

THE UTILIZATION OF APLITE IN LADLE DESULFURIZATION
OF CAST IRON

by

Max Bolotsky

A Thesis Submitted as Partial Fulfillment
for the Degree of

MASTER OF SCIENCE

in

METALLURGICAL ENGINEERING

Approved:

H. V. White
In Charge of Major Work

H. V. White
Head of Major Department

E. P. Horro
Dean of Engineering Division

Director of Graduate Studies

Virginia Polytechnic Institute

June, 1940

LD

5655

V855

1940

B646

C.2

125478

ABSTRACT

The desulfurizing powers of apfite, apfite-soda ash mixtures, and apfite-dehydrated lime combinations when added to a ladle of cast iron were tested. Ladle conditions were simulated by melting cast iron in a crucible and introducing the reagent mixtures into the molten metal by means of a cast iron cup and steel rod.

It was found that in every case the desulfurizing power was appreciably below that of soda ash and did not warrant testing the mixture to determine its effect upon the corrosion of ladle refractory linings.

ACKNOWLEDGMENTS

The writer would like to express his appreciation to the following persons for having contributed to his thesis investigation: Dominion Minerals Corp., Washington, D. C., who suggested the problem; W. Levi, Radford Foundry, Radford, Virginia, who generously supplied the soda ash (Purite) and part of the sulfur analysis apparatus and materials; Dr. R. J. Holden, head of the Geology Department, V. P. I., for the dehydrated lime; J. W. Whittemore and P. S. Dear, head and professor, respectively, of the Ceramic Engineering Department, V. P. I., for having allowed the use of the facilities of their department and for assistance whenever requested; and Prof. H. V. White, head of the Department of Metallurgical Engineering, V. P. I., for his assistance and suggestions throughout the investigation.

Table of Contents

| | | |
|-----|--|----|
| I. | THE INTRODUCTION | 1 |
| II. | THE REVIEW OF THE LITERATURE | 4 |
| A. | The Mechanism of Ladle Desulfurization and the Desulfurizing Action of Various Reagents | 4 |
| 1. | How Ladle Desulfurization of Cast Iron with Soda Ash is Carried on | 4 |
| 2. | The Chemical Reactions Involved using Soda Ash | 4 |
| 3. | The Desulfurizing Actions of the consti- tuents of Aplite | 9 |
| a. | The Mineralogy and Composition of Aplite | 9 |
| b. | "Basicity" and Desulfurization | 9 |
| c. | The Action of Silica | 10 |
| d. | The Action of Alumina | 13 |
| e. | The Action of CaO | 14 |
| f. | The Action of Na ₂ O and K ₂ O | 14 |
| g. | The Action of Fe ₂ O ₃ | 14 |
| 4. | Feldspars As Desulfurizing Agents | 15 |
| 5. | The Removal of Sulfur and Inclusions by the use of Slags and Dispersion | 16 |
| a. | The Effects of Dispersing Slags in iron | 16 |
| b. | The Removal of Sulfur | 17 |
| c. | The Removal of Inclusions | 17 |
| 6. | Other Reagents that Are Used for Ladle Desulfurization | 19 |

Table of Contents (cont'd.)

| | | |
|------|--|----|
| 7. | The Work of the U. S. Bureau of Mines on Desulfurization | 23 |
| | a. Blast Furnace Studies | 23 |
| | b. Development of Calcium Carbide (CaC_2) | 23 |
| B. | The Effect of Desulfurizing Reagents on the Ladle Refractory Lining | 24 |
| | 1. The Extent of the Corrosion | 24 |
| | 2. The Mechanism of Attack | 25 |
| | 3. Methods Proposed to Overcome the Corrosion | 27 |
| | a. Using a Better Refractory | 27 |
| | b. Using Other Reagents or Reagent Mixtures | 29 |
| III. | EXPERIMENTAL | 30 |
| | A. Materials | 31 |
| | 1. Aplite | 31 |
| | 2. Soda Ash | 31 |
| | 3. CaO | 31 |
| | 4. Cast Iron | 32 |
| | B. Apparatus | |
| | 1. Melting Furnace | 32 |
| | 2. Preheating Furnace | 32 |
| | 3. Crucibles | 32 |
| | 4. Device Used to Introduce the Reagent | 36 |
| | C. Method of Sulfur Analysis | 37 |
| | D. Method of Procedure | 40 |
| | 1. General Procedure | 40 |

Table of Contents (cont'd.)

| | | | |
|-----|-------------|--------------------|----|
| 2. | Test 1 | 42 | |
| | a. | Introduction | 42 |
| | b. | Procedure | 42 |
| | c. | Discussion | 42 |
| 3. | Test 2 | 43 | |
| | a. | Introduction | 43 |
| | b. | Procedure | 43 |
| | c. | Discussion | 43 |
| 4. | Test 3 | 46 | |
| | a. | Introduction | 46 |
| | b. | Procedure | 46 |
| | c. | Discussion | 47 |
| 5. | Test 4 | 47 | |
| | a. | Introduction | 47 |
| | b. | Procedure | 48 |
| | c. | Discussion | 48 |
| 6. | Test 5 | 51 | |
| | a. | Introduction | 51 |
| | b. | Procedure | 52 |
| | c. | Discussion | 52 |
| IV. | Discussion | 55 | |
| | A. | General Discussion | 55 |
| | B. | Reccommendations | 57 |
| V. | Conclusions | | |

List of Tables

| | | |
|------------|--|----|
| Table I. | The Composition of the Aplite | 31 |
| Table II. | The Sizes and Weights of Couplings and Plugs | 36 |
| Table III. | Desulfurizing Power of Soda Ash - Aplite Mixtures of Total Amounts, 10 Pounds per ton | 44 |
| Table IV. | Desulfurizing Power of Soda Ash - Aplite Mixtures of Total Amounts, 10 Pounds Per Ton | 44 |
| Table V. | Effect of Aplite on the Desulfurizing Power of Soda Ash | 49 |
| Table VI. | Effect of Aplite on the Desulfurizing Power of Soda Ash | 49 |
| Table VII. | Desulfurizing Power of Large Amounts of Aplite With and Without Lime | 53 |

List of Illustrations

A. Photographs

- Fig. 1 -- The Melting Furnace 33
- Fig. 2 -- The Preheating Furnace 34

B. Drawings

- Fig. 3 -- Method of Adding Reagent Mixtures
to Melts 35
- Fig. 4 -- Evolution Method Apparatus For
Sulfur Analysis 39

C. Graphs

- Fig. 5 -- Desulfurizing Power of Soda Ash -
Aplite Mixtures of Total Amounts
10 Pounds Per Ton 45
- Fig. 6 -- Effect of Aplite on the Desulfurizing
Power of Soda Ash. Soda Ash, 10 Pounds
Per Ton 50
- Fig. 7 -- Desulfurizing Power of Large Amounts
of Aplite With and Without Lime 54

I. THE INTRODUCTION

The desulfurization of cast iron is a problem of international metallurgical importance. Desulfurization, e.g. reduction in the sulfur content by the addition of suitable reagents or slag forming materials to molten cast iron, is practiced in England, France, Germany, Italy, Japan, and other countries as well as in the United States.

Benefits of sulfur reduction are increased tensile and transverse strength and improved machinability (1). During the usual desulfurizing process slag inclusions are said to be washed out of the metal, thus producing iron of greater fluidity. This enables the iron to be cast at lower temperatures or into intricate shapes (2) (3). For these reasons desulfurization is being practiced more and more by foundries that produce superior cast iron.

Desulfurization of cast iron is done by addition of a reagent either to the charge of the melting furnace or into a reservoir of the molten metal. It is done usually in the forehearth of a cupola furnace or in a teapot reservoir ladle.

A strongly basic material is the reagent employed. Soda ash (Na_2CO_3) is considered by many to be the best and is widely used. It is an efficient desulfurizer but, like any basic material, introduces the evil of severe refractory corrosion. So severe is the attack of the highly alkaline slag on the siliceous refractory linings usually employed in the fore-

hearth and ladle that the life of the lining is reduced from weeks to days.

Although originated for the improvement of cast iron, desulfurization in the ladle has recently achieved increased importance through application to pig iron. By performing the bulk of sulfur removal in a reservoir ladle instead of in the blast furnace, it is possible to produce pig iron of low silicon content. The making of this basic pig iron enables the operator to run his blast furnace at lower temperatures, thus saving in fuel, time, and operation costs (4). And the iron is equal to the regular type in the making of steel and even superior for casting certain types of cast iron. In England pig iron desulfurization in ladles with soda ash is already being done by the Brassert Process.

In the United States the Bureau of Mines has worked on sulfur removal from pig iron. A new reagent, calcium carbide (CaC_2), has been tried in both pig and cast iron. It has been found to be even more efficient than soda ash when introduced properly and to eliminate abnormal refractory corrosion also. The problem of its proper introduction has not yet been completely solved, however.

