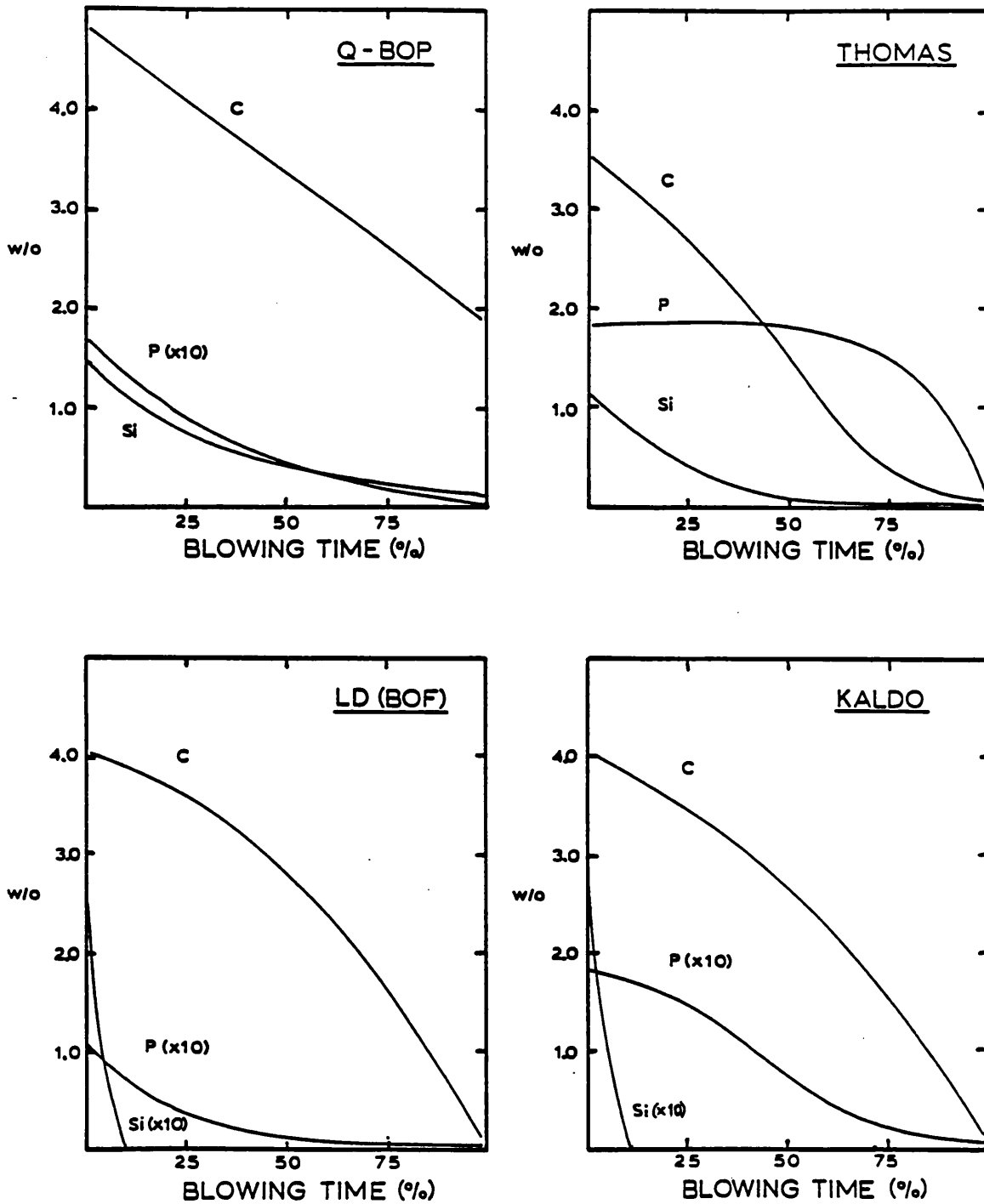


Figure 2.1 Generalized Solute Refining Sequences for Some Basic Oxygen Steelmaking Practices.

Anomalies in predicted behavior are generally explained with reference to important operational features such as the ratio of scrap to hot metal charge, blowing and flux additions practice, and slag development rate and composition path. The equilibrium explanation of refining sequence fails to clarify complex and unusual observations where unique contacting situations produce metastable reaction behavior and attainment of non-equilibrium states. This is particularly true with attempts to explain phosphorus reaction behavior in the complex gas-metal-slag emulsions produced in top and bottom blowing and with powder injection treatments.

It is generally accepted that in modern basic oxygen steelmaking converters, dephosphorization proceeds primarily within the slag-metal emulsion. Early observations by Kozakevitch,²⁵³ Meyer,²⁵⁴ and Chatterjee²⁵² confirm this and later studies by Schurmann and co-workers^{248, 249, 251} and Bardenheuer²⁵⁰ have attempted to model dephosphorization reaction rates on the basis of metal droplet formation and granule circulation within the emulsion. Observations indicate that, for a given charge, the phosphorus refining rate increases with droplet formation and dispersion, both of which are primarily a function of blowing rate and lancing conditions. The bath is gradually dephosphorized by recirculation of refined droplets and subsequent mixing of these droplets with the bath.

Chatterjee²⁵² claims that formation of the emulsion tends to promote dephosphorization at the expense of decarburization and that much higher decarburization rates are achieved in the absence of the emulsified slag. Kootz²⁴⁷ observed that dephosphorization in basic steelmaking converters occurs at much higher residual carbon levels than anticipated from thermodynamic equilibrium and claimed that phosphorus removal can be promoted by formation of highly oxidized basic slags through raising lance heights and

using a soft blowing technique. These claims are confirmed by the work of Schoop and co-workers²⁴⁸⁻⁹ who observed that hard blowing favors decarburization while soft blowing promotes dephosphorization. Schurmann²⁴⁸ explains these observations by hypothesizing that dephosphorization can occur only at a slag-metal interface within the emulsion while decarburization can occur at either a slag-metal or gas-metal interface. Riboud²⁵⁵ maintains that from observations of basic oxygen converter refining behavior, the dephosphorization and decarburization reactions appear to be independent reactions for all practical purposes. Whatever the case may be, it is clear that the refining sequence in basic oxygen converters does not necessarily follow thermodynamic equilibrium predictions and that kinetic factors are responsible.

This disparity between process observations and thermodynamic predictions of refining behavior is even more pronounced in the case of bottom blown converters with lime injection, such as the Q-BOP process. Dephosphorization proceeds to completion at relatively low slag oxidation potentials and high residual carbon levels in the bath. Turkdogan²¹⁸ and Kor,²¹⁷ as well as Fruehan²²⁰ have resorted to rather exotic reaction mechanisms in an attempt to explain such observations with a "quasi-equilibrium" approach. They postulate that dephosphorization proceeds via a gas phase mechanism in which volatile phosphorus species form which react with injected lime and are prevented from reversion by a sluggish back reaction. Turkdogan and Kor²¹⁷ provide some experimental evidence to apparently support this hypothesis, but they fail to convincingly substantiate these claims and ignore crucible-alloy side reactions in their experiments. Fruehan's²²⁰ work suffers from similar inadequacies in interpretation and experimental technique. Recently, Nozaki²³² has provided an explanation of the Q-BOP dephosphorization reaction mechanism

in which he proposes localized oxidation of iron at the tuyeres to form calcium ferrite. This is reduced as it rises in the metal bath and oxidizes silicon, phosphorus and carbon. The phosphorus and silicon which are oxidized are then assimilated into the top slag layer before reversion occurs.

Dephosphorization refining mechanisms in top blown and bottom blown converters will be discussed in detail in a subsequent section. However, it is important to emphasize that thermodynamic arguments alone cannot account for observed reaction sequences and proper understanding of the dynamic kinetic features of the reaction system are required.

B. Gas-Metal-Solid Reaction Kinetics

The reaction kinetics of dephosphorization of iron alloys by solid lime and oxidizing gases were studied by Yoshii,²⁰⁹ Fujii,²¹⁰ and Kawai.²¹¹ Yoshii, using lime crucibles, found that the rate of dephosphorization increased with increasing oxygen potential and oxygen delivery rate to the alloy surface. All of his data appear to lie within the regime of oxygen transport control. Fujii studied the reaction using magnesia crucibles and found that the rate of dephosphorization increased with increasing lime charge and oxygen blowing rate. When the system was not saturated with respect to calcium oxide, the reaction rate decreased with oxygen blowing, presumably due to lime dilution and subsequent reduction in dephosphorization driving force. At low phosphorus levels, the rate appeared to be phosphorus transport controlled in the alloy since increased blowing rate and lime addition had no effect on the reaction. With carbon containing alloys, dephosphorization occurred at high carbon levels although at a slower rate than when carbon was absent. From these results, it appears that carbon and phosphorus can be oxidized simultaneously providing lime is present at the gas-metal interface.

Kawai's results appear to contradict Fujii's findings since these workers observed no dephosphorization prior to the completion of decarburization. In addition, they observed an apparent requirement for an incubation period in which alloy oxygen content rises to a minimum level prior to the onset of dephosphorization. However, in Kawai's work a lime crucible was used and the alloy surface was directly exposed to the gas phase. Thus, decarburization could occur at the point of gas-metal contact while dephosphorization was essentially restricted to the crucible-metal interface. Adsorbed oxygen was obviously consumed by the decarburization reaction prior to reaching the crucible surface, the preferred reaction site for dephosphorization. In Fujii's work, lime powder was initially charged on the alloy surface and presumably adsorbed oxygen from the gas reacted with alloy phosphorus and was "captured" by either the lime particles or a lime-rich slag. Considerable dephosphorization occurred due to the large surface area provided for dephosphorization by the lime particles. It is obvious from these results that the phosphorus oxidation reaction is competitive with decarburization provided that a chemical potential driving force is established for dephosphorization. As will be seen later, the reduction or reversion of calcium phosphate in contact with iron-carbon alloys is very slow due to a solid-state reaction mechanistic barrier and the forward reaction is thus favored.

C. Slag-Metal Reaction Kinetics

Previous studies of slag-metal dephosphorization reaction kinetics have tacitly assumed that the actual refining reaction occurs as an interfacial, heterogeneous, two liquid phase, mass transfer process. Classical kinetic theory analysis has been applied to obtain reaction "rate constants" and "order", an approach which is only suitable for homogeneous single-phase reactions. Thus, much confusion has been generated due to

this failure to distinguish between chemical rate constants and mass transfer coefficients. General disregard for the complex, multi-component, slag phase relationships prevails as with the equilibrium studies discussed in Part A. The importance of liquid hydrodynamic factors, reaction contact conditions and geometry, and thermodynamic driving force have been casually ignored and a general lack of appreciation and understanding of the variety of reaction regimes and potential rate limiting factors exists. Because of such limitations, rather than comparing previous studies and accepting published data at face value, it is best to reconstruct what verifiable information exists regarding the dephosphorization reaction so as to provide a sound basis for proceeding. With this attitude in mind, it is possible to reap maximum benefits from previous studies in spite of their limitations.

Kawai²¹² and co-workers studied the dephosphorization kinetics of calcium oxide-wustite slags and found that the "apparent rate constant" increased with increasing lime content. Due to this compositional dependence, these workers assumed that mass transport in the slag phase was rate limiting. In studies of phosphorus reversion or reduction from slags, the rate was much slower than phosphorus transfer during oxidation. It is interesting to note that these workers observed no significant transfer of oxygen during phosphorus reversion although iron was oxidized and transferred to the slag.

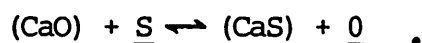
Aratani and Sanbongi²¹³ studied slag dephosphorization kinetics using $\text{CaO-SiO}_2\text{'FeO'}$ ternary type slags and found that the maximum observed phosphorus refining rate occurred within the boundary of the dicalcium silicate saturation "nose", a phase region which coincides with the calcium silico-phosphate saturation surface. In general, observed rates were independent of alloy phosphorus content ($\%P > 0.2$) and slag oxidation state

(%FeO > 10) and, within the homogeneous liquid region, dependent on lime content. As with the observations of Kawai and co-workers, the phosphorus reversion or reduction rate was considerably slower.