Many reagents and slags other than soda ash have been experimented with by investigators. These include reagents alone and mixtures of reagents and soda ash. Among these has been feldspar. But although the desulfurizing power of the materials was investigated, little attention was

paid to the effect of their use on refractory corrosion.

Studies of the corrosion of refractories by soda ash ladle slag have been performed at the Virginia Polytechnic Institute by Dear and Haff. Their results were read by the Dominion Minerals Corporation who then suggested the use of aplite, a soda containing feldspar mineral, as a desulfurizing reagent. Their belief was that its use might reduce refractory corrosion.

It was the purpose of this investigation, then, to determine the sulfur reducing power of aplite when used alone or with soda ash in a ladle of cast iron and to learn the effect of aplite-soda ash mixtures on refractory corrosion.

II. THE REVIEW OF THE LITERATURE

A. The Mechanism of Ladle Desulfurization and the Desulfurizing Action of Various Reagents

1. How ladle desulfurization of cast iron with soda-ash is carried on

It has been stated as theory and proven by widespread practice that iron as tapped from the cupola is not in physicochemical equilibrium with such impurities contained in it as iron sulfide (FeS) and manganese sulfide (MnS). These inclusions can be removed by the introduction into the molten metal of a reactive slag (5). Soda ash is the material widely used for this purpose.

This slag forming reagent, either in the form of fused blocks (Purite) or a compressed and bonded powder, is thrown into a teapot reservoir ladle of the molten cast iron. Almost immediately there is a violent boiling action as the Na_2CO_3 fuses and liberates CO_2 . The evolution of this gas plus other gases formed in the desulfurizing reactions and the stream of iron flowing into the ladle are the means by which the reagent is dispersed through the metal (6).

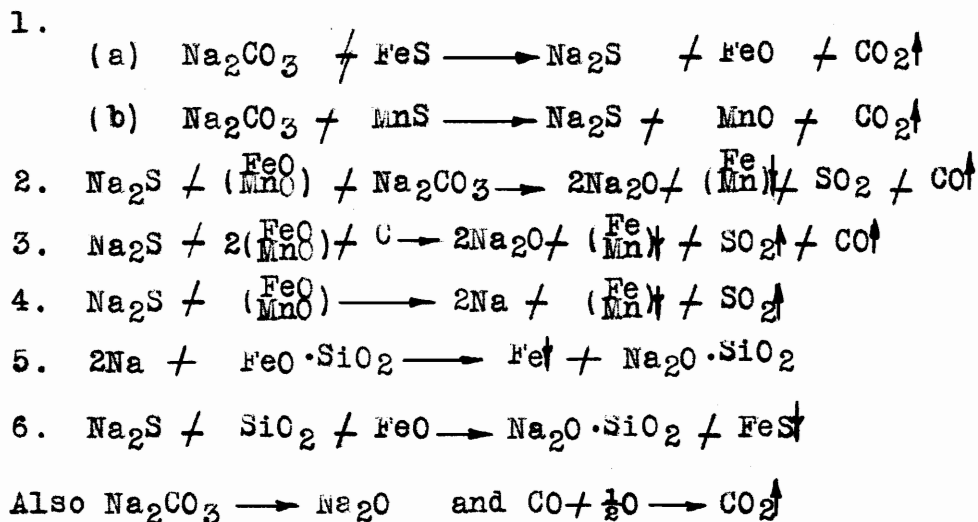
2. The chemical reactions involved using soda ash

Evans (7), Colclough (8), Girardet and Lelievre (9), and other investigators state that the reactions occurring in

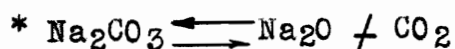
soda ash desulfurization are both varied and complex. Search in the literature revealed that practically no work has been done toward determining thermodynamic and reaction rate data. The reactions given by investigators are admitted to be probable and to be considered from the standpoint of the end results only.

The uncertainty about the exact reactions taking place are illustrated by the four sets of equations that have been put forth by the Mathieson Alkali Company, makers of "Purite," at four different times:

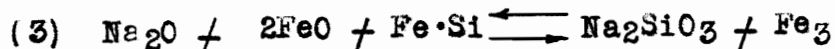
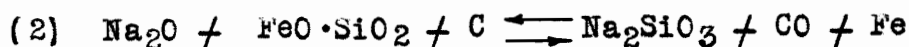
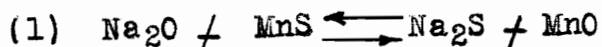
In 1928 (10)



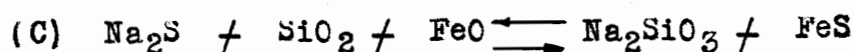
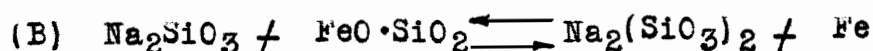
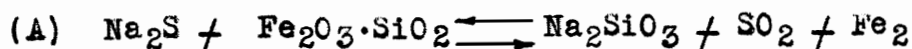
In 1929 (Na₂CO₃ Used As Slag In Air Furnace) (11)



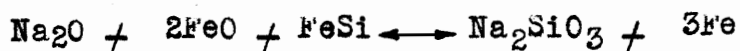
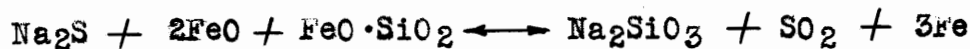
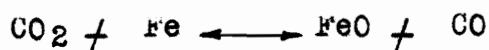
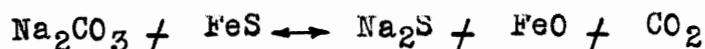
Primary Reactions



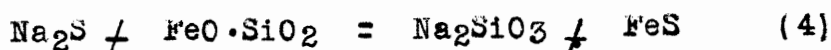
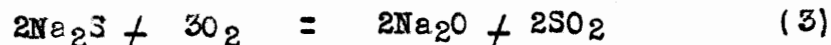
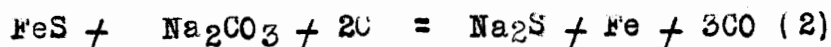
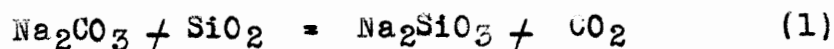
Secondary Reactions



In 1934 (12)



In 1938 (Pig Iron † by Evans) (7)



Evans' (13) description of the above, the most recent of the four sets of equations, is given in brief to present a more complete picture of the process:

The major portion of the sulfur in pig iron is assumed

* Described but not listed

† Pig iron is similar to cast iron in composition

to occur as iron sulfide (FeS) and manganous sulfide (MnS). The FeS is soluble in molten iron and the MnS is an insoluble compound suspended in the metal bath.

Reaction (1)-- This represents all combinations between the Na_2CO_3 and slag or entrapped silicates in all molten cast iron. It includes silicon (Si) from the iron and silica (SiO_2) from the ladle refractory lining. MnS is removed at the same time and with the same speed by a mechanical scrubbing action.

Reaction (2)-- This includes any reaction with MnS and illustrates the true desulfurizing process. Its speed depends on the amount of siliceous inclusions and sulfur present, the more the sulfur, the faster the reaction. Silicates slow down this reaction and an excess will practically end it.

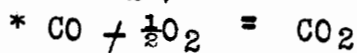
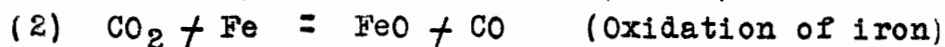
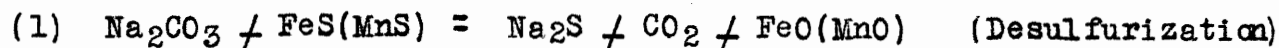
Reaction (3)-- This represents any conversion of sulfides in the slag to gases. Most of the sulfur in the slag is oxidized.

Reaction (4)-- This is taken to represent all manner of reversion of sulfur from the slag back into the metal bath. The speed increases as the total acids in the slag increase.