Mori and co-workers²¹⁴ studied the reaction rate between low basicity, LD-type slags and iron-phosphorus alloys and found that the dephosphorization rate increased with increasing basicity. As in previous studies, the reversion rate was found to be slower than the dephosphorization rate. Oxygen transport was found to be much faster than that of phosphorus and had very little influence on the dephosphorization rate. A significant hydrodynamic feature was observed in this work. In a comparison of rates observed with inductively stirred melts and unstirred reaction systems, the reaction rate increased with stirring and slag-metal equilibrium was approached more rapidly. Mori hypothesized that the rate controlling mechanism in dephosphorization appeared to be phosphate transport in the slag. Such conclusions were also drawn from the results of two independent Russian studies in which phosphorus transport in the slag was found to be rather slow and dephosphorization reaction kinetics were enhanced by slag stirring.^{268, 269}

Takenouchi and co-workers²¹⁵ studied the effects that various fluxes or fluidizers have on slag-metal dephosphorization kinetics with lime and fluorite-based slags. They assumed that the reaction is either chemically controlled or diffusion controlled and hypothesized that dephosphorization rates should increase with increased lime activity and slag fluidity. By keeping slag silica at a minimum and using fluidizers to lower slag liquidus temperatures and reduce viscosity, these workers attempted to optimize slag-metal refining rates. It is interesting to note that calculated mass transfer coefficients in this study are significantly higher than those observed in comparable studies although no inductive

stirring was utilized. The addition of alkali and alkaline earth metal oxides enhanced dephosphorization kinetics. In associated experiments, both sulphur and phosphorus were simultaneously refined with residual dissolved oxygen acting as an oxidant. At very low oxygen potentials, the sulphur reaction was found to enhance dephosphorization by a coupled reaction with lime which provides a source of oxygen for dephosphorization:



Gaye and Riboud²¹⁶ studied slag-metal dephosphorization kinetics of alloy droplets in contact with oxidizing slags during emulsification. They observed very fast dephosphorization rates which were significantly enhanced by decarburization and gas-induced emulsification which caused fragmentation of the alloy droplets. Dephosphorization was completed in a matter of seconds while decarburization proceeded much more slowly. In fact, the phosphorus reaction kinetics during decarburization of Fe-C-P alloys were significantly faster than with iron-phosphorus alloys while decarburization was impeded by the oxidation of phosphorus. These observations indicate that under such contacting conditions the two reactions are parallel and competitive rather than sequential in nature.

More recent studies of slag-metal dephosphorization kinetics have utilized rather exotic flux additives not normally associated with conventional concepts of slag systems. While these reaction studies are generically of the slag-metal type of system, they more appropriately fall under the heading of external refining of hot metal and are discussed in the following section.

D. External Hot Metal Refining Kinetics

While there is no fundamental reason for distinguishing between dephosphorization reaction mechanisms in basic steelmaking furnaces, where

blast furnace hot metal is converted, and in external refining furnaces or ladles, this appears to be the current fashion, particularly in Japan. In recent studies, the presumption has been made that some novel reaction chemistry has been discovered which permits refining of phosphorus under "reducing" conditions (i.e. refining of carbon-saturated alloy). Such a naive approach has been taken recently in several timely reviews by Fuwa,²⁰⁷⁻⁸ Tiwary²⁵⁶ and Smillie.²⁵⁷ Very few of those studies reviewed are worth citing as they are generally of empirical engineering quality and have little scientific value. Nevertheless, a critical review of this work is made with the intention of clarifying fundamental understanding of the dephosphorization reaction mechanism during hot metal refining.

External refining pretreatment of hot metal is not a new phenomenon. On the contrary, hot metal mixers have traditionally been used for blending and refining of blast furnace iron to maintain uniformity in alloy charges to steelmaking furnaces. In a dated paper, Davies²⁰⁶ has reviewed the history of pre-refining treatments and claims that such practices have existed for over one hundred years, where hot metal silicon and phosphorus contents were problematic. Such pretreatments are desirable since reducing alloy silicon content reduces the metallurgical burden of high slag volumes and improves thermal efficiency. In addition, pretreatment avoids problems with meeting specifications with high carbon heats. The open hearth flush slag practice is one example of a prominent pretreatment practice, and Elliott²⁰⁵ has studied the refining behavior of phosphorus during this operation. Two slag practices, such as the LD-AC and Kaldo processes are yet additional examples of hot metal prerefining treatments utilized to remove silicon and phosphorus prior to decarburization. The current undue attention being directed toward hot metal dephosphorization studies in Japan is an immediate result of inadequate understanding of the phosphorus

reaction mechanism and misconceptions which persist within the literature.

In early basic open hearth practice, a rather common mistake was to oxidize the metal bath too quickly with the flush slag. This tended to initiate the onset of the decarburization boil, prior to silicon and phosphorus removal, with the result being failure to achieve adequate refining prior to reaching the carbon end-point. From prerefining experiences at Brymbo works, Davies²⁰⁶ claimed that the extent of phosphorus removal during pretreatment is dependent on the timing and onset of carbon boil, and that little dephosphorization occurs after initiation of the boil. Various contacting techniques were studied, addition of mill scale and lime to runners and ladles, oxygen injection with lime addition to ladles and powder injection with oxygen in a prerefining furnace. Davies claimed that ladle treatment was impractical due to slag-metal emulsification and the violent nature of the reactions. Thus a specially designed refining furnace with powder injection facilities was utilized. From these experiences it was possible to completely eliminate phosphorus at high residual carbon levels.

While North American and European steelmakers have no current justification for resorting to external dephosphorization treatments of hot metal due to low phosphorus ores and charges to the BOF, the Japanese are burdened with high phosphorus Australian ores and high hot metal-to-scrap ratios charged to furnaces. In addition, due to the current practice of recycling LD slag to the blast furnace, there is a build-up of phosphorus in the steelmaking process which cannot be adequately removed by conventional means. This situation is further complicated by recent Japanese trends toward the use of lower slag volumes which further restrict refining capacity in the BOF. Since a large percentage of Japanese steel production is continuously cast, additional problems are created with the

high tapping temperatures required by continuous casting streams since a reduction in phosphorus refining efficiency results. Thus, the present emphasis in Japan on external refining of phosphorus is a specific requirement which has evolved from the particular form of steelmaking practice. However, since these practices produce what are commonly referred to as "ultra-pure" steels, the commercial availability of such grades may lead to stricter residual requirements in certain applications and will certainly generate potential markets for such steels. Thus, renewed interest in external dephosphorization has been generated world-wide within the past few years.

In North American steelmaking practice, conventional wisdom has dictated the utilization of high silicon hot metal for the heat requirements in melting scrap charged to the BOF. However, recent theoretical mass and energy balance treatments of BOF operations by separate workers²⁵⁸⁻²⁶¹ have concluded that the traditional conception of silicon oxidation as a cheap source of heat input is unfounded and that the actual energy recovery efficiency for melting of scrap is rather poor. In addition, the use of high silicon hot metal charge leads to many adverse effects such as excessively high operating temperatures, increased slopping, large slag volumes, high sensible heat losses, increased lime charging requirements and oxygen consumption, reduction in lining life, increased iron losses to the slag, and problems with carbon end-point control.

Since slag refining behavior and capacity for sulphur and phosphorus removal is generally fixed by slag basicity and volume, within the context of external refining pretreatment, there is no need for the presence of a slag during converting if the refining capacity is not required. Recent practice in Japan has taken this approach in pilot studies of "slagless

converting" or Nippon Steel's "Slag Minimum Refining Process", where decarburization is performed either in the presence of a small volume of very basic slag or in the absence of any slag. Based on preliminary results,²⁶² both silicon and phosphorus can be removed prior to decarburization by close control of oxidation via mill scale and oxygen input. Lime charging requirements are reduced dramatically, iron yield is improved, and, due to reduced acid slag exposure, lining life is extended and process control is improved.

Current dephosphorization reaction studies in Japan have looked at rather exotic reactants to achieve phosphorus removal prior to the onset of significant decarburization, presumably without any historical perspective of preliminary refining treatments with more conventional slag systems and process operations. Soda ash, carbonate and sulfate treatments,^{224-5, 227, 241-2} oxychloride and fluoride fluxes,²²⁸⁻²³⁰ carbide-fluoride solutions²³¹ and alkali metal based fluxes²³³⁻⁹ have been studied empirically and attempts to offer theoretical explanations for observed reaction behavior have led to misleading and incorrect formulations. Quasi-chemical equilibrium interpretations of reactions far removed from equilibrium have been proposed with complete disregard for underlying kinetic features and the dynamic nature of the reaction system. Phosphorus reaction formulations and reaction products are postulated without any solid evidence and, in certain cases, these "equilibrium" treatments contradict known thermodynamic data.

The problem that plagues virtually all of these exotic pretreatment schemes is that the dephosphorization reaction product is unstable and phosphorus readily reverts back to the metal after addition of the reagents. Additional problems exist with the strong temperature dependence of these reactions and endothermic decomposition of the reactants when

contacted with hot metal in the case of carbonates, sulfates, halides and alkali oxides. Extreme refractory corrosion, ventilation, and atmospheric control problems are encountered with scaling up such processes and these are unlikely to compete successfully on an industrial scale. More conventional reaction schemes using recycled slag and mill scale are likely to supersede such exotic pretreatments.

Only one recent Japanese study of prereducing treatment with recycled LD slag has attempted phosphorus refining prior to decarburization within a conventional refining environment. Both desiliconization and dephosphorization were observed prior to decarburization when hot metal was contacted with an oxidized basic slag while the metal was impeller-stirred. The authors were at a loss to explain observed behavior on the basis of thermodynamic arguments.^{221, 222}

A summary of selected kinetic studies of the dephosphorization reaction is presented in Table 2.1 as a way of comparing previous work. For each study listed, the maximum observed value for the "apparent mass transfer coefficient" of phosphorus is given along with pertinent experimental information.

Table 2.1: Summary of Previous Dephosphorization Kinetics Studies

Study (Ref.)	Alloy Composition (%)		Slag System	Oxidation Source	Hydro-dynamic Conditions	Temp. Range (°C)	Apparent Mass Transfer Coefficient (cm/s)
	Phosphorus	Other Solutes					
Fujii(210)	0.24-0.38 0.25-0.3	- <u>C</u> :2.0-2.5	CaO(s) "	Gas (O ₂)	Induction Stirring	1600 1450-1600	0.032 0.052 ($k_c=0.043$)
Kawai(211)	- 0.3-0.35	- <u>C</u> :0.6-1.1	CaO(s) "	Gas (H ₂ /H ₂ O)	Induction Stirring	1593-1700	0.003 0.002 ($k_c=0.014$)
Kawai(212)	0.225	-	CaO-FeO (50%CaO)	Slag ('FeO')	Induction Stirred	1600	0.028
	0.37	-	CaO-FeO (40%CaO)	"	"	"	0.030
	-	<u>Si</u> :0.5	CaO-SiO ₂ -MgO + 8%P ₂ O ₅	Reversion Experiments	"	1590	0.042 $k_{Si}=0.033$)
Aratani(213)	0.3	<u>O</u> :0.05	CaO-FeO (45%CaO)	Slag ('FeO')	No Stirring	1600	0.040 ($k_o=0.020$)
	0.3	<u>O</u> :0.07	CaO-SiO ₂ -FeO	"	"	1550	0.016 ($k_o=0.012$)
	-	-	CaO-SiO ₂ -FeO + 3.54% P ₂ O ₅	Reversion Experiment	"	"	0.029
Mori(214)	0.3-0.4	<u>O</u> :0.03-0.10	LD Slags (CaO/SiO ₂ =0.5-1.76)	Slag ('FeO')	Induction Stirring - No Stirring	1570 1680	0.026
	0.006-0.01	<u>O</u> :0.034-0.153	LD Slags + P ₂ O ₅	Reversion Experiments	"	"	0.020 0.023
Takenouchi(215)	0.085	0.009	CaO-CaF ₂ -FeO + Fluxes	Slag ('FeO')	No Stirring	1600	0.131
	0.011-0.014	<u>S</u> :0.013-7 <u>O</u> :0.007.04	"	Residual <u>O</u>	"	"	0.125 ($k_s=0.159$)
Riboud(216)	1.5	-	CaO-SiO ₂ -Al ₂ O ₃ -FeO (N _O /N _{Fe} =1.43)	Slag ('FeO')	Forced Convection (Falling Drop)	1550	0.021
	1.5	<u>C</u> :2.5	"	"	"	"	0.074 ($k_c=0.008$)
Jahanshahi(191)	0.12	<u>O</u> :0.23	CaO	Residual <u>O</u> + Gas(O ₂)	Induction Stirring	1600	0.78
	0.12	<u>O</u> :0.23	CaO-CaF ₂ -SiO ₂	"	"	"	0.66
	0.11	<u>C</u> :4.31	CaO-CaF ₂	"	"	"	No Reaction ($k_c=0.040$)

Table 2.1: Summary of Previous Dephosphorization Kinetics Studies (cont.)