Colclough (4), in his article describing the use of soda ash in the Brassert Process, lists the following set of reactions:

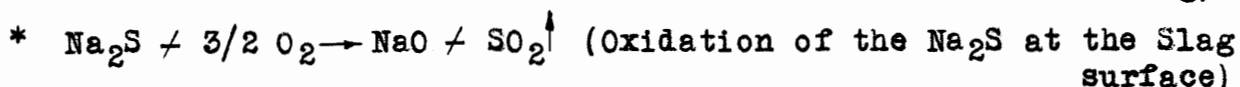
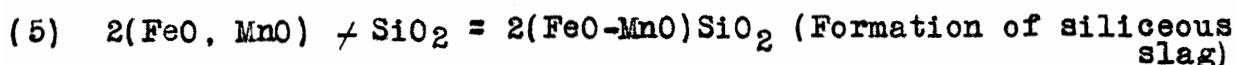
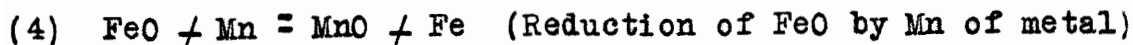
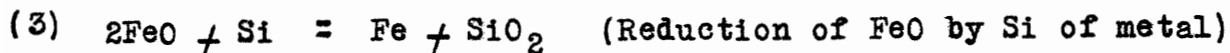
Primary Reactions

(Formation of Na_2S , FeO, and MnO)



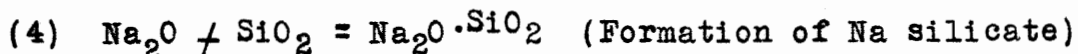
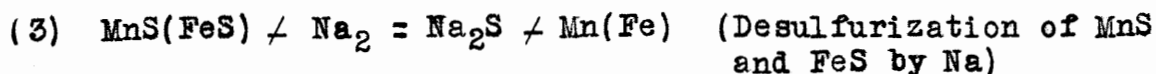
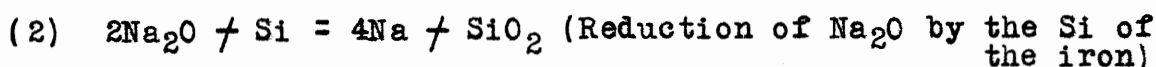
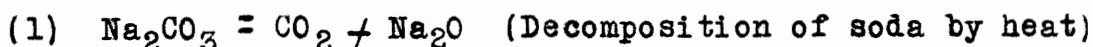
Secondary Reactions

(Formation of silicates of Fe and Mn)

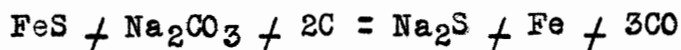


Joseph, Scott, and Tenenbaum (6) consider the soda ash reactions in cast iron to be as proposed by Colclough.

Le lievre (14) proposes reactions for pig iron which differ from both Evans and Colclough:



Girardet and Lebevre (9) studied the desulfurization of cast iron with Na₂CO₃ by means of the reaction:

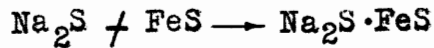


They state that metallic Na is produced during the action and it is the metallic Na which reacts with the sulfides.

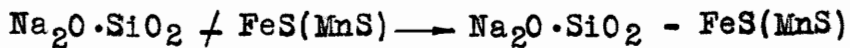
Oelsen and Middel (15) made a comprehensive study of the efficiency and limits of this method to gain a practical basis for its application. They say that an appreciable reduction of the soda to metallic Na begins only after the

* Described but not listed

sulfur content has been reduced to less than .05%. Na_2S is said to be a solvent for FeS , thus giving rise to the equation:



Korber and Oelsen (16) through extensive laboratory studies and plant tests have found that $\text{Na}_2\text{O} \cdot \text{SiO}_2$ has some desulfurizing action. Hence still another equation may be written:



3. The desulfurizing actions of the constituents of aplite

a. The Minerology and Composition of Aplite -- Kraus, Hunt, and Ramsdell (17) describe aplite as being "an extremely fine and even-grained rock consisting largely of quartz and orthoclase (feldspar) with a very subordinate amount of dark material." It occurs as dikes, e.g. fissures in larger rock bodies containing intrusions of igneous material. The mineral is termed acid by Kraus, Hunt, and Ramsdell, which refers to the silica content. The aplite used in the investigation consisted of silica (SiO_2), 59.90%; alumina (Al_2O_3), 23.78%; calcium oxide (CaO), 6.20%; sodium oxide (Na_2O), 6.31%; Potassium oxide (K_2O), 2.96%; and ferric oxide (Fe_2O_3), .19%.

b. "Basicity" and Desulfurization -- It is a generally accepted fact that increased "basicity" improves desulfurization (18). "Basicity" is defined as the ratio of bases to acids, in the case of blast furnace slags this being $(\text{CaO} + \text{MgO})$ to $(\text{SiO}_2 + \text{Al}_2\text{O}_3)$ (19). Recent work by Holbrook and Joseph of the U. S. Bureau of Mines (20) has shown, however, that

there is no simple relationship between "basicity" and the power to remove sulfur from iron. It was shown that "to relate basicity and desulfurization MgO cannot be combined with CaO as 'total bases', nor can Al_2O_3 be combined with SiO_2 as 'total acids.' Moreover, Al_2O_3 cannot be ignored in computing 'basicity', as is frequently done. Each oxide has its own effect on desulfurization, and the degree of the effect is not constant for all ranges of composition."

c. The Action of Silica -- Although there has not been accumulated thermodynamic and reaction rate proof, it has been the experience of many investigators (13) (9) (21) (15) (16) that soda ash when added to cast iron will react first with any silica in the metal, such as siliceous cupola slag, before combining with the sulfur. This is given by Evans (22) as the reason for the erratic results generally found with desulfurizing tests in blast-furnace transfer ladles. He explains that since the soda ash reacts first with entrained silicates in and furnace slag accompanying the metal, variations in the amounts of these constituents produce variations in sulfur reduction.

The Mathieson Company (23) states that ordinarily one pound per ton of Purite is required to neutralize entrained slag and cupola slag coming with the iron. They (24) warn that for efficient results the silica contents of the slag should not exceed 30%. With an appreciable increase above 40%, reaction (4) of Evans will take place and the sulfur will go back into the iron.

Wood, Barrett, and Holbrook (25) of the Bureau of Mines say that return of sulfur from the slag to the metal will take place after desulfurization unless the slag and metal are separated at the proper time. This is attributed mainly to the silica taken by the slag from oxidation of part of the silicon in the metal and by corrosion of the siliceous ladle lining.

Nevertheless, two patents (26) (27) have been taken out in France (1936 and 1937) for the desulfurization of steel by means of an alkaline base such as Na_2CO_3 and a compound such as SiO_2 , Al_2O_3 , or TiO_2 . The purpose of the compound is to form with the base a compound stable at a high temperature. The compound (SiO_2 , Al_2O_3 or TiO_2) is to be added in amount insufficient to saturate the base. The same principles that apply to alkali desulfurization of cast iron are true also for steel.

Moreover, a method (28) for adding alkali or alkaline earth metals into a bath of molten metal for alloying or purifying has recently been patented that involves, in the case of purification (or desulfurization), SiO_2 or Al_2O_3 to the metal. The alkali is formed into an elongated core which is surrounded by a closely fitting tube consisting of the metal of the bath or of fluxes, such as SiO_2 or Al_2O_3 .

Korber and Oelsen (16) in 1938 and Middel and Oelsen (15) in 1939 during their intensive investigation into the mechanism of soda ash sulfur reduction studied the stability

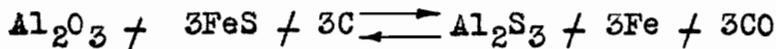
at 1300° to 1400° C. of the Na₂S formed. They concluded that the Na₂S is stable at these temperatures in the presence of the melt and does not require any flux, such as Na₂O·SiO₂ to keep it dissolved in the slag. The authors advise that for maximum sulfur reduction, it is best to use soda ash alone, free from silica.

Nevertheless, Korber and Oelsen (16) did discover that Na₂O·SiO₂ has some desulfurizing action since it may react to form Na₂S and tends to dissolve out FeS from the batch. In the following year (15) Middel and Oelsen furnished quantitative evidence of this. Describing sodium silicate to be a good desulfurizer, they state that it can absorb about 5% sulfur at a final content in the iron of .05% and about 8% at a .1% final sulfur. They found that the desulfurizing action of silicates depends largely on the temperature; increase of temperature from 1200° to 1500° C. (for the same initial sulfur content) increases the final sulfur to about twice the amount and the ratio (S_{Na}) : (S_{Fe}) to 4-5 times.

That Na₂O·SiO₂ had desulfurizing power was believed already in 1927 by Bardenheuer and Osterman (29). They described desulfurization by alkali oxides as occurring by slag formation in the presence of Si or Mn. The authors state that alkali silicate melts can hold 20%- 30% Na₂S and 30% - 40% MnS. However, the end of the soda reaction is reached when no free alkali oxide is present in the Na₂SiO₃ slag formed.

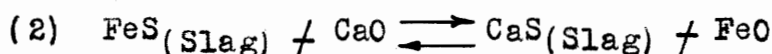
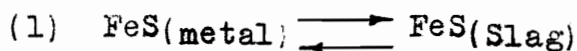
d. The Action of Alumina -- Alumina (Al_2O_3) is often considered an acid constituent of slags (19). Metallfrax (30) considers Al_2O_3 basic in listing the compound among the constituents of a patented basic desulfurizing slag. Recent work of the U. S. Bureau of Mines, described in the section on "Basicity and Desulfurization" has shown that it is incorrect to prophecy the desulfurizing power of Al_2O_3 , or any oxide, by its basicity or acidity.

There is disagreement as to whether or not Al_2O_3 has desulfurizing power. It is the opinion of Bardenheuer and Osterman (29) that Al_2O_3 slags have no advantage over SiO_2 slags. Geller and Bardenheuer (31) go further and say that desulfurization with Al_2O_3 does not take place. Joseph and Holbrook (32) in 1935 found that the substitution of alumina for silica improved sulfur removal over the temperature range $1440^\circ - 1560^\circ \text{C}$. In an extensive investigation of blast-furnace slags carried on the following year by these engineers of the Bureau of Mines (33), this was corroborated. Additional evidence is furnished by Mikulinsku and Umova (34) who found that above 1400°C the following reaction proceeds to the right:



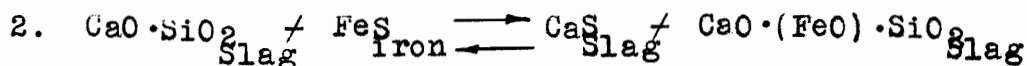
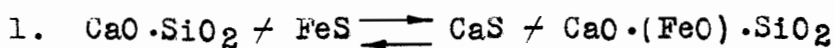
The adding of Al_2O_3 to an alkaline base in desulfurization in order to form a compound with the base has already been mentioned (26) (27). Its addition in the form of a tube surrounding the alkali has also been described (28). The actions of $\text{Al}_2\text{O}_3 \cdot \text{Na}_2\text{O}$ and $\text{Al}_2\text{O}_3 \cdot \text{SiO}_2$ were not found in the literature.

e. The Action of CaO -- The usual assumption about the desulfurizing action of CaO is that sulfur removal takes place by diffusion of FeS from the metal into the slag where it reacts with CaO (35). This may be expressed as follows:



Recent ^{work} of the Bureau of Mines (36) has, however, indicated that the above reactions are not correct. The action is supposed instead to consist of reduction of CaO to metallic calcium, which then enters the metal phase and transports CaS to the slag phase.

It is stated by Tammann and Samson-Himmelstjerna (37) that in the open hearth steel making furnace, CaO combined with SiO₂ has no desulfurizing action. Nevertheless, the Bureau of Mines (38) is at present studying the equilibrium conditions in the following two reactions of the blast-furnace, which are listed as desulfurizing reactions:



f. The Action of Na₂O and K₂O -- The mechanism of Na₂O desulfurization has been covered in the sections describing the action of soda ash. K₂O acts similarly to Na₂O.

g. The Action of Fe₂O₃ -- The amount of Fe₂O₃ in aplite is negligible. However, as FeO is formed when soda ash is used, it might be well to tell of its effect. According to

R. I. 3419 of the Bureau of Mines (38) FeO has an adverse effect on desulfurization (in blast-furnace slags). This has long been known, the report states, but quantitative data have been lacking. Study of the reactions given previously indicates that FeO favors the reintroduction of the sulfur from the Na₂S back into the metal as FeS. This is one reason Wood, Barrett, and Holbrook (25) warn that in alkali treatment the slag must be separated from the metal at the proper time. They say it is "conceivable" that some of the resulfurization may be caused by an increase in the ferrous oxide content of the slag as a result of atmospheric oxidation.

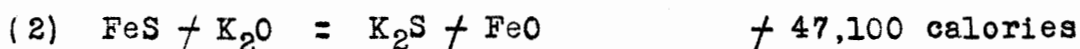
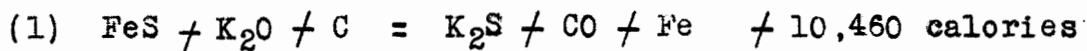
4. Feldspars as desulfurizing agents

Thorough review of the literature from 1926 to 1940 has unearthed only three mentions of the use of feldspars in sulfur reduction. Of these, one is a French patent (1933) (39) for the refining of metals by means of a finely divided solid slag. Feldspar is one of the fluxes listed to give fluidity to the slag.

In 1930 the use of Italian lavas rich in leucite (a feldspathoid, $KAl(SiO_3)_2$) and containing 9-11% K₂O was advocated by Possenti (40). Tests were made on one kilogram crucible melts of cast iron previously made up with FeS and containing only about .1% manganese to avoid desulfurization by manganese. A mixture of one kilogram of iron containing .18% phosphorus and .8% sulfur, 333 grams of leucite of 9% K₂O, and 100 grams of CaO gave a slag containing 1.25% sulfur, and the iron dropped

to .10% phosphorus and .965% sulfur (It is evident that there has been a typographical error and that either the initial sulfur content was 8% or the final was .0965%. The latter is probably the case.). Another test on one Kilogram of iron with 1.42% P and 1.10% S, 250 grams of leucite of 17.5% K₂O (achieved by magnetic concentration), and 50 grams of CaO gave a slag containing 1.85% S, and the iron fell to .75% P and .062% S. The sulfur was said to be in the slag as K₂S.

In 1934 the reactions for sulfur reduction with feldspars (Potassium containing) were given by Guedras (41). Stating that leucite and feldspar have been used as desulfurizing agents, he lists the following reactions by which complete desulfurization can be achieved with a potassium salt (leucite):



5. The removal of sulfur and inclusions by the use of slags and dispersion

a. The Effects of Dispersing Slags In Iron -- In order to hasten the reaction between a molten metal and the slag Perrin suggested dispersing the slag in the liquid metal. In such emulsions the contact is very intimate and forces the reactions to an equilibrium almost instantly (42). By the Perrin process deoxidation, dephosphorization, desulfurization,

and inclusion removal are possible (43).

b. The Removal of Sulfur -- Ordinarily soda ash and other desulfurizing reagents are simply thrown into the ladle of iron. The evolution of gases and flow of metal into the ladle are thought sufficient to give good dispersion of the reagent throughout the metal. That many do not agree with this belief is shown by the large number of devices and methods that have been patented for more efficient dispersion of the desulfurizing material. Fifteen were found in the literature.

Among the more recent work done on this problem is that of Joseph, Scott, and Tenenbaum (6), who desulfurized 800 pound melts of cast iron by introducing caustic soda into the ladle by means of steel pipe. A short section of $1\frac{1}{2}$ inch pipe was threaded at one end, which then screwed into a cap. The cap was drilled and threaded to allow the introduction of a cold-rolled 10-foot rod. Several pipe nipples were then filled with fused caustic, screwed onto the rod one at a time, and introduced below the surface of the metal.

By dispersing the reagent mechanically in the iron, it is also possible to use ordinary open hearth (44) and other basic slags (55) for desulfurization in a ladle.

c. The Removal of Inclusions -- The removal of inclusions from cast iron during desulfurization with soda ash is claimed to be the second of the two-fold benefit from its use. According to Hennig (46) the iron oxides are removed from the iron

by the boiling action of the CO_2 passing through the metal. It has been shown in practice that soda ash treated metal is more machinable and has greater fluidity (1) (2) (3). Recent experiment conducted at the Radford Foundry, Radford, Virginia, bear this out (47). The cause is laid in part to the washing away of inclusions, and microscopic evidence (2) is said to verify this.

Another use of dispersed slags is for inclusion removal. According to Viandon (43) in refining iron the non-metallic inclusions can be eliminated by mixing intimately molten artificial slag with the molten metal, the slag carrying along the impurities from the metal. A. N. S. patent (48) describes such a procedure for iron and steel with the exception that the purifying slag is that of the furnace in which the steel is produced, the metal being poured through the separated slag after deoxidation. Another patent (49) involves adding to steel 1% of finely divided slag forming materials consisting largely of alumina and advises adding the material to the ingot mold.

Although the inclusion content of cast iron is judged by the behavior of the iron, there appears to be no reliable method of exact inclusion analysis. It has been found by two investigators (50) that microscopic determination disagrees with the electrolytic method. Moreover, the recently developed electrolytic-iodine method of Scott (51) when applied by Joseph, Scott, and Tenenbaum (6) evidenced that caustic soda did not

reduce the inclusion content of cast iron. This is contrary to other microscopic evidence (2) as well as the supposed cause of better machinability and fluidity of soda treated cast iron.