Study (Ref.)	Alloy Composition (%)		Slag System	Oxidation Source	Hydro-dynamic Conditions	Temp. Range (°C)	Apparent Mass Transfer Coefficient (cm/s)
	Phosphorus	Other Solutes					
Present work	0.193	$\underline{C}$:0.417	CaO-FeO	Slag ('FeO')	Induction Stirring	1600	0.063 ($k_c=0.011$)
Inoue(224)	18.23	-	Na ₂ CO ₃	Carbonate	Mechanical Stirring	1300	0.002
	0.849	$\underline{C}$:4.75	"	"	"	1250	0.014
	0.2	"	"	"	"	"	0.014
Suito(225)	0.1	$\underline{S}$:0.05	Na ₂ CO ₃ -	Carbonate-Sulfate	Mechanically Stirred	1250-	0.036
	-	$\underline{C}$:4.75	Na ₂ SO ₄	Reversion Experiments	"	1350	($k_s=0.015$)
	-	$\underline{C}$:4.75	3Na ₂ O.P ₂ O ₅			1250	0.0006
Inoue(144)	0.1	$\underline{S}$:0.05	CaCO ₃ -	Carbonate-Sulfate	Mechanically Stirred	1250-	0.047
	"	$\underline{C}$:4.8 (graphite sat.)	CaSO ₄			1450	
	"	$\underline{Si}$:0.5	"	"	"	"	0.006
	"	$\underline{Mn}$:0.6	"	"	"	"	($k_{Si}=0.006$)
	"	$\underline{Cr}$:8.0	"	"	"	"	0.017
	"	$\underline{C}$:4.8 (unsat.)	"	"	"	1350	($k_{Mn}=0.022$)
	"	"	"	"	"	"	No Reaction
	-	$\underline{C}$:4.8	CaCO ₃ -Fe ₂ O ₃	Slag ('FeO')	"	"	0.017
	-	"	3CaO.P ₂ O ₅	Reversion Experiments	"	1250	($k_c=0.008$)
	-	"	3CaO.P ₂ O ₅ + CaF ₂	"	"	1350	0.012
Inoue(229)	0.18-0.24	$\underline{S}$:0.14 -0.66	CaO-CaCl ₂	Coupled Transport of Oxygen	Natural Convection	1250-1350	0.018
	"	$\underline{C}$:4.8	CaO-CaCl ₂	Fe ₂ (SO ₄) ₃ MnO ₂ CaSO ₄ CaCO ₃ FeO	"	1250-1350	0.046
	0.20	$\underline{S}$:0.14	CaO-CaCl ₂ -SiO ₂	Gas (O ₂)	Gas Injection	1350	0.006 ($k_c=0.004$, $k_s=0.054$)

III. OUTLINE OF WORK AND EXPERIMENTAL APPROACH

As seen in the review of previous dephosphorization reaction studies, our present understanding of the reaction mechanism and interpretation of experimental and operational observations is inadequate. This situation arises from a combination of factors: confusion of equilibrium and kinetic effects, complete disregard for hydrodynamic mass transport principles and complimentary chemical thermodynamic potential gradients, confusion over "mass transfer coefficients" and chemical reaction "rate constants", and ignorance with regard to complex slag phase equilibria and the associated complexity of the heterogeneous reaction systems encountered in such studies.

Rather than attempt to burden the literature with yet another kinetic study and repeat previous work, maximum benefit could be derived from reconstructing a picture of phosphorus reaction behavior based on previous observations of various reaction schemes. Having provided such a basis for proceeding, it was desirable to test our conceptual understanding of the dephosphorization reaction mechanism with selected experiments.

Since it is exceedingly difficult to match laboratory reaction conditions with a particular steelmaking practice due to problems with matching contact conditions, stirring effects, and temperature and chemical potential gradients, a laboratory study which provided the most remarkable example of the relative importance of kinetic rather than thermodynamic reaction features seemed appropriate.

In order to achieve this end, the interactions of phosphorus, silicon and carbon during oxidation refining seemed to be of fundamental interest, and initially, the levitation melting technique was utilized for timed sampling of various alloys during oxidation with both gas and slag phases. Because the initial contacting period and reaction geometry with this

technique are relatively undefined, a more conventional contacting method was ultimately desired. Since the establishment of diffusion gradients and precipitation of reaction products at the slag-metal interface was considered likely in a less turbulent environment, and it was important to establish the influence of such features on reaction behavior, a crucible containment method was selected to compliment the initial levitation studies.

Initial studies involved contacting an iron-phosphorus alloy containing various amounts of carbon and silicon with a highly oxidized calcium ferrite slag. For comparison, some of these alloys were levitated in the presence of an unoxidized lime-based slag and oxidized via introduction of an oxidizing gas. In addition, timed crucible-quenching experiments were performed to study phosphorus and silicon interactions during oxidation with a calcium ferrite slag. Since removal of phosphorus simultaneously with carbon and silicon must certainly occur under non-equilibrium conditions, the kinetics of reversion of phosphorus due to reduction of calcium phosphate by iron-carbon alloy was also investigated.

Experimental details are described in Section IV and the results and discussion of reaction mechanisms is presented in Sections V and VI, respectively.

IV. EXPERIMENTAL DETAILS

In this section, experimental details are provided for both levitation melting experiments and crucible containment experiments. While the apparatus and procedures for the levitation kinetic experiments were very similar to those described previously in Part A, and will not be repeated, general experimental procedures are given in Section A. In Section B, details are presented for the crucible containment studies.

A. Levitation Kinetic Studies

A general discussion of the levitation technique, experimental apparatus design, alloy and slag sample preparation procedures and sample analysis is provided in the preceding study of equilibrium experiments presented in Part A. Experimental procedures for the kinetic studies were quite similar to the equilibrium studies, with the notable exception that drop quenching of the levitated sample was performed at various stages of the reaction, prior to the attainment of equilibrium, and the alloy sample was subsequently analyzed for phosphorus, carbon and silicon while the slag sample was recovered for further analysis. Carbon was analyzed by the standard combustion method while silicon and phosphorus were analyzed by the inductively coupled plasma photometry method.¹⁹⁴ Similar procedures were used for the phosphorus reversion studies.

B. Crucible Containment Studies

Although the levitation technique enables one to study slag-metal reaction behavior under turbulent conditions during the initial stages of contact, it is rather difficult to obtain quantitative information from such experiments due to considerable uncertainties in reaction geometry and temperature during such short reaction periods. For quantitative information, a conventional crucible containment contacting technique is preferred where contact conditions and geometry are relatively well

defined. In addition, salient reaction features such as diffusional gradients and reaction product formation at the interface can be readily observed when they occur. Initially, timed sample quenching experiments were considered necessary to establish the nature of transport or interfacial reaction problems prior to timed bath sampling experiments. It was desirable to determine whether suitable and representative sampling of the bath was possible under such quiescent reaction conditions where diffusional processes may be rate limiting or reaction product formation may occur at the slag-metal interface.

1. Experimental Apparatus

A high temperature lanthanum chromite tube furnace was used for all crucible containment studies. Constant temperature control was provided by a Eurotherm P.I.D. controller (30 amp / 240 v) and furnace temperature was monitored with the use of a Pt-6Rh / Pt-30Rh thermocouple and digital voltmeter. The chromite elements were connected in two parallel sets of three elements in series, and approximately 22 amps of power were required for continuous operation at 1600°C.

A mullite furnace reaction tube (46 mm I.D.) was used with water cooled brass end caps as seals which permitted control over the furnace atmosphere. These fittings permitted the introduction of controlled gas atmospheres, sampling and viewing of the experimental crucible, and thermocouple temperature measurement. Specially fabricated magnesia reaction crucibles (10 mm I.D., 50 mm long) were placed within fabricated magnesia protection crucibles (20 mm I.D., 65 mm long) and supported on an alumina platform which was machined to fit the end of a mullite thermocouple protection tube (8 mm O.D., 90 cm long). The crucible assembly was introduced at the furnace bottom and brought into the reaction zone using the thermocouple tube as a support. A diagram of the experimental assembly

is shown in Figure 4.1. In all experiments, high purity argon was used as a furnace purging gas.

Initial experiments were attempted using commercially available labware for reaction crucibles. High purity recrystallized alumina, beryllia and recrystallized magnesia were tried and none of these materials was found to be suitable for containing high FeO slags, even for short reaction times. Either rapid attack, or permeation and breaching of these crucibles occurred within the duration of an experiment.

While, according to established phase equilibria, magnesia should have relatively limited solubility in these slags, the porosity and purity of commercially available grades rendered them unsuitable for experiments with high FeO slags. These slags readily attack the silicate glass bond used in sintering this material and the presence of calcium oxide impurity in the material introduces complications of crucible-alloy side reactions with phosphorus. Previous studies have been significantly influenced by such interactions.^{217, 218, 220} For this reason, it was necessary to develop a method for fabricating high density and high purity magnesia crucibles for continuation of this work. The method of preparation is described in Appendix C.

2. Experimental Procedure

Initially, four grams of alloy were charged to the magnesia reaction crucible and this was placed within a magnesia protection crucible on the alumina pedestal support. The bottom furnace cap was removed and the crucible assembly was inserted and slowly raised into the furnace hot zone so as to avoid thermal shock. Approximately two grams of pre-fused slag were pressed into 5 mm diameter pellets for charging to the crucible. For the initiation of slag-metal contact, the top furnace port was opened, a quartz tube (8 mm I.D.) was located over the magnesia reaction crucible,

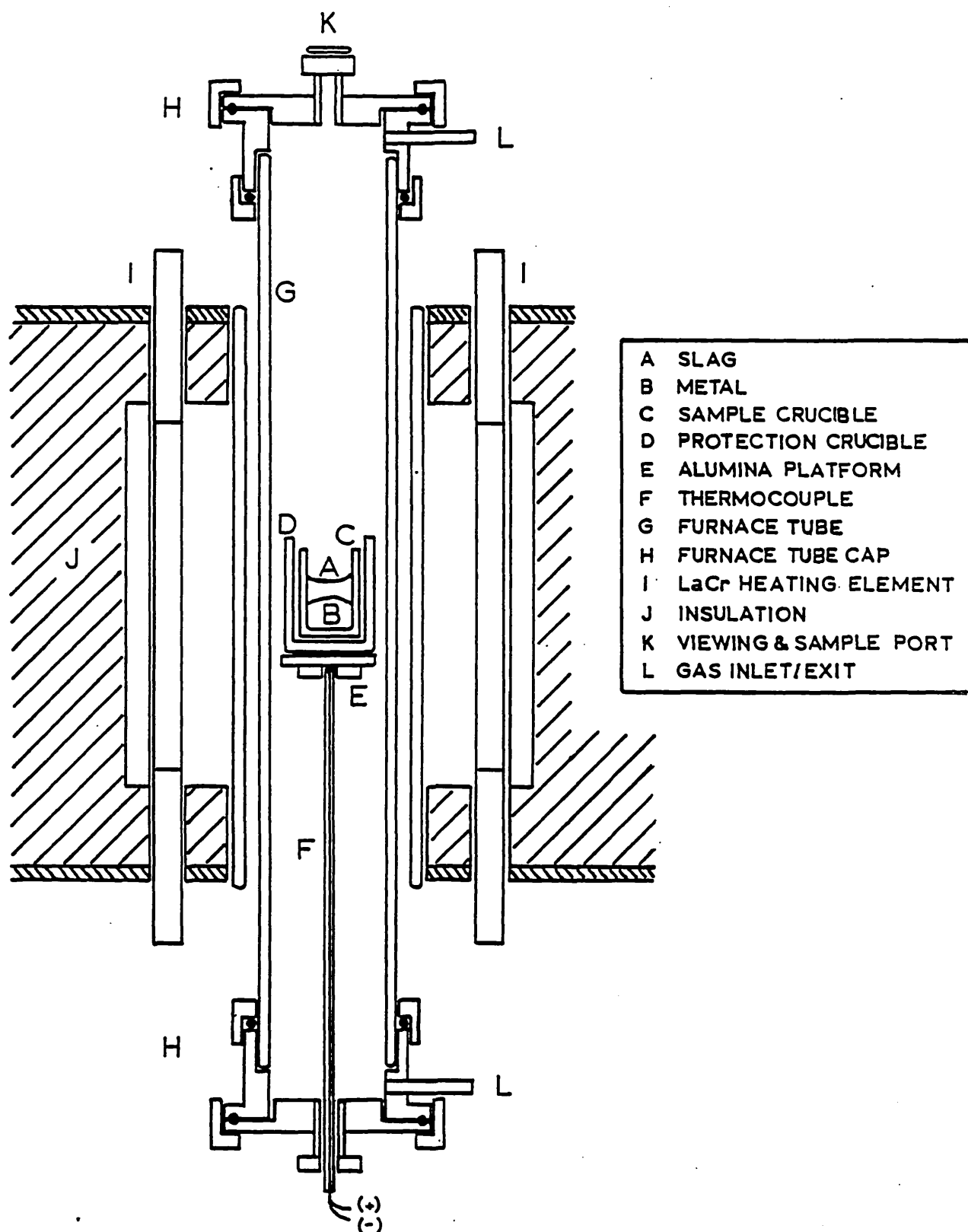


Figure 4.1 The Experimental Assembly Utilized in Crucible Quenching Experiments.

and the slag pellets were dropped onto the melt surface using the tube as a guide. The tube was then removed and the furnace cap replaced. Completion of the slag fusion was used as the initial contact time, since this occurred well within 30 seconds, and timed samples of the entire crucible-alloy-slag sample were taken at appropriate intervals over a thirty minute period by quenching the reaction crucible in the furnace cold zone.

3. Sample Treatment and Analysis

Each crucible sample was sliced in the axial direction with a silicon carbide slitting wheel. One half of the sample was rough polished, then vacuum impregnated with casting resin so as to maintain the integrity of the friable slag phase in contact with the alloy and crucible. The superfluous crucible material was cut away so that the specimen could be mounted within a standard metallographic specimen die. After mounting in bakelite, the sample was polished to metallographic standard for subsequent optical and electron microscope evaluation.