6. Other Reagents That Are Used For Ladle Desulfurization

There have been a host of reagents and mixtures of reagents patented or advised for use in the desulfurization of metals. The following list of reagents and reagent mixtures for sulfur removal from cast and pig* irons in the ladle has been found in the literature:

1. Soda ash (Na_2CO_3)
2. Na_2CO_3 and CaF_2 (52)
3. Na_2CO_3 (dehydrated), NaNO_3 (dehydrated), and CaF_2 (53)
4. Na_2CO_3 , CaCO_3 , and CaF_2 (54)
5. Na_2CO_3 (25%), CaF_2 (25%), and CaCO_3 (50%) (4)*
6. Na_2CO_3 (15-30%); CaO , limestone and (or) dolomite (30-80%); and CaF_2 (5-30%) (55)
7. Mixture of $1/4 - 1/6$ CaF_2 and Na_2CO_3 plus a greater amount of CaCO_3 (56)*
8. Na_2CO_3 and ground CaCO_3 (57) (58)
9. Na_2CO_3 (50%) and FeSi (50%) (59)
10. Na_2CO_3 in a slag (45)
11. NaHCO_3 (.5 - .1%) (21)
12. Mixtures of NaOH and CaCO_3 (60)

* Pig iron

13. NaNO_3 and wood ash (61)*
14. NaCl (.5% moist), FeSi (.02% containing 85% Si), and charcoal (.05% ground wood) (62)
15. Na_2SiF and powdered Al plus a metallic deoxidizer such as Si, Ti, or Al (63)
16. Alkali metal chlorate, preferably KClO_3 , and MnO_2 , Na_2CO_3 , NaF , and H_3BO_3 (64)
17. Alkali carbonate and CaF_2 (2 - 40%) (65)
18. Alkali metal fluoride (such as NaF) and CaO (CaCO_3 and cryolite also) (66)
19. Mixture of carbon and an alkali metal compound in the molten condition (Na_2CO_3 and C with Na_2O) (67)
20. Alkali metal in a tube of slag forming substance (SiO_2 , Al_2O_3) (28)
21. Double fluoride of an alkali metal and a non-alkali metal plus Al powder (68)
22. Hydride of an alkali, alkaline earth, or rare earth metal (up to 2%). Mixtures of these hydrides with the corresponding silicides may also be used (69)
23. Metallic calcium agglomerated in the molten form with solid subdivided iron to form a mechanical mixture. Other similar mixtures of alkali and heavier metals may also be used (70)
24. Calcium carbide (71)
25. Beryllium (72)

* Pig iron

26. Cerium with Al, Ca, Mg, or Si (73)
27. Silicides of Ca, Mg, and Ba (74)
28. A Li, Ca, Si composition (75)
29. Si - Ti (20% Ti) or Ca - Si - Al or Si - Ca and Na_2CrO_2 or Na_2CO_3 (43)
30. Basic slag containing CaO (55%), SiO_2 plus CaF_2 (25%), and Al_2O_3 or Na_2O (30)*
31. Suitable basic slag (76) (77)*
32. Basic slag of Fe, FeO, and CaO (78)
33. Manganese (77)*
34. Green slag containing 29.7% Mn (79)*

The following are reagents and reagent mixtures that were listed for use in sulfur removal from steel only. This does not mean that they are not applicable to cast and pig irons.

1. Sodium vapour (80)
2. Hydrogen gas (81)
3. Beryllium (82)
4. Na_2CO_3 , and a compound such as Al_2O_3 , SiO_2 , or TiO_2 (27)
5. Alkali metal carbonate and Al_2O_3 , TiO_2 , or SiO_2 (26)
6. Na_2CO_3 , BaO_2 , KMnO_4 , and NaClO_3 (83)
7. Alkali carbonate and (BeO_2 or $\text{K}_2\text{M}_2\text{O}_8$ or MnO_2) (84)
8. Iron with Ti (15 - 25%), C (1.5 - 5%), Si (up to 3.5%), and Al (up to 3%), the C being $\frac{1}{4}$ of the Ti (85)

A brief general review on the merits of these reagents and mixtures is proper at this time. It is the opinion of several investigators that reducing conditions are necessary (29)(30)(76)

or at least very helpful (86) for sulfur reduction by use of alkali carbonates. The alkali chlorides are also said to be effective only in the presence of reducing materials (86). In the case of pig iron, however, the carbon content is said by Oelsen and Middel (15) to be a sufficiently strong reducer for the FeO formed in the slag so that no other reducing agents (Si or Mn) are required for the soda.

The above paragraph explains Na_2CO_3 mixtures that contain Si, Mn, or their combinations with iron and other metals and other reducing agents. Another reason given for the addition of Si with the reagent is to protect the Si of the metal (29). Fe - Si in the amount of 50% is said by one investigator (59) to increase desulfurization with Na_2CO_3 .

The addition of lime to soda ash has been found to be beneficial by several investigators (4) (21) (58) (59). As partially summed up by Colclough (4) in describing a mixture of soda ash, lime, and fluorspar, "The mixture...also increases the efficiency of the Na_2CO_3 as measured in pounds of sulfur removed per pound of carbonate used, by providing bases to combine with the silica which is formed in the secondary reactions (See Section II, a)....and thereby liberating the whole of the sodium base for combination with sulfur." This is in addition to desulfurization by the lime itself, and the slag produced is of such fluidity as to be readily skimmed from the surface of the metal. The purpose of the fluorspar

and other fluxes is to make the CaO or CaCO_3 fluid, in which condition the latter can react with and remove sulfur (87).

It might also be proper to note, before continuing, that Na_2CO_3 is considered by at least one investigator (87) to be the best desulfurizer of the alkali carbonates.

7. The Work of the U. S. Bureau of Mines on Desulfurization

a. Blast Furnace Studies -- For several years the Blast Furnace Studies Section, Metallurgical Division, U. S. Bureau of Mines has been carrying on desulfurization studies in connection with the blast furnace. This includes articles on "Effect of Temperature On the Desulfurizing Action of Manganese in Basic Pig Iron" and "Effect of Replacing Lime With Magnesia On the Desulfurizing Action of Blast Furnace Slag" (88); and "The Thermodynamic Properties of Sulfur and Its Inorganic Compounds" (89).

Other work, which has already been referred to, dealt with "Silica and Alumina In Iron Ores" (32); "The Relative Desulfurizing Powers of Blast Furnace Slags" (19) (18); and "Equilibrium Conditions in Desulfurizing Reactions" (38).

b. Development of Calcium Carbide (CaC_2) -- The use of calcium carbide by the Bureau of Mines for sulfur reduction in pig iron and cast iron has been briefly mentioned in the Introduction and elsewhere (25). Calcium carbide, in the form of briquetted mixtures with NaCl or other reagents, was introduced below the surface of molten pig iron in crucibles

by means of a graphite rod and holder, or graphite dispersing unit. Melts of 200-300 grams, 1600 grams, 8 pounds were desulfurized in this manner. Salt (NaCl) was found to be the best dispersing material.

When the carbide was tried at several steel plants by adding in the usual methods--throwing into the bottom of the ladle, metal stream in the runner, and so forth--the results were unsatisfactory. A large dispersing unit was then built to treat one-ton charges of cast iron in the ladle. When tried this time, the results were superior to those achieved by use of an equal weight of soda ash (about 10 pounds per ton).

B. The Effect of Desulfurizing Reagents on the Ladle Refractory Lining

1. The Extent of the Corrosion

The usual type of ladle lining refractory in use where desulfurization with soda ash is carried on is a fire-clay, acid in nature. When soda ash is added to the ladle, a slag that is very basic and very fluid is produced. So great is the attack of this highly alkaline fluid slag on the refractory linings that the life of the lining is often reduced from weeks to days. In one foundry (90), for example, where six weeks service was regularly obtained from ladle linings, the addition of 0.20% of soda ash reduced the refractory life to one week. Again, at the Radford, Virginia, plant of the

Lynchberg Foundry Company, the ladle life, because of soda ash desulfurization, is only about 10 to 12 heats (91).

2. The Mechanism of Attack

Dear (92), Hoff (91), and recently Parker (93) of V. P. I. have investigated the attack of soda ash slag on ladle refractories. Dear studied the physical structure of the ladle brick used at a particular foundry; Hoff investigated the resistance of various types of refractory bricks, acid and basic, to the penetration of the slag under static conditions; and Parker reinvestigated Hoff's recommendations under dynamic conditions by means of a rocking furnace.

The brick studied by Dear and considered the average foundry ladle brick by Hoff and Parker, is a ladle brick currently used in open-hearth practice, (94) (95) as well as in foundries. This is a siliceous fireclay of relatively low refractoriness (94) (95). Beginning at 2200° F Dear determined a 120% increase in bulk volume over that of the original.

It is this bloating characteristic of the brick that makes for its use in ladle linings since at high temperatures the plastic mass fills in all joints, thus sealing the lining effectively (95). But this plasticity at high temperatures when the lining is subjected to the action of soda ash also makes for severe corrosion.

The mechanism of attack is well described by Dear in the following paragraphs:

"The glass, the cristobolite (a polymorphic form of SiO_2) and the other forms of silica in the brick were taken in solution first, followed by the finely divided mullite ($3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$) and clay body. The presence of well-crystallized mullite needles as the persistent solid phase at the slag-refractory interface indicated that the liquid at the contact surface was enriched with Alumina (Al_2O_3).

"The condition throughout the contact area is somewhat as follows: (a) a very fluid, highly basic liquid grading back through (b), a liquid of increased viscosity in which the content of iron and manganese oxides and alumina appears to be greater, to (c), a liquid of relatively high viscosity at the interface, caused by solution of refractory enriching the alumina and silica content to the point where abundant mullite takes place. Immediately behind this viscous layer is the vesicular layer of the refractory where more or less localized penetration and fluxing occurs. This is pictured as the 'condition gradient' before each tilting of the ladle.