Microprobe analysis of samples was performed on a Cambridge Geoscan microscope. A gallium phosphide standard (30.76 %P) and the phosphorus K_{α} line were utilized for analysis at the 2θ angle of $82^{\circ}20'$. Since phosphorus levels were generally quite low, long count times and high beam currents were required. Unfortunately, these procedures increased the background noise and reduced sensitivity. The beam current was 140 uAmps at 15 KV providing a 30 nAmp specimen current. One hundred second count times were required and a minimum of five readings were taken for each point analyzed. Under such conditions, the phosphorus standard gave a 4000 counts per second reading, while the background yielded 5 counts per second (equivalent to 0.04 %P). Thus, while detection limits of ± 0.002 %P have been reported, a sensitivity of only ± 0.04 %P was actually obtained.

Microprobe analysis of previously analyzed phosphorus alloy standards yielded very good agreement with classical colorimetric trace analysis methods.

V. RESULTS

In this section, the experimental data for slag-metal oxidation kinetic experiments are presented in graphical form in Figures 5.1 through 5.3 for levitation studies. In Figure 5.4, the reversion kinetic behavior for tetracalcium phosphate and iron-carbon alloys is given. The changes in phosphorus, carbon and silicon concentrations with oxidation time are presented for each alloy studied. Tabulated data for these reaction studies are presented in Appendix B.

For timed quenching experiments of slag-metal-crucible samples, only one sample set was analyzed due to instrument technical problems which prevented analysis of the remaining samples within the time frame of this study. It is the intention of the author to make these results available in a future publication on the subject. Although the results of the analysis are inconclusive, the presence of phosphorus diffusion gradients was established at various quench times. Significant analytical problems were encountered in trying to analyze the trace phosphorus content of calcium-containing slags due to interference of the calcium K_{β} and phosphorus K_{α} lines. The solution to this problem has not been achieved as of the date of publication of this document.

A critical discussion of the results of this study in light of previous reaction studies and observed refining behavior is presented in Section VI.

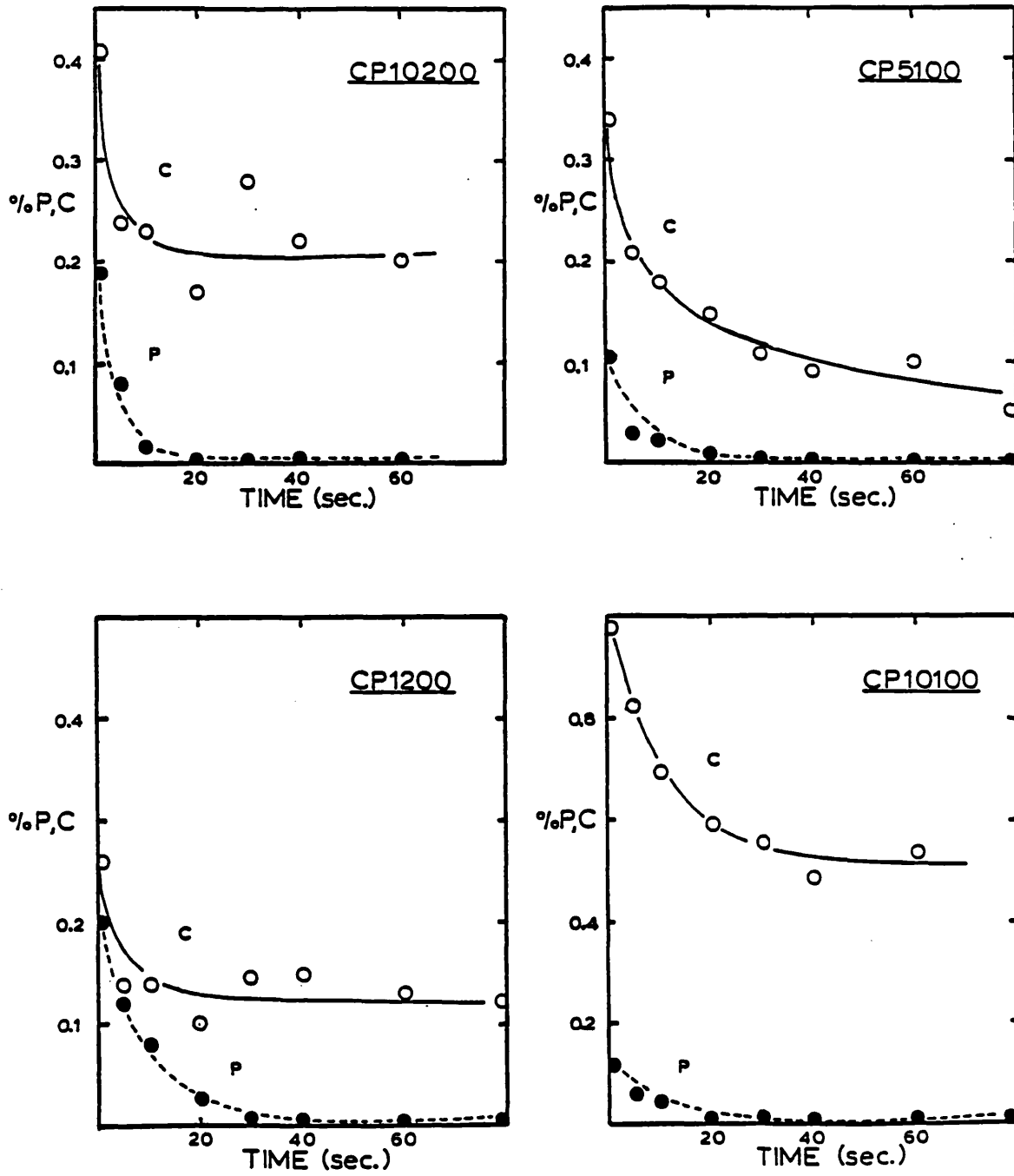


Figure 5.1 Slag-Metal Oxidation Behavior of Selected Fe-P-C Alloys.

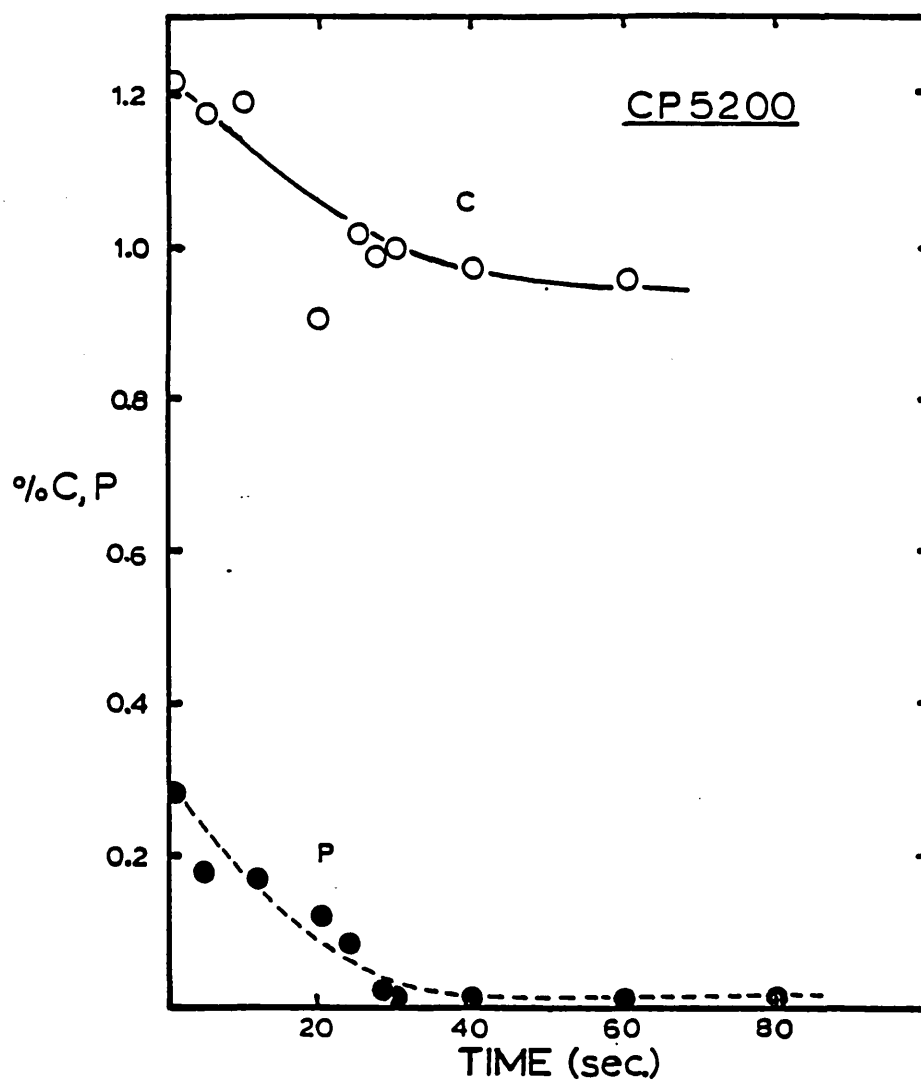


Figure 5.1 (cont.) Slag-Metal Oxidation Behavior of Selected Fe-P-C Alloys.

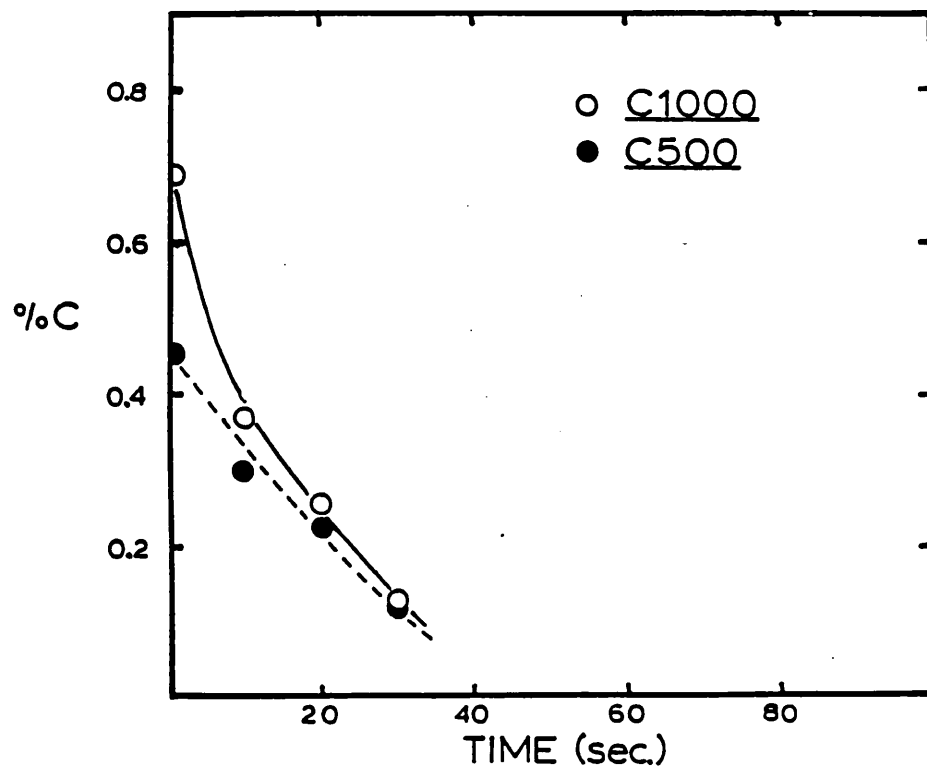


Figure 5.2 Slag-Metal Oxidation Behavior of Selected Fe-C Alloys.