"When the ladle is tilted, the very fluid, highly reactive liquid slag moves down the back wall and up the front wall. Mechanical erosion is then effective. The flow of fluid slag washes away the dissolved and corroded material, exposing fresh areas of refractory for subsequent attack. Pouring completed, the ladle is returned to the normal position. The reactive slag, reversing its travel, moves up the back wall and

down the front wall, washing the freshly exposed areas and bringing up less saturated slag liquid to renew the interfacial corrosion."

3. Methods Proposed to Overcome the Corrosion

a. Using a Better Refractory -- As a result of his studies, Dear suggests using a brick of higher alumina content. Such a brick would give rise to more mullite formation in the slag-refractory contact area, greater viscosity of the residual slag, and a smaller amount of interstitial glass, and would, therefore, provide more resistance to attack.

This was corroborated by both Hoff and Parker, who advocate using hard burned, super-duty fireclay brick. Such a brick would be resistant to soda ash attack because of the reasons above. It would also overcome shrinkage at high temperatures and thus slag penetration at the joints, the reason which prohibits the use of most super-duty firebrick. In regard to cost, Hoff states that "comparing its cost with that of brick similar to those used in the ladle under study, and considering the cost of the labor required for relining and the time lost while the ladle is out of service, a life double that was obtained would more than justify its use."

To overcome refractory corrosion Offutt (96) suggests using a special fired refractory made by the A. P. Green Fire Brick Co., Mexico, Missouri. This brick shows expansion on being heated to 2912° F. However, since his tests indicated

that no mortar tested offered as good a resistance to the soda slag as did the better refractories, he advocates having all mortar joints as thin as possible.

Offutt states that in almost every case the special brick have shown lower costs than other refractory materials. Lining costs of \$.05 per ton are not considered to be too high, he says, and the special brick costs are below this.

Boles and Blackburn (94) object to using this brick because of the lack of a satisfactory joint mortar. They advocate a special plastic which is to be rammed onto the ladle and then dried thoroughly. According to Boles and Blackburn "these plastics give a hard, dense, refractory lining--one that is free of joints and uniformly resistant to the cutting action of soda ash and soda slags."

Excellent service is claimed for the lining. Examples are three months service in one foundry for the cover of a teapot ladle and cleaner iron in another foundry where rammed linings were used.

According to Offutt plastics offer no advantage over first-quality stiff mud brick. He says "Plastic refractories have been tried on a good many occasions largely because a monolithic lining is possible. Plastic materials are installed green and upon being heated to 2800° F., shrinkage cracks will develop, defeating the purpose. A plastic is easier, however, to install, particularly in small ladles. The fusion point of plastic is no higher than that of first-quality fire brick and

many of the same weaknesses are pronounced in plastic linings for mixer ladles. A plastic lining will not be as dense, due to the granular structure, as is desirable to counteract the action of the soda slag. Plastic linings have been used with some success in various foundries, but the service cost has been found to be about the same as for first-quality stiff mud brick."

b. Using Other Reagents or Reagent Mixtures -- There is very little in the literature on decreasing ladle refractory corrosion by change or modification of the reagent. There appears to have been a search by investigators primarily for cheaper or more efficient reagents. An example is the development of calcium carbide by the Bureau of Mines (25).

Colclough (4), however, states after a series of experimental tests, that considerable advantage may be obtained by the use of other agents in conjunction with soda ash. He says that the materials added may act under certain conditions as desulfurizers and also form a slag which has a lower fluxing action on the lining. A mixture of Na_2CO_3 , 25%; CaF_2 , 25%; and CaCO_3 (50%) is advocated.

III. EXPERIMENTAL

The purpose of the investigation was to determine if apelite alone, or in combination with soda ash, had desulfurizing power when added to a ladle of cast iron. If it did, the effect on ladle lining refractories was to be determined.

Originally it had also been intended to investigate the effect of adding the apelite on the inclusion content of the cast iron. The literature (Section II, 5) has indicated beneficial results from "washing" molten iron with a slag. This was not done, however, for two reasons: first, the literature shows that no reliable method for exact inclusion determination is available (Section II, 5); and second, the experimental results were such that it was not justified.

The desulfurization procedure consisted of melting three pound batches of cast iron in fireclay crucibles in a ceramic fusion furnace and introducing the reagent into the molten iron by means of a holder and rod similar to that used by Joseph, Scott, and Tenenbaum (6). A preheating furnace was used to take the crucibles containing the batches up to 1400° F in order to pass the inversion temperatures of the silica in the crucibles very slowly and thus eliminate the danger of cracking. The sulfur contents before and after treatment were determined by means of the evolution method.

A. Materials

1. Aplite

The aplite was secured at V. P. I. from the Ceramic Engineering Department. It is of the following composition, of which the chemical composition is listed on Page 23 of Bulletin Number 35, Engineering Experiment Station Series, V.P.I. (97):

Table I. The Composition of the Aplite

| | Loss on Igni- tion (%) | SiO ₂ (%) | Al ₂ O ₃ (%) | Fe ₂ O ₃ | CaO (%) | MgO (%) | Na ₂ O (%) | K ₂ O (%) | P.C.E.* |
|-----------------------|---------------------------------|-------------------------|---------------------------------------|--------------------------------|------------|------------|--------------------------|-------------------------|---------|
| % | 0.70 | 59.90 | 23.78 | .193 | 6.20 | nd | 6.31 | 2.96 | |
| Mols Per 100 Grams | | 1.004 | 0.235 | 0.001 | 0.111 | 0 | 0.102 | 0.032 | 6-7 |
| Mol Fraction | | 0.676 | 0.158 | 0.0007 | 0.075 | 0 | 0.069 | 0.022 | |

Considering the Al₂O₃ basic the silicate degree of the aplite is 2.07.

The source of the aplite was the Dominion Minerals Corporation, 719, 15th Street, Washington D. C.

2. Soda Ash

Purite (Na₂CO₃), furnished by W. Levi, metallurgist of the Radford Foundry, Radford, Virginia, was used in the investigation.

3. CaO

The CaO was furnished by Dr. R. J. Holden, head of the Geology Department, V. P. I. It was prepared by calcining a partially calcined lime for four hours at 875° C.

* Pyrometric Cone Equivalent or softening point. In degrees fahrenheit, 2260°

4. Cast Iron

The cast iron was secured from the V. P. I foundry. The iron was in the form of pulley blanks, three of which made up three pounds. Two cast irons were used in the investigation, since the first supply was exhausted. Each iron was all poured from one ladle so as to insure uniform sulfur content.

B. Apparatus

1. Melting Furnace

The furnace used to melt the iron is shown in Fig. 1. It is a ceramic fusion furnace, built by the Ceramic Engineering Department, V. P. I. Pyrofax gas and compressed air were used to raise the temperature to about 2300° F, after which oxygen was introduced to raise the temperature to the melting point of the iron. The temperature of the iron was measured by means of a thermocouple.

2. Preheating Furnace

This furnace is shown in Fig. 2. It is a Westinghouse muffle electric furnace and is controlled by an automatic thermostat.

3. Crucibles

These were Battersea Crucibles. They are highly siliceous clay English crucibles, capable of withstanding temperatures somewhat above that of the melting point of cast iron. See Fig. 3.