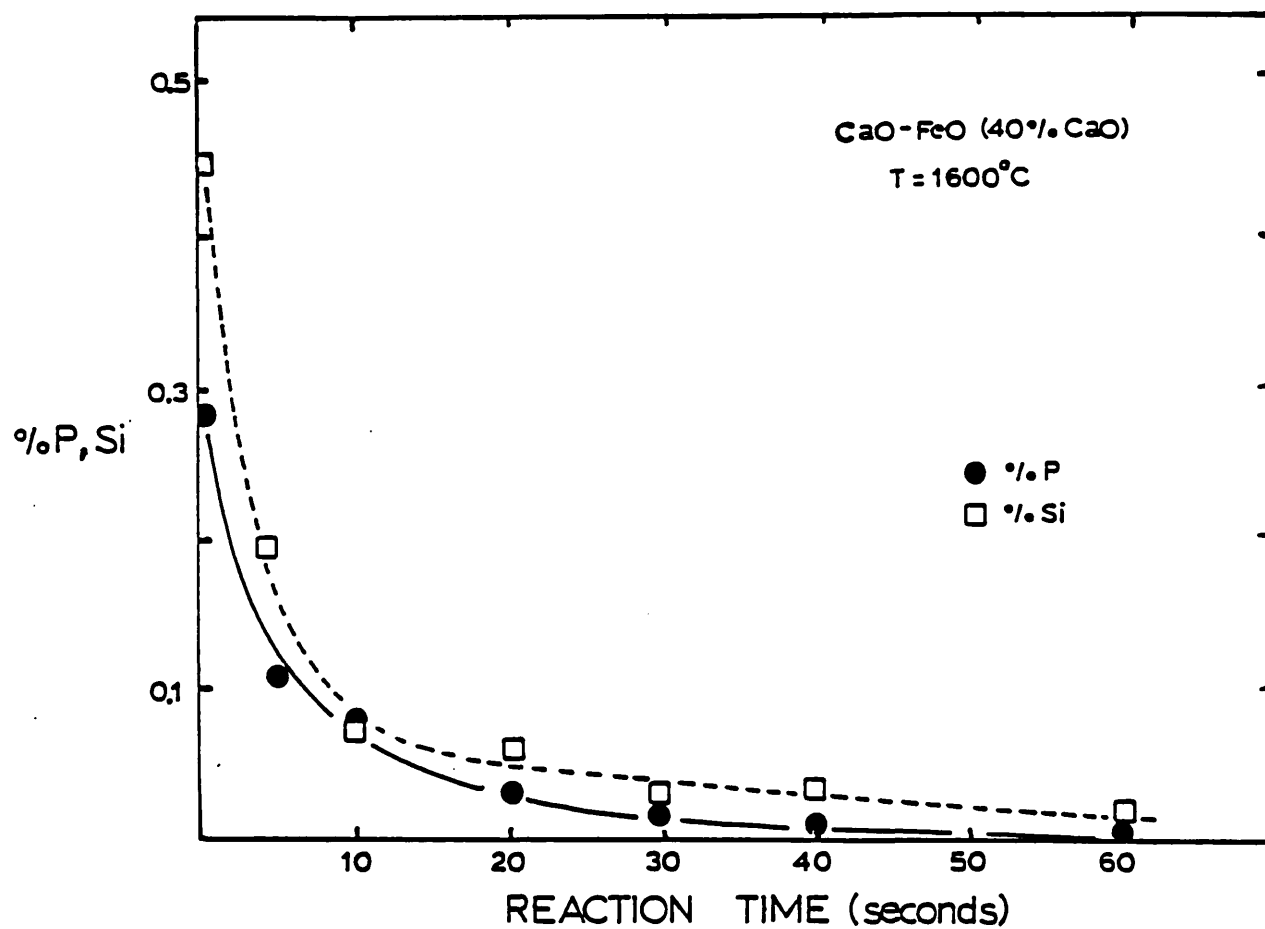


Figure 5.3 Slag-Metal Oxidation Behavior of Fe-P-Si Alloy.

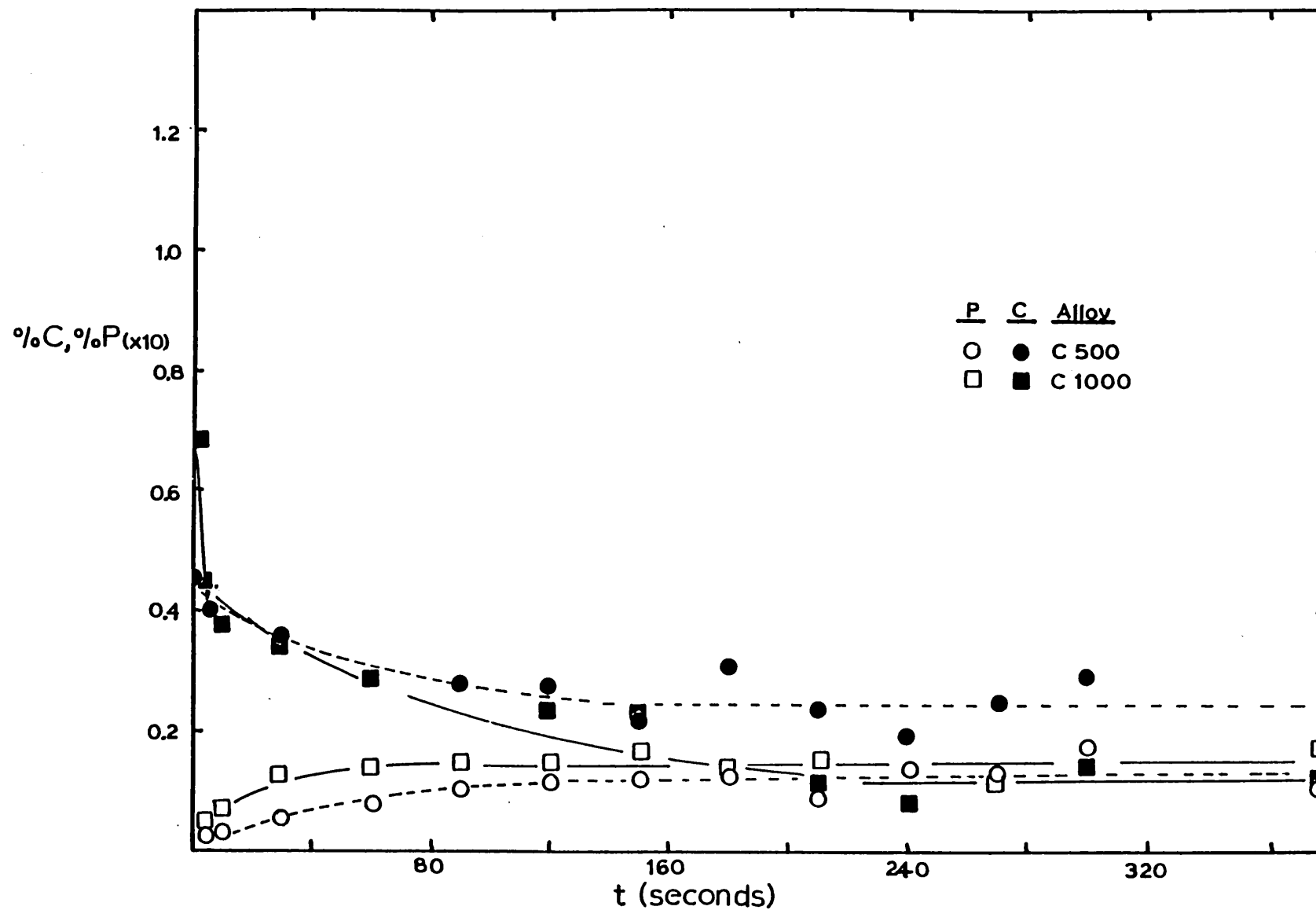


Figure 5.4 Phosphorus Reversion Behavior of Tetracalcium Phosphate and Fe-C Alloys.

VI. DISCUSSION OF RESULTS

As seen previously in the review of dephosphorization kinetics literature, some workers have observed that simultaneous removal of silicon, carbon and phosphorus during oxidation of iron alloys was possible, providing suitable reaction conditions were met. These observations have been made in the flush slag open hearth practice, during the emulsion refining period in top blown converters, in the Kaldo practice and in early hot-metal pretreatment studies. More recently, attention has focused on such refining behavior in Q-BOP or bottom blown converters, with lime injection practice and in external hot-metal refining studies with a variety of fluxes. Present understanding of the refining behavior of carbon, silicon and phosphorus during oxidation of iron alloys cannot adequately explain these observations of simultaneous reaction, and it was the intent of this study to provide a self-consistent reaction model which would clarify dephosphorization behavior.

Within this section, the results of the present work are discussed in conjunction with previous kinetic studies. By incorporating our present understanding of the role of complex slag phase relationships, provided by the results of the equilibrium study presented in Part A, a consistent and comprehensive picture of the phosphorus refining reaction is presented which explains previous inconsistencies and clarifies apparent contradictions in observed and predicted reaction behavior.

A. Oxidation of Fe-P-C Alloys

As seen from the results presented for oxidation of Fe-P-C alloys with calcium ferrite slag, in each case phosphorus was removed to trace levels even with relatively high residual carbon levels which considerably exceed those predicted from equilibrium considerations. The rate of dephosphorization was, in each case, comparable to the rate of decarburization and, in

some cases, surpassed the rate of decarburization. This behavior was observed even when the initial molar ratio of phosphorus to carbon varied from 1:3 to 1:20. This would suggest that the dephosphorization reaction proceeds at a much faster rate than the decarburization reaction when oxidation proceeds via a slag-metal interface.

On the basis of the present study, it appears that the initial decarburization rate, under such conditions, is directly proportional to the amount of slag oxygen available and is inversely proportional to the initial phosphorus content of the alloy. In contrast, the initial dephosphorization rate is independent of the initial carbon content and slag weight. These results demonstrate that phosphorus is highly competitive with carbon for slag oxygen. The dependence of the decarburization rate on the initial phosphorus content and initial slag weight indicates that the decarburization reaction is probably controlled by oxygen transport to the metal surface. The initial dephosphorization rate appears to be independent of the initial carbon content and initial slag weight. It is the author's opinion that under such contacting conditions the dephosphorization rate is primarily dependent on the slag-metal interfacial area. This agrees with the work of Esin,²⁸⁴ where the rate of dephosphorization was found to be area dependent. Unfortunately, there is considerable uncertainty in estimating the slag-metal interfacial contact area under such reaction conditions. In virtually every case, the slag and metal emulsified upon contact. Thus, the area of slag-metal contact substantially increased and could not be measured with any degree of accuracy, making quantitative measurements of mass transfer coefficients virtually impossible. Minaev reported similar problems in this regard.²⁴⁵

B. Oxidation of Fe-P-Si Alloys

While evidence has shown that the carbon and phosphorus reactions

during oxidation are parallel and simultaneous under certain contacting conditions, it has been generally assumed that silicon and phosphorus oxidation are sequential, with desiliconization occurring prior to the initiation of dephosphorization. This implicit understanding is based on an equilibrium thermodynamic approach to the two oxidation reactions. The concept of parallel and competitive reactions involving silicon and phosphorus was postulated during the course of this work with the provision that a significant chemical potential driving force is initially created for dephosphorization and that any kinetic barriers inhibiting the phosphorus reaction are eliminated. This theory was tested and the results presented in the previous section follow the predicted behavior where both phosphorus and silicon are simultaneously oxidized and incorporated into the slag phase. The parallel reaction was promoted by the highly basic and oxidizing character of the slag and the turbulent hydrodynamic conditions produced with this contacting method. The slag phase reaction product has not been identified to date although it is thought to be a calcium silico-phosphate solid solution, as predicted by known phase equilibria presented previously in Part A.

C. Comparison of Present Work with Previous Studies

In a previous unpublished study of gas phase oxidation of levitated Fe-P-C alloys in the presence of basic slags, Jahanshahi¹⁹¹ observed that no dephosphorization occurred prior to decarburization. Kawai and co-workers²¹¹ also observed that, during gas phase oxidation of Fe-P-C alloys contained in lime crucibles, decarburization was completed prior to the initiation of dephosphorization. In a closely related study, Fujii²¹⁰ obtained simultaneous reaction of carbon and phosphorus, at comparable rates, during oxygen blowing onto the surface of an Fe-P-C alloy when lime powder was charged on the metal surface. Riboud²¹⁶ also observed simul-

taneous reaction of carbon and phosphorus during oxidation of Fe-P-C alloy with oxidized basic slags. The rate of dephosphorization was much faster than that of decarburization and exceeded the rate of dephosphorization of Fe-P alloys under similar conditions. The presence of phosphorus actually impeded the decarburization reaction. It is interesting to note that, in a related study of decarburization kinetics of iron alloy droplets immersed in oxidized basic slags, Gare²²⁶ observed that the presence of phosphorus dramatically inhibited the decarburization reaction and that phosphorus was preferentially oxidized. In a related study, Aleev and Grigoryan have reported that, when diffusional mass transport control is eliminated in slag-metal contact, trace levels of phosphorus exert a profound influence on retarding the decarburization rate.²²³ They claim that this is due to surface tension factors.

Such apparent inconsistencies are readily explained if one considers the fundamental nature of the two refining reactions and possible slag-metal and gas-metal transport mechanisms. Dephosphorization obviously requires a slag-metal interface for transfer of phosphorus to occur by way of reaction with calcium oxide. The gas phase phosphorus transport mechanisms proposed previously^{217, 218, 220} do not hold up to close scrutiny.^{191, 283} On the other hand, decarburization requires a gas-metal interface, since either CO or CO₂(g) is formed during oxidation of dissolved carbon. Since oxidation of alloys can occur either through the gas phase or by way of an oxidizing slag, by promoting one form of oxidation over another, either the phosphorus reaction is favored, as in the case of oxidation with basic slags, or the carbon reaction is promoted, by encouraging the gas-metal reaction. While decarburization can also occur with slag phase oxidation of alloys, from the results of the present study and those of Riboud²¹⁶ and Gare,²²⁶ it appears that the phosphorus

reaction is highly competitive with carbon over the oxygen provided via a basic slag phase, and that dephosphorization occurs preferentially at the expense of decarburization, when a significant chemical potential driving force exists for phosphorus removal.

This reaction model agrees with process observations. In top blowing, where emulsification of the slag and metal promote dephosphorization at the expense of decarburization,²⁵² soft blowing favors dephosphorization whereas hard blowing favors decarburization²⁴⁷⁻⁹ due to promotion of slag-metal or metal-gas reactions, respectively. Both Davies²⁰⁶ and Elliott²⁰⁵ noted that the promotion of carbon boil and gas-metal reaction had a major influence on the degree of dephosphorization and desiliconization achieved during preliminary refining. They observed that proper control over the slag oxidation state was necessary so as to promote slag-metal transfer prior to the onset of carbon boil. Similar requirements were cited in recent studies of continuous prerefining processes in Japan.^{221, 222, 262}

Observations of simultaneous and parallel reaction of phosphorus and silicon during oxidation are less numerous. In most basic oxygen steel-making practices, desiliconization is completed prior to the initiation of dephosphorization. The reason for this is primarily due to the mechanism of lime dissolution in steelmaking converters. Silicon oxidation readily occurs via a gas-metal or slag-metal oxidation reaction, in similar manner to decarburization, but desiliconization via a gas phase always occurs simultaneously with fayalite slag formation as a reaction product. Since the dephosphorization reaction requires the presence of lime in order to provide a chemical potential driving force, no dephosphorization is observed during converter desiliconization since there is initially no thermodynamic driving force for phosphorus removal prior to the onset of

lime dissolution. If lime is placed in solution during the initial stages of oxidation, simultaneous reaction will occur as shown by the results of the present study. Similar observations have been made in two-slag, LD-AC processes,²⁷²⁻³ with pretreatments using recycled LD slags^{221, 222} and simultaneous additions of powdered lime with oxygen^{240, 271} or mill scale.^{206, 244}

Based on the known stability of the calcium silico-phosphate solid solution, as discussed in Part A of this work, it is most likely that, during oxidation, both silicon and phosphorus are simultaneously incorporated into a solid solution reaction product, providing lime is initially present at the metal-slag interface. It is interesting to note that microstructural observations have shown that phosphorus is initially incorporated into a dicalcium silicate solid solution when solid lime or lime-rich slag is contacted with Fe-P-Si alloys during oxidation.²⁷¹⁻³ In this regard, both Aratani²¹³ and Ono²⁴³ have reported enhanced dephosphorization rates when refining slags approached the dicalcium silicate saturation surface.

D. Phosphorus Reversion Behavior

While these reaction models for simultaneous dephosphorization, decarburization and desiliconization are able to explain important kinetic features which enable simultaneous oxidation of the three solutes, perhaps the most important kinetic feature when considering these reactions is the explanation for the rather slow phosphorus reversion rates observed in slag-metal contacting. As seen from the results of this study, only slight reversion of phosphorus occurs when tetracalcium phosphate is contacted with iron-carbon alloys. These results agree with the observations of Inoue and Suito²²⁶ who observed only slight reversion of phosphorus when tricalcium phosphate was reduced with carbon saturated iron at 1350°C.

Shiomi and co-workers²⁴⁶ treated low basicity phosphate slag with both silicon and carbon and found rather slow phosphorus reduction rates. In both cases, iron oxide was reduced prior to phosphorus and phosphorus reversion was initiated upon the formation of an iron alloy which adsorbed reduced phosphorus. Yakavlev and co-workers²⁷⁰ observed that the reduction of phosphate slags with both lump and powdered aluminum was also rather slow.

Rather important kinetic features underlie these observations since thermodynamic equilibrium considerations alone cannot explain such behavior. However, careful consideration of the complexity of phosphate slag phase equilibria is essential. In considering the reduction of the refractory calcium phosphates or calcium silico-phosphates or slags close to saturation with these phases, rather complex heterogeneous reactions would be anticipated with phase contact problems and metastable reaction situations almost certainly encountered. If Fe-C or Fe-Si alloy is contacted with any of these refractory phases, some slight reversion of phosphorus would be expected from a surface reaction at the contact interface. However, a reaction product layer of either solid lime or dicalcium silicate would immediately form and pose a barrier to further contact. Thus a solid-state diffusion mechanism would become rate limiting and very little reaction would occur within a finite time period.

In the case of heterogeneous slags, where the liquid is saturated with respect to any of these refractory phases and phosphorus has rather limited true solubility in the liquid phase, even greater problems of phase contact would occur and essentially no reversion would be observed. This scenario is particularly valid in the case of slags saturated with respect to the calcium silico-phosphate solid solution. Several workers have observed independently that phosphorus has a very limited solubility in liquids

saturated with this phase¹²⁹⁻¹³¹ and Ono¹³⁰ has found that segregation and differential floatation of the solid solution occurs due to the difference in densities of this phase and associated liquids.

These unusual features of phosphorus slag systems are thought to be responsible for observations of refining behavior during bottom blowing with lime injection and in hot metal oxidation via a flux or slag phase. When no stable refractory-type reaction product forms, reversion occurs immediately following phosphorus oxidation, unless oxidizing reagents are continuously added to satisfy the reaction with carbon or other oxidizable solutes. This is one reason why pretreatments with soda ash are unlikely to be successful.^{225, 241-2}

Understanding the importance of such metastable contacting conditions is essential for characterizing phosphorus refining during hot metal pretreatments and obviously requires knowledge and appreciation of slag phase relationships. Without selection of those unique conditions which are made possible by the complex phase equilibria of phosphate slag systems, hot metal refining of phosphorus would not be possible, and it is for this very reason that so many papers which have appeared recently in the Japanese literature on quasi-chemical reaction mechanisms are of such little scientific value.

In order to provide the reader with a useful model for predicting phosphorus reaction behavior within the context of a variety of reaction situations, the author has provided a schematic outline in Appendix D which attempts to clarify observed behavior and delineate various reaction schemes which may be encountered in actual practice.

VII. SUMMARY AND CONCLUSIONS

Initial results have demonstrated that dephosphorization and decarburization proceed simultaneously and in parallel fashion when Fe-P-C alloys are oxidized via a slag phase containing significant amounts of lime in solution. Based on the present findings and previous studies, it appears that promotion of slag-metal oxidation favors dephosphorization at the expense of decarburization whereas promotion of gas-metal oxidation inhibits dephosphorization.

Rather similar requirements are necessary for simultaneous refining of silicon and phosphorus, where lime dissolution kinetics are not dependent on in-situ slag formation of a fayalite liquid, and a chemical potential driving force for dephosphorization initially exists upon initiation of slag-metal oxidation.

Due to the character of complex phosphate slag phase equilibria and the refractory nature of the dephosphorization reaction products, unique, metastable contacting situations are possible which promote dephosphorization even when it is thermodynamically unfavorable.

Both hot metal pre-treatments and basic steelmaking converter reaction behavior can be coherently and consistently explained through the use of the reaction model proposed in this study which is complementary to the phase equilibrium data presented in Part A of this work.

VIII. APPENDICES

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APPENDIX A.

Slag-Metal Equilibrium Data.

Table A.1: Slag and Metal Compositions for Timed-Oxidation Experiments.

Sample	%P _{Fe}	%P ₂ O ₅	%FeO	%CaO	%SiO ₂	%MgO	Other
MO1	0.111	0.00	12.4	-	-	87.8	-
MO2	0.116	0.00	28.4	-	-	71.9	-
MO3	0.111	0.00	48.4	-	-	51.6	-
MO4	0.107	0.12	64.2	-	-	35.7	-
MO5	0.114	0.02	75.5	-	-	24.5	-
MO6	0.116	0.04	79.0	-	-	20.9	-
MO7	0.127	0.00	80.6	-	-	19.5	-
MO8	0.123	0.01	82.4	-	-	17.5	-
MO9	0.135	0.00	85.7	-	-	14.4	-
M10	0.131	0.00	92.3	-	-	7.8	-
M11	0.131	0.00	87.5	-	-	12.5	-
M12	0.136	0.03	87.2	-	-	12.8	-
M13	0.134	0.05	90.4	-	-	9.6	-
M14	0.143	0.04	90.7	-	-	9.3	-
D01	0.007	2.22	6.8	54.6	-	36.4	-
D02	0.018	2.65	20.5	46.1	-	30.7	-
D03	0.033	1.81	34.0	38.5	-	25.7	-
D04	0.024	1.70	53.1	27.1	-	18.1	-
D05	0.018	1.48	67.8	18.4	-	12.3	-
D06	0.025	1.10	72.5	15.8	-	10.5	-
D07	0.041	0.78	72.2	13.2	-	8.8	-
C01	0.001	2.16	34.4	63.4	-	-	-
C02	0.001	1.67	50.6	47.7	-	-	-
C03	0.000	1.32	60.8	37.9	-	-	-
C04	0.001	1.12	68.9	29.9	-	-	-
C05	0.035	0.64	71.7	27.6	-	-	-
C06	0.042	0.53	74.7	24.8	-	-	-
MF01	0.053	1.73	8.8	-	-	2.7	MgF ₂ 86.8
MF02	0.052	1.48	20.0	-	-	2.4	76.1
MF03	0.041	1.84	32.5	-	-	2.0	63.7
MF04	0.036	1.19	47.4	-	-	1.5	49.9
MF05	0.045	0.86	68.9	-	-	0.9	29.3
MF06	0.101	0.19	74.7	-	-	0.8	24.4
MCF01	0.064	1.66	10.1	-	-	22.1	CaF ₂ 66.2
MCF02	0.013	2.61	19.6	-	-	19.5	58.4
MCF03	0.010	2.62	36.7	-	-	15.2	45.5
MCF04	0.011	1.68	48.5	-	-	12.5	37.4
MCF05	0.010	1.15	64.4	-	-	8.6	25.8
MCF06	0.001	0.96	75.9	-	-	5.8	17.4

Table A.1: (Cont.)

Sample	%P _{Fe}	%P ₂ O ₅	%FeO	%CaO	%SiO ₂	%MgO	Other
CS101	0.031	3.86	11.2	68.0	17.0	-	-
CS102	0.005	3.29	19.1	62.1	15.5	-	-
CS103	0.008	2.67	31.8	52.4	13.1	-	-
CS104	0.000	2.07	46.6	41.1	10.3	-	-
CS105	0.000	1.66	56.1	33.8	8.4	-	-
CS106	0.000	1.38	62.8	28.7	7.2	-	-
CS107	0.001	1.17	66.4	26.0	6.5	-	-
CS201	0.086	1.73	11.9	60.4	25.9	-	-
CS202	0.045	2.38	21.5	53.3	22.8	-	-
CS203	0.014	2.40	31.6	46.2	19.8	-	-
CS204	0.001	1.97	47.4	35.4	15.2	-	-
CS205	0.000	1.55	55.5	30.1	12.9	-	-
CS206	0.003	1.29	62.3	25.5	10.9	-	-
CS207	0.002	1.11	66.5	22.6	9.7	-	-
CS301	0.059	1.34	6.8	55.1	36.7	-	-
CS302	0.042	1.48	15.2	50.0	33.3	-	-
CS303	0.023	8.04	46.5	30.3	20.2	-	-
CS304	0.016	1.75	61.6	22.0	14.7	-	-
CS305	0.015	1.52	66.8	19.0	12.7	-	-
CS306	0.060	0.69	75.1	14.5	9.7	-	-
CS307	0.061	0.60	78.6	12.5	8.3	-	-
CS401	0.089	0.95	33.8	32.6	32.6	-	-
CS402	0.043	1.49	47.6	25.5	25.5	-	-
CS403	0.029	1.26	66.3	16.2	16.2	-	-
CS404	0.109	0.25	78.1	10.8	10.8	-	-
CS405	0.050	0.97	53.9	22.6	22.6	-	-
CS406	0.088	0.54	65.3	17.1	17.1	-	-
CS407	0.086	0.54	61.1	19.2	19.2	-	-
CS408	0.077	0.56	67.3	16.1	16.1	-	-
CS501	0.124	0.16	8.3	36.6	55.0	-	-
CS502	0.116	0.32	17.9	32.7	49.1	-	-
CS503	0.095	0.79	43.1	22.5	33.7	-	-
CS504	0.080	0.81	60.1	15.6	23.4	-	-
CS505	0.074	0.79	69.9	11.7	17.6	-	-
CS506	0.061	0.76	74.9	9.7	14.6	-	-
CS507	0.101	0.33	77.9	8.7	13.1	-	-
DS101	0.056	1.99	7.8	43.3	18.0	28.9	-
DS102	0.041	2.18	17.3	38.7	16.1	25.8	-
DS103	0.014	2.31	29.1	32.9	13.7	22.0	-
DS104	0.012	1.84	44.9	25.6	10.7	17.1	-
DS105	0.008	1.53	54.7	21.0	8.8	14.0	-
DS106	0.025	1.12	61.2	18.1	7.5	12.1	-
DS107	0.018	1.03	65.8	16.0	6.6	10.6	-

Table A.1: (Cont.)