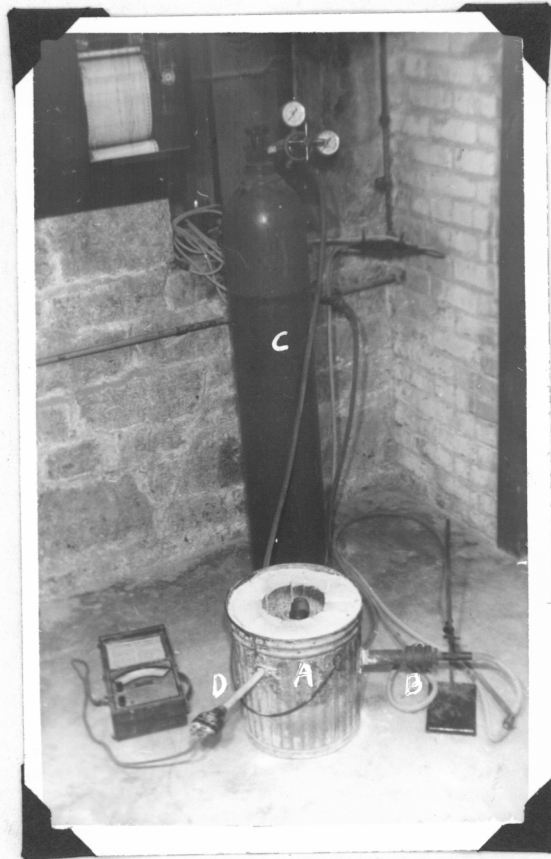


Fig. 1 The Melting Furnace

A. Furnace

B. Burner

C. Oxygen Supply

D. Thermocouple

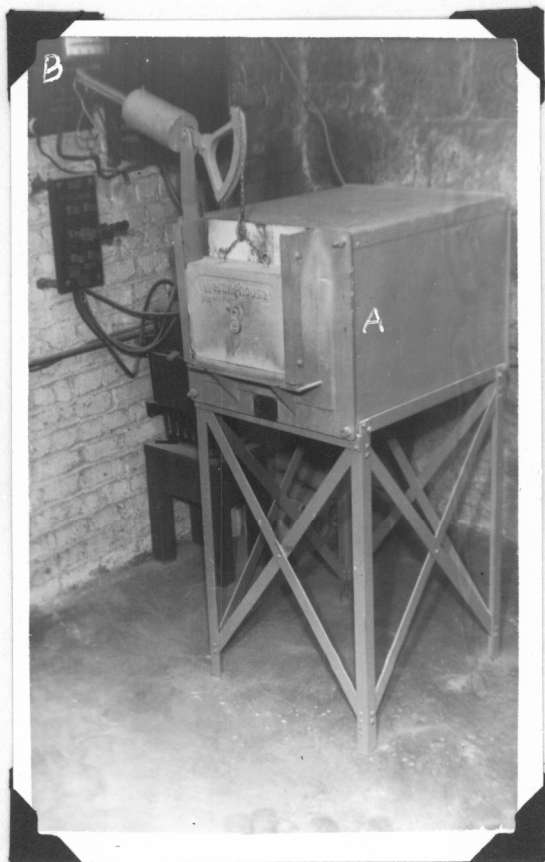


Fig. 2 -- The Preheating Furnace

A. Furnace

B. Pyrometer and Thermostat

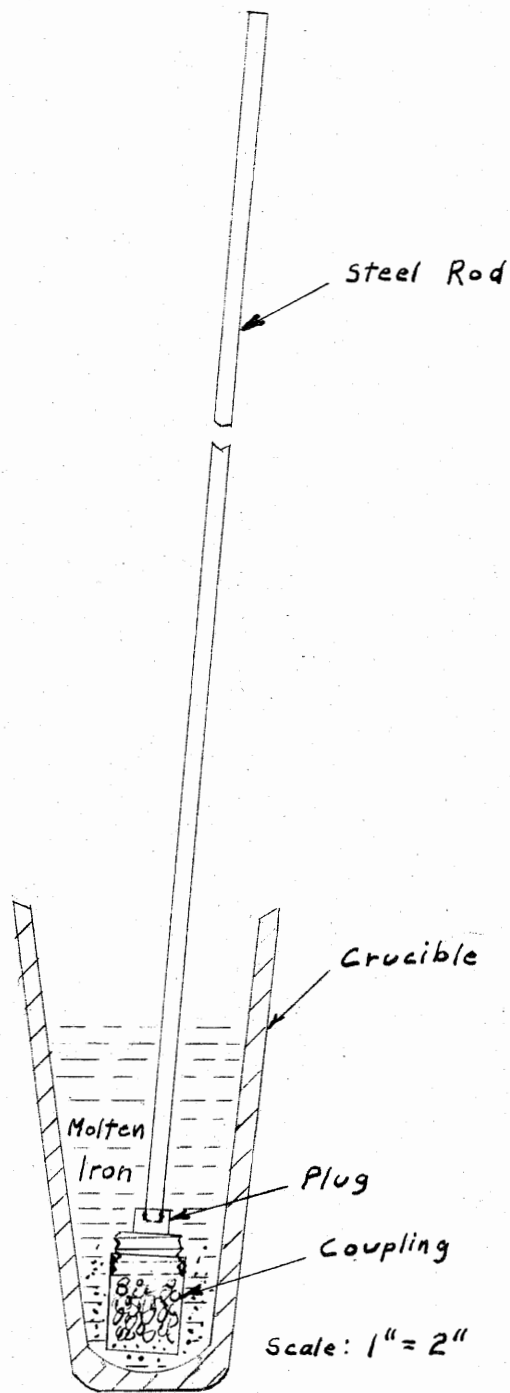


Fig. 3 - Method of Adding Reagent
Mixtures to Melts

4. Device Used To Introduce The Reagent

This device (Fig. 3) was patterned after that used by Joseph, Scott, and Tenenbaum (6), the difference being that the cup was of cast iron instead of steel. The apparatus for each desulfurization consisted of a four foot steel rod, one quarter of an inch in diameter, threaded at one end and a cast iron coupling and plug. The plug, which was drilled and tapped, screwed into the coupling, and the rod screwed into the plug. The reagent was placed in the coupling and introduced into the metal by means of the rod.

Two sizes of couplings and plugs were used and one size of plug and nipple, the latter being used as a "coupling." The sizes and weights of "couplings" and plugs were as follows:

Table II. The Sizes and Weights of Couplings & Plugs

| Number | Description of "Coupling" | Description of Plug | Weight of Coupling and Plug |
|--------|---------------------------|---------------------|-----------------------------|
| 1 | 3/4 " Coupling | 3/4 " Plug | 1/8 lb. |
| 2 | 3/4 " Nipple, 2" long | 1 " Plug | 1/4 lb. |
| 3 | 1 1/2 " Coupling | 1 1/2 " Plug | 5/8 lb. |

Since each set of "couplings" and plugs was purchased at the same store, each set was assumed to be of the same sulfur content.

C. Method of Sulfur Analysis

The method of analysis used was the evolution method. In brief it consisted of evolving the sulfur of the cast iron as H_2S , absorbing the gas in an ammoniacal solution of $CdCl_2$, liberating the sulfur as H_2S again with HCl , and oxidizing the liberated gas with a standard iodate solution, starch being used as the indicator.

Although this method is not as accurate as the gravimetric method, which is the second of the two methods generally used in sulfur analysis, it was chosen for two reasons. This method is much faster than the gravimetric and relative results were sufficient for drawing accurate conclusions from the experimental work.

The chief cause of inaccuracy in the evolution method is the fact that most cast irons do not give up all their sulfur as hydrogen sulfide. As Lundell, Hoffman, and Bright (98) say, "It is well known that the evolution method is not as trustworthy and accurate as the gravimetric oxidation method, owing to the fact that it may not conform to the assumptions that all the sulfur is evolved as hydrogen sulfide, and that this alone is responsible for the consumption of iodine. The method is, however, so extremely simple and rapid that it is exclusively used in works control, and very generally also in the analysis of material sold."

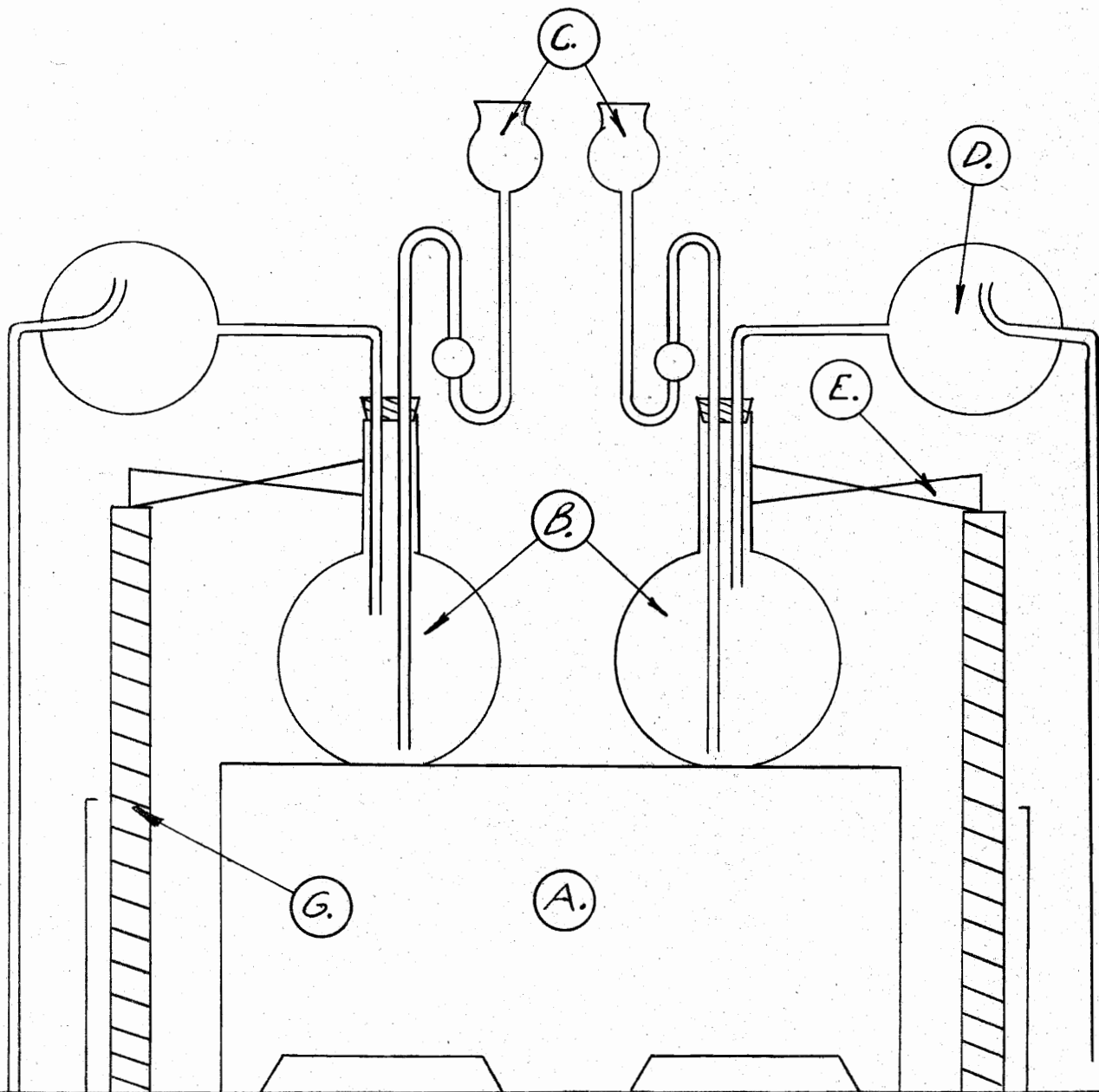
Since all the cast iron melts were allowed to cool at the same rate, and otherwise similarly treated, it should follow, therefore, that the same error be true of each melt. Accordingly, the results should be accurate relatively.