Sample	%P _{Fe}	%P ₂ O ₅	%FeO	%CaO	%SiO ₂	%MgO	Other
DS201	0.088	1.06	7.5	38.4	27.4	25.6	-
DS202	0.039	2.03	16.5	34.2	24.4	22.8	-
DS203	0.018	2.09	28.1	29.3	20.9	19.5	-
DS204	0.017	1.68	43.7	22.9	16.4	15.3	-
DS205	0.014	1.34	52.2	19.5	13.9	13.0	-
DS206	0.021	1.09	59.0	16.8	12.0	11.2	-
DS207	0.019	0.93	62.2	15.5	11.1	10.3	-
DS301	0.084	1.28	8.6	32.5	36.1	21.6	-
DS302	0.071	1.37	18.2	29.0	19.3	32.2	-
DS303	0.054	1.39	28.6	25.2	28.0	16.8	-
DS304	0.028	1.44	44.3	19.5	21.7	13.0	-
DS305	0.031	1.12	52.9	16.6	18.4	11.1	-
DS306	0.029	0.97	59.8	14.1	15.7	9.4	-
DS307	0.030	0.89	66.3	11.8	13.1	7.9	-
DS401	0.054	0.92	68.2	9.3	15.4	6.2	-
DS402	0.119	0.18	34.0	19.7	32.9	13.2	-
DS403	0.102	0.51	49.1	15.1	25.2	10.1	-
DS404	0.036	0.97	66.2	9.9	16.4	6.6	-
DS405	0.108	0.30	78.2	6.5	10.8	4.3	-
DS406	0.120	0.17	51.6	14.5	24.1	9.6	-
DS407	0.115	0.22	71.8	8.4	14.0	5.6	-
DS408	0.100	0.59	39.6	17.9	29.9	12.0	-
DCS101	0.057	2.58	9.9	56.0	17.5	14.0	-
DCS102	0.029	2.95	20.2	49.2	15.4	12.3	-
DCS103	0.006	2.82	31.0	42.4	13.2	10.6	-
DCS104	0.003	2.10	46.8	32.7	10.2	8.2	-
DCS105	0.002	1.70	56.6	26.7	8.3	6.7	-
DCS106	0.007	1.41	62.6	23.0	7.2	5.8	-
DCS107	0.003	1.12	68.7	19.3	6.0	4.8	-
DCS201	0.016	3.25	8.6	49.4	26.4	12.3	-
DCS202	0.009	2.99	18.8	43.8	23.5	11.0	-
DCS203	0.002	2.61	30.9	37.3	20.0	9.3	-
DCS204	0.005	1.97	47.1	28.5	15.3	7.1	-
DCS205	0.003	1.52	56.0	23.8	12.7	5.9	-
DCS206	0.007	1.26	62.2	20.5	11.0	5.1	-
DCS207	0.009	1.06	66.6	18.1	9.7	4.5	-
DCS301	0.124	0.19	9.2	43.5	36.3	10.9	-
DCS302	0.083	0.91	16.2	39.8	33.2	9.9	-
DCS303	0.062	1.56	31.9	31.9	26.6	8.0	-
DCS304	0.036	1.60	47.7	24.3	20.3	6.1	-
DCS305	0.028	1.35	55.7	20.6	17.2	5.2	-
DCS306	0.028	1.17	64.1	16.7	13.9	4.2	-
DCS307	0.088	0.51	68.9	14.7	12.3	3.7	-

Table A.1: (Cont.)

Sample	%P _{Fe}	%P ₂ O ₅	%FeO	%CaO	%SiO ₂	%MgO	Other
DCS401	0.085	0.87	34.9	25.7	32.1	6.4	-
DCS402	0.057	1.30	60.9	15.1	18.9	3.8	-
DCS403	0.071	0.76	56.5	17.1	21.4	4.3	-
DCS404	0.103	0.32	67.2	13.0	16.2	3.2	-
DCS405	0.111	0.23	59.7	16.0	20.0	4.0	-
DCS501	0.101	0.06	33.1	23.4	33.4	10.0	-
DCS502	0.073	0.52	58.6	14.3	20.4	6.1	-
DCS503	0.065	0.70	75.2	8.5	12.1	3.6	-
DCS504	0.093	0.20	67.6	11.3	16.1	4.8	-
DCS505	0.115	0.01	83.8	5.7	8.1	2.4	-
DCS601	0.076	1.11	38.8	22.5	30.0	7.5	-
DCS602	0.091	0.62	59.0	18.2	20.2	2.0	-
DCS603	0.033	1.10	66.0	14.8	16.4	1.6	-
DCS604	0.094	0.24	75.3	11.0	12.2	1.2	-
DCS605	0.071	0.40	75.7	10.8	12.0	1.2	-

Table A.2: Slag and Metal Compositions for Slag-Metal Equilibration Experiments

Sample	%P _{Fe}	%P ₂ O ₅	%FeO	%CaO	%SiO ₂	%MgO
CSB201	0.080	1.61	11.0	61.2	26.2	—
CSB202	0.034	3.32	20.5	53.4	22.9	—
CSB203	0.026	3.61	29.5	46.8	20.0	—
CSB204	0.007	4.39	38.9	39.7	17.0	—
CSB205	0.007	4.38	48.3	33.1	14.2	—
CSB206	0.010	4.54	56.5	27.3	11.7	—
CSB207	0.020	4.45	67.6	19.6	8.4	—
DSB201	0.081	1.72	10.8	36.7	26.2	24.5
DSB202	0.056	2.60	19.6	32.6	23.3	21.8
DSB203	0.046	3.03	28.8	28.6	20.5	19.1
DSB204	0.024	3.90	38.9	24.0	17.2	16.0
DSB205	0.025	4.29	48.0	20.0	14.3	13.4
DSB206	0.029	3.86	59.1	15.6	11.1	10.4
DSB207	0.033	3.94	67.0	12.2	8.7	8.2
DCSB201	0.054	2.63	9.7	49.1	26.3	12.3
DCSB202	0.039	3.14	19.3	43.4	23.3	10.9
DCSB203	0.013	4.00	28.1	38.0	20.4	9.5
DCSB204	0.007	4.73	41.2	30.3	16.2	7.6
DCSB205	0.009	4.53	48.0	26.6	14.2	6.6
DCSB206	0.018	4.29	57.6	21.4	11.4	5.3
DCSB207	0.037	3.07	20.5	42.8	22.9	10.7
DCSB208	0.021	3.60	29.8	37.3	20.0	9.3
CS2P101	0.192	1.46	10.1	70.7	17.7	—
CS2P102	0.122	4.13	19.5	61.1	15.3	—
CS2P103	0.062	6.45	28.0	52.5	13.1	—
CS2P104	0.007	8.54	36.4	44.0	11.0	—
CS2P105	0.019	8.21	45.6	36.9	9.2	—
CS2P106	0.052	7.14	55.9	29.5	7.4	—
CS2P107	0.051	7.24	64.7	22.5	5.6	—
DS2P101	0.177	2.08	10.6	41.9	17.5	28.0
DS2P102	0.178	2.10	19.5	37.6	15.7	25.1
DS2P103	0.163	2.75	29.0	32.8	13.7	21.8
DS2P104	0.104	5.09	38.3	27.2	11.3	18.1
DS2P105	0.085	5.92	47.1	22.5	9.4	15.0
DS2P106	0.083	6.04	56.4	18.0	7.5	12.0
DS2P107	0.089	5.88	65.2	13.9	5.8	9.2
DCS2P101	0.198	1.23	10.4	56.5	17.7	14.1
DCS2P102	0.192	1.48	19.9	50.3	15.7	12.6
DCS2P103	0.093	5.43	29.0	42.0	13.1	10.5
DCS2P104	0.104	5.00	37.9	36.5	11.4	9.1
DCS2P105	0.059	6.77	46.2	30.1	9.4	7.5
DCS2P106	0.048	7.32	55.7	23.7	7.4	5.9
DCS2P107	0.073	6.39	66.0	17.7	5.5	4.4

Table A.2: (Cont.)

Sample	%P _{Fe}	%P ₂ O ₅	%FeO	%CaO	%SiO ₂	%MgO
CS2P201	0.112	4.19	3.9	64.4	27.6	—
CS2P202	0.110	4.49	13.2	57.7	24.7	—
CS2P203	0.050	7.11	18.1	52.3	22.4	—
CS2P204	0.042	8.21	26.6	45.7	19.6	—
CS2P205	0.053	7.94	39.2	37.0	15.9	—
CS2P206	0.117	4.87	64.3	21.6	9.2	—
CS2P207	0.096	5.25	56.8	26.6	11.4	—
CS2P208	0.122	3.82	19.4	53.8	23.1	—
CS2P209	0.071	6.20	65.2	20.0	8.6	—
DS2P201	0.168	2.14	8.5	37.5	26.8	25.0
DS2P202	0.121	4.04	14.0	34.4	24.6	23.0
DS2P203	0.102	4.85	22.9	30.4	21.7	20.2
DS2P204	0.094	5.22	31.9	26.4	18.9	17.6
DS2P205	0.110	5.10	43.2	21.7	15.5	14.5
DS2P206	0.114	5.04	53.0	17.6	12.6	11.8
DS2P207	0.126	4.41	65.1	12.8	9.2	8.5
DCS2P201	0.136	3.32	6.5	50.5	27.1	12.6
DCS2P202	0.090	5.32	11.9	46.3	24.8	11.6
DCS2P203	0.028	8.15	16.3	42.3	22.7	10.6
DCS2P204	0.034	8.49	26.6	36.4	19.5	9.1
DCS2P205	0.055	7.70	39.6	29.5	15.8	7.4
DCS2P206	0.056	7.84	49.0	24.2	13.0	6.0
DCS2P207	0.051	8.15	59.1	18.4	9.8	4.6
CS2P301	0.155	2.77	9.7	52.6	35.0	—
CS2P302	0.131	3.69	19.7	46.0	30.1	—
CS2P303	0.110	4.36	28.9	40.1	26.7	—
CS2P304	0.086	5.25	37.9	34.1	22.7	—
CS2P305	0.079	5.58	47.3	28.3	18.9	—
CS2P306	0.096	4.98	56.7	23.0	15.3	—
CS2P307	0.170	2.28	68.3	17.7	11.8	—
DS2P301	0.159	2.64	10.0	31.4	34.9	21.0
DS2P302	0.153	2.84	20.0	27.7	30.8	18.5
DS2P303	0.146	3.13	28.9	24.5	27.2	16.3
DS2P304	0.101	4.74	38.3	20.5	22.8	13.7
DS2P305	0.094	5.13	47.7	17.0	18.9	11.3
DS2P306	0.105	4.66	57.4	13.7	15.2	9.1
DS2P307	0.144	3.31	68.0	10.3	11.5	6.9
DCS2P301	0.169	2.26	9.7	42.3	35.2	10.6
DCS2P302	0.167	2.35	20.3	37.0	30.9	9.3
DCS2P303	0.109	4.45	29.1	31.9	26.6	8.0
DCS2P304	0.126	3.88	38.4	27.7	23.1	6.9
DCS2P305	0.130	3.78	48.0	23.1	19.3	5.8
DCS2P306	0.132	3.69	57.5	18.6	15.5	4.7
DCS2P307	0.117	4.30	67.0	13.8	11.5	3.5

Table A.2: (Cont.)

Sample	%P _{Fe}	%P ₂ O ₅	%FeO	%CaO	%SiO ₂	%MgO
CS4P201	0.315	2.82	31.8	45.7	19.6	-
CS4P202	0.095	9.65	29.6	42.5	18.2	-
CS4P203	0.335	2.11	30.6	47.1	20.2	-
CS4P204	0.134	9.96	24.9	45.6	19.5	-
CS4P205	0.091	11.68	30.5	40.5	17.3	-
CS4P206	0.114	10.82	55.5	23.6	10.1	-
CS4P207	0.145	9.35	46.4	31.0	13.3	-
CS4P208	0.336	2.18	18.2	55.7	23.9	-
CS4P209	0.097	11.80	31.2	39.9	17.1	-
CS4P210	0.160	9.10	58.0	23.0	9.9	-
CS4P211	0.195	7.60	70.8	15.1	6.5	-
CS4P212	0.164	9.50	51.2	27.6	11.8	-
DS4P201	0.252	5.37	21.4	30.8	22.0	20.5
DS4P202	0.186	8.07	26.5	27.5	19.6	18.3
DS4P203	0.199	7.63	38.5	22.6	16.2	15.1
DS4P204	0.190	7.99	48.7	18.2	13.0	12.1
DS4P205	0.224	6.58	61.6	13.4	9.6	8.9
DS4P206	0.231	6.37	72.6	8.8	6.3	5.9
DS4P207	0.292	3.82	14.5	34.3	24.5	22.9
DS4P208	0.270	4.68	22.7	30.5	21.8	20.3
DCS4P201	0.094	11.82	8.2	44.8	24.0	11.2
DCS4P202	0.059	13.54	16.2	39.4	21.1	9.8
DCS4P203	0.077	12.75	40.9	26.0	13.9	6.5
DCS4P204	0.140	10.02	56.9	18.5	9.9	4.6
DCS4P205	0.194	7.65	70.3	12.3	6.6	3.1
DCS4P206	0.079	12.47	18.5	38.7	20.7	9.7

APPENDIX B

Slag-Metal Kinetic Data
Table B.1: Oxidation Studies of Iron-Phosphorus-Carbon Alloys

Alloy	Reaction Time(sec)	%P	%C	Metal Weight	Slag Weight
CP10200	0	0.193	0.417	-	-
	5	0.038	0.245	0.4041	0.0427
	10	0.009	0.243	0.5448	0.0511
	20	0.008	0.179	0.8127	0.0515
	30	0.005	0.288	0.8505	0.0538
	40	0.006	0.229	0.9543	0.0571
	60	0.005	0.208	1.1175	0.0521
CP5100	0	0.104	0.342	-	-
	5	0.016	0.217	0.8474	0.0723
	5	0.024	0.211	0.9718	0.0552
	8	0.014	0.138	0.9411	0.0525
	10	0.016	0.180	0.7129	0.0551
	20	0.010	0.202	0.9081	0.0735
	20	0.012	0.132	0.9251	0.0770
	30	0.023	0.158	0.9160	0.0744
	30	0.006	0.123	0.7369	0.0627
	35	0.013	0.113	0.8581	0.0737
	40	0.001	0.104	0.8888	0.0784
	45	0.018	0.141	0.9463	0.0686
	60	0.004	0.113	-	-
	80	0.009	0.063	0.8975	0.0837
CP1200	0	0.205	0.264	-	-
	5	0.124	0.140	0.8856	0.0426
	10	0.078	0.144	0.9654	0.0489
	20	0.026	0.125	0.8471	0.0549
	30	0.009	0.157	0.9308	0.0625
	40	0.020	0.160	0.9259	0.0649
	60	0.027	0.132	0.9411	0.0659
	80	0.008	0.131	0.9319	0.0666
	100	0.008	0.096	0.9308	0.0667
	120	0.009	0.061	0.9393	0.0687
	150	0.009	0.096	0.9293	0.0693
	150	0.008	0.065	0.8654	0.0658

Table B.1: Oxidation Studies of Iron-Phosphorus-Carbon Alloys

Alloy	Reaction Time(sec)	%P	%C	Metal Weight	Slag Weight
CP10100	0	0.118	0.974	-	-
	3	0.077	0.712	0.9955	0.0603
	5	0.055	0.827	0.9864	0.0556
	10	0.059	0.618	1.0629	0.0604
	10	0.043	0.698	1.0124	0.0588
	20	0.015	0.595	1.0845	0.0676
	30	0.021	0.428	0.9459	0.0670
	30	0.012	0.554	0.9928	0.0678
	40	0.010	0.487	0.9676	0.0666
	60	0.004	0.529	1.0740	0.0775
	80	0.006	-	-	-
	120	0.009	0.184	0.9140	0.0859
	120	0.027	0.227	0.9245	0.0711
	120	0.028	0.203	0.9734	0.0764
	150	0.024	0.223	0.8998	0.0556
	180	0.022	0.0945	0.8870	0.0816
CP5200	0	0.286	1.210	-	-
	5	0.182	1.171	0.6031	0.0380
	12	0.173	1.210	0.6788	0.0352
	20	0.120	0.908	0.9758	0.0561
	25	0.088	1.022	1.0770	0.0454
	28	0.021	0.972	1.2505	0.0476
	30	0.026	0.999	1.1068	0.0585
	40	0.005	0.939	-	-
	60	0.006	0.924	-	-
	80	0.004	-	-	-

Table B.2: Oxidation Studies of Iron-Carbon Alloys

Alloy	Reaction Time (sec)	%C	Metal Weight	Slag Weight
C500	0	0.451	-	-
	10	0.358	0.8675	0.0941
	10	0.350	0.8737	0.0907
	20	0.230	0.9036	0.0970
	30	0.138	0.9713	0.0792
C1000	0	0.684	-	-
	10	0.375	0.8786	0.0602
	20	0.256	0.9263	0.0922
	30	0.140	0.9254	0.0806

Table B.3: Oxidation of Iron-Phosphorus-Silicon Alloys

Alloy	Reaction Time (sec)	%P	%Si	Metal Weight	Slag Weight
Fe-P-Si	0	0.298	0.446	-	-
	5	0.104	0.194	1.0474	0.0524
	10	0.078	0.067	0.9689	0.0498
	20	0.031	0.062	1.0014	0.0586
	30	0.027	0.032	0.9906	0.0512
	40	0.005	0.035	0.9829	0.0597
	60	0.005	0.017	1.0029	0.0600

Table B.4: Phosphorus Reversion Studies

Alloy	Reaction Time (sec)	%P	%C	Metal Weight	Slag Weight
CP500	0	-	0.451	-	-
	5	0.008	0.458	0.9355	0.0437
	10	0.005	0.403	1.0308	0.0347
	30	0.006	0.358	1.0935	0.0356
	60	0.003	0.389	0.8974	0.0387
	120	0.012	0.272	0.7877	0.0377
	150	0.013	0.219	0.9476	0.0512
	180	0.010	0.321	0.9359	0.0512
	210	0.005	0.240	0.9161	0.0526
	240	0.014	0.190	0.8759	0.0515
	270	0.018	0.262	0.7995	0.0505
	300	0.022	0.307	0.8145	0.0566
CP10000	0	-	0.684	-	-
	5	0.009	.452	0.9594	0.0445
	30	0.017	0.350	0.9026	0.0321
	60	0.0098	0.287	0.7588	0.0299
	90	0.011	-	0.8564	0.0377
	120	0.0149	0.232	0.9820	0.0459
	150	0.022	0.227	0.8822	0.0418
	180	0.009	-	0.8686	0.0465
	210	0.009	0.111	0.9120	0.9642
	240	0.009	0.086	0.8942	0.0514
	270	0.008	0.519	0.7620	0.0459
	300	0.018	0.153	0.8243	0.0560

APPENDIX C

Crucible Fabrication Technique*

Due to the lack of commercially available magnesia labware of suitable purity and density, an attempt to fabricate high purity, high density magnesia crucibles was undertaken based on the previous work of Atlas.²⁷⁴ Limited additions of lithium halide salts were used as sintering aids and very high density magnesia (exceeding 95% theoretical) could be obtained with rapid firing schedules at low temperatures. However, in following Atlas' technique, severe specimen cracking occurred due to high dimensional shrinkage during densification and residual stresses introduced in green specimens due to excessive die friction. Additional problems were encountered due to the hygroscopic nature of treated powders, powder batch variations and exceptionally high compaction ratios. This required significant changes in raw material pretreatment prior to final pressings in order to optimize densification of specimens. Additional optimization of firing schedules was made in order to refine the process and avoid excessive cracking and shrinkage while maintaining high fired densities. The general procedure is given below, although certain details are omitted pending possible application for patent rights.

Raw Material: Both technical and Analar grade magnesia powder was used as starting material. This powder is calcined precipitated $\text{Mg}(\text{OH})_2$ and is very fine (1 μm diameter). It contains minimal metallic impurities and traces of sulfate as a major contaminant.

Slurry Preparation: Five hundred grams of magnesia powder was mixed with one liter of distilled water in a blender to form a thick slurry.

Approximately five grams of lithium halide salt was dissolved in

*Please note: Specific details of the powder pretreatment operations are omitted so as not to jeopardize the status of any pending patent applications. Details will be described in a future publication.

distilled water and added to the magnesia slurry while stirring. The mixture was stirred for approximately thirty minutes and a hot-air dryer was then utilized for evaporating excess water and the mixture was stirred for approximately one hour until a paste-like mass was formed. This was transferred to a pyrex container and then dried overnight at 150°C.

Calcining Treatment: Prior to use, the dried slurry was calcined under optimum conditions so as to chemically activate the magnesia powder. After calcining, the magnesia was cooled and stored under a dry atmosphere. Prior to final use in fabrication, the pretreated powder was crushed immediately preceeding its usage.

Isostatic Pressing: Cold isostatic pressing was the preferred method for obtaining sufficient green densities for final sintering and good densification upon firing.

Die design. A female mandrel design was used to maintain uniformity in the crucible internal diameter. Aluminum alloy mandrels were machined and tapered to various shapes and the final designs were optimized taking the powder handling characteristics into consideration. A polyurethane elastomer (Cil-monothane A-40, Compounding Ingredients Ltd., Manchester) was used as the preferred die bag and end cap material.

Die loading. The mandrel and bag were cleaned with acetone and then sprayed with a PTFE coating and a silicone mold releasing agent so as to prevent pressed specimens from sticking to the die. The die bag was attached to the mandrel with jubilee clips and powder was charged to the die and lightly packed in place. Initially, it was necessary to vacuum degas the die prior to pressing. In this procedure a cotton ball was placed in the die before sealing with an

end cap and elastic band. A needle syringe was inserted in the gap created by the cotton and a vacuum was applied to the die. This procedure was bypassed by improving the powder pretreatment handling and processing method.

Pressing. Several die bags were placed in a wire basket and loaded into the pressing chamber. These were pressed simultaneously at 30,000 psi and the pressure was released slowly so as to avoid shattering of specimens during decompression and rupturing of the die bags.

Firing: Crucibles were carefully removed from the mandrels and stored in a dry atmosphere prior to firing. Crucibles were placed in a refractory brick box which protected them from the direct radiation of the furnace heating elements and were loaded into a muffle furnace at room temperature. The furnace temperature was raised by periodic ramping and brought to 1400°C within two hours. After maintaining this temperature for approximately thirty minutes, the furnace was shut off and the crucibles were slowly cooled in-situ to room temperature. Post-fired densities routinely exceeded 93% of theoretical values with proper powder treatment. Whiteway²⁷⁵ quotes this density as an indicator of excellent slag resistance and crucibles produced with this technique were able to contain calcium ferrite melts without breaching and were superior to commercially available material.

APPENDIX D

Dephosphorization Rate Limiting Mechanisms in Slag-Metal Systems

- I. Iron-Phosphorus Alloys (No carbon, silicon, manganese, chromium or other oxidizable solute elements).
 - A. Slags with large phosphorus capacity.
 1. Low Phosphorus Alloys: Rate is limited by phosphorus transport in the metal to the slag-metal interface.
 2. High Phosphorus Alloys: Rate is limited by phosphorus transport from the slag-metal interface to the bulk slag; where a solid dephosphorization product is formed, rate is limited by dissolution or mechanical removal of this solid from the interface.
 - B. Slags with low phosphorus capacity.
 1. Low Phosphorus Alloys: Phosphorus transport in the metal has no problem keeping up with the slag-metal reaction since this is rather slow due to the low driving force for the reaction; phosphorus or lime transport in the slag is rate limiting.
 2. High Phosphorus Alloys: Slag is quickly saturated with phosphorus and reaction stops as it either reaches equilibrium or a solid dephosphorization product forms which inhibits further reaction with the bulk slag.
- II. Iron-Phosphorus-Carbon Alloys (No oxidizable solute other than carbon and phosphorus).
 - A. Highly oxidized slags
 1. Large Phosphate Capacity (Dephosphorization product is essentially non-reducible by Fe-C alloy).
 - a. Low Phosphorus Alloy: Simultaneous reaction of carbon and phosphorus with reaction controlled by phosphorus transport in the metal.
 - b. High Phosphorus Alloy: Phosphorus preferentially oxidized and reaction controlled by either oxygen transport in the slag to the slag-metal interface, phosphate transport away from the slag-metal interface to the bulk slag, or removal of solid dephosphorization product from the interface.
 2. Low Phosphate Capacity Slag (Dephosphorization product is readily reduced by Fe-C alloy).
 - a. Very little dephosphorization with considerable decarburization.
 - b. Dephosphorization accompanied by equally rapid reversion with very little overall dephosphorization.
 - B. Less oxidizing slags
 1. Large Phosphate Capacity Slag
 - a. High Phosphorus Alloy: Phosphorus preferentially oxidized and rate controlled by oxygen transport in the slag to the interface or transport of the phosphate formed away from the interface.

- b. Low Phosphorus Alloys: Rate controlled by phosphorus transport in the metal to the slag-metal interface
 - 2. Low Phosphate Capacity Slag
 - a. High Phosphorus Alloy: Simultaneous reaction of phosphorus and carbon with rate controlled by phosphate transport in the slag or removal of solid phosphate product from the interface.
 - b. Low Phosphorus Alloy: Simultaneous reaction until phosphorus transport in the metal becomes rate limiting and decarburization overtakes the phosphorus reaction.
 - C. Non-Oxidizing Slags (e.g. Electric Furnace Slags). Dephosphorization and decarburization proceed at a very slow rate controlled by coupled transport reactions at the slag-metal interface which involve oxygen or ion transport.
- III. Multicomponent Iron-Phosphorus Alloys (Oxidizable solutes, such as silicon, manganese or chromium, are present).
 - A. Basic Oxidizing Slags: Initially these solutes are oxidized, consuming slag oxygen and creating local variation in slag composition. Their oxidation products diffuse away from the interface into the bulk slag. In each case, phosphorus will be simultaneously oxidized but the dephosphorization reaction may be impaired either by phosphorus transport in the alloy, the competition for slag oxygen or a reduction in slag phosphate capacity due to localized composition variations in the slag caused by the oxidation of these solutes. In the case of chromium, a solid oxidation product may form which blocks further reaction from occurring. Gradually these inhibitions to dephosphorization are reduced as the solutes are removed and, providing there is sufficient oxygen remaining in the slag, the metal-slag reaction follows the behavior outlined in Part I or II above.
 - B. Non-Oxidizing Slags: Very little reaction can occur as any phosphorus in the slag is readily reduced by an exchange reaction at the interface.

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