In order to check the analytical determinations, several analyses were duplicated at the Radford Foundry by the evolution method. It was found that the results checked very well. (See Table IV)

The apparatus used for the analyses is shown in Fig. 4. The total apparatus was three times that shown in the drawing, e.g. there were six Kejdal Traps and so forth.

Legend

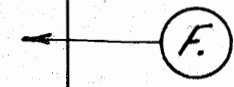
- (A) Electric Heater
- (B) 500cc Florence Flask
- (C) Thistle Tube
- (D) Kejdal Trap
- (E) Flask Support
- (F) 400 c.c. Tall Beaker
- (G) Insulating Board



Evolution Method-Apparatus
For Sulphur Analysis

Max Bolotsky - May 26, 1940
Metallurgical Engineering
Department - V.P.I.

Scale: 1" = 3"



Table

D. Method of Procedure

1. General Procedure

The experimental work consisted of five tests. In each case the reagents were weighed, mixed, and rammed into the coupling cups on one day and melting and desulfurization were carried on during the following day.

The couplings and some of the plugs were galvanized. Before using, the zinc coatings were removed by one hour immersion in 1-1 HCl. After this they were rinsed and dried.

The clean plugs were then drilled and tapped.

The reagents were used in the powdered form in order to attain intimate mixtures. The apfite was already in a fine state but the soda ash had to be pulverized. In order to eliminate moisture, the apfite was thoroughly dried.

Weighing of the reagents was now done. Thorough mixing was accomplished and the mixtures were then rammed into the couplings. After screwing in the drilled and tapped plugs, the filled reagent cups were placed in a dessicator to prevent the absorption of moisture. This precaution was taken to eliminate the possibility of rapid evolution of steam later, with an accompanying spattering of iron.

At this time the cast iron charges were placed in the crucibles and the crucibles were introduced into the Westinghouse furnace. The temperature was slowly raised so as to pass the inversion temperatures of the silica in the crucibles

very slowly and thus prevent the danger of cracking. The crucibles were left in the furnace all night with the thermostat set at 1600° F.

The next day melting and desulfurization were carried on. After bringing the temperature of the melting furnace up to about 1800° F, a crucible was transferred from the preheating furnace to the fusion furnace. The initial heating of the fusion furnace required ten minutes. Another thirty minutes was necessary to take the iron up to its melting temperature and a little farther, to 2600° F, where the iron was very fluid. Oxygen was introduced into the burner at 2300° F. to accomplish this.

Desulfurization now followed. A prepared reagent mixture was taken out of the dessicator and a rod, previously threaded, was screwed into the plug. With this device, the reagent mixture was held below the surface of the metal in the crucible. The rod was withdrawn when the coupling and plug had melted and entered the melt.

Desulfurization was allowed to continue for ten minutes, after which the burner was cut off. After five minutes of cooling in the furnace, the crucible was removed and allowed to cool in air to room temperature.

Another crucible was transferred from the Westinghouse furnace, which was kept at 1600° F till all desulfurizations had been done, and the above procedure was followed again.

Sulfur analysis of each melt was the final step.

2. Test 1

a. Introduction -- From the Review of the Literature it appeared that in all probability aplite could not be substituted for soda ash on an equal weight basis, both with and without the Na_2CO_3 . To verify this, however, and also to gain experience with the method of procedure, a test was run.

Mixtures of aplite and soda ash totaling 10 pounds per ton were used (See Table III). This amount of soda ash alone and the same quantity of aplite alone were also tested. Ten pounds per ton was chosen because this amount of soda ash is often used in practice (7) and also because several investigators who have studied soda ash desulfurization have recommended this quantity (99) (100) (12).

b. Procedure -- The procedure was as described in the section General Procedure. The small size couplings and weights were used to hold the reagent mixtures. Several rods were used since the melting of the plug destroyed the rod threads.

c. Discussion -- In this test the influence of the sulfur content of the couplings and plugs was considered negligible since the total weight of each coupling plus plug was only one twenty-fifth of the weight of the melt. Each melt weighed three and one-eighth pounds before melting but due to slag formation during the fusing, the actual weight of each melt was about three pounds.

It was evident from the results (See Table III and Fig. 5) that something had been in error. Whenever 10 pounds per ton of soda ash is added to cast iron ordinarily, there is a large sulfur reduction. Practically no sulfur reduction had taken place in any of the melts.

3. Test 2

a. Introduction -- The slag formed during the melting had not been removed prior to desulfurization. It was decided to repeat Test 1, this time removing the slag.

b. Procedure -- Test 1 was repeated with the exception that the slag formed during the melting was removed from each crucible with the aid of a bent steel sheet. This slag consisted of burned-in-sand from the sand mold in which the iron had been cast and iron oxide formed during the heating.

Hereafter, in all the following tests, this slag was removed.

c. Discussion -- Table IV and Fig. 5 show the results of Test 2. It was evident that aplite could not be substituted for soda ash on an equal weight basis. In addition it was seen that aplite in the amount of 10 pounds per ton had negligible desulfurizing power.

A check on the results is given by a table in reference (12). Interpolation indicates that 10 pounds per ton of soda ash alone ordinarily should lower an initial sulfur content of .116% to .063%. This checks well with the final sulfur content secured, .065%.

Table III. DESULFURIZING POWER OF SODA ASH - APLITE
MIXTURES OF TOTAL AMOUNTS, 10 POUNDS PER TON

Note: Slag formed during melting not removed

| Melt Number | Percent Soda Ash | Percent Aplite | Pounds Per Ton Soda Ash | Pounds Per Ton Aplite | Grams Soda Ash | Grams Aplite | Percent Sulfur |
|-------------|------------------|----------------|-------------------------|-----------------------|----------------|--------------|----------------|
| 0* | 0 | 0 | 0 | 0 | 0 | 0 | 0.116 |
| 1 | 100 | 0 | 10 | 0 | 6.8 | 0.0 | 0.091 |
| 2 | 75 | 25 | 7.5 | 2.5 | 5.1 | 1.7 | 0.095 |
| 3 | 50 | 50 | 5 | 5 | 3.4 | 3.4 | 0.113 |
| 4 | 25 | 75 | 2.5 | 7.5 | 1.7 | 5.1 | 0.090 |
| 5 | 0 | 100 | 0 | 10 | 0.0 | 6.8 | -- |

Table IV. DESULFURIZING POWER OF SODA ASH - APLITE
MIXTURES OF TOTAL AMOUNTS, 10 POUNDS PER TON

Note: Slag formed during melting removed

| Melt Number | Percent Soda Ash | Percent Aplite | Pounds Per Ton Soda Ash | Pounds Per Ton Aplite | Grams Soda Ash | Grams Aplite | Percent Sulfur | |
|-------------|------------------|----------------|-------------------------|-----------------------|----------------|--------------|----------------|-----------------------|
| | | | | | | | My Analyses | Radford Foundry Check |
| 0* | 0 | 0 | 0 | 0 | 0 | 0 | 0.116 | 0.115 |
| 6 | 100 | 0 | 10 | 0 | 6.8 | 0.0 | 0.065 | 0.068 |
| 7 | 75 | 25 | 7.5 | 2.5 | 5.1 | 1.7 | 0.081 | 0.081 |
| 8 | 50 | 50 | 5 | 5 | 3.4 | 3.4 | 0.093 | 0.094 |
| 9 | 25 | 75 | 2.5 | 7.5 | 1.7 | 5.1 | 0.099 | -- |
| 10 | 0 | 100 | 0 | 10 | 0.0 | 6.8 | 0.104 | -- |

* Iron Before Desulfurization

Per cent Sulfur in Metal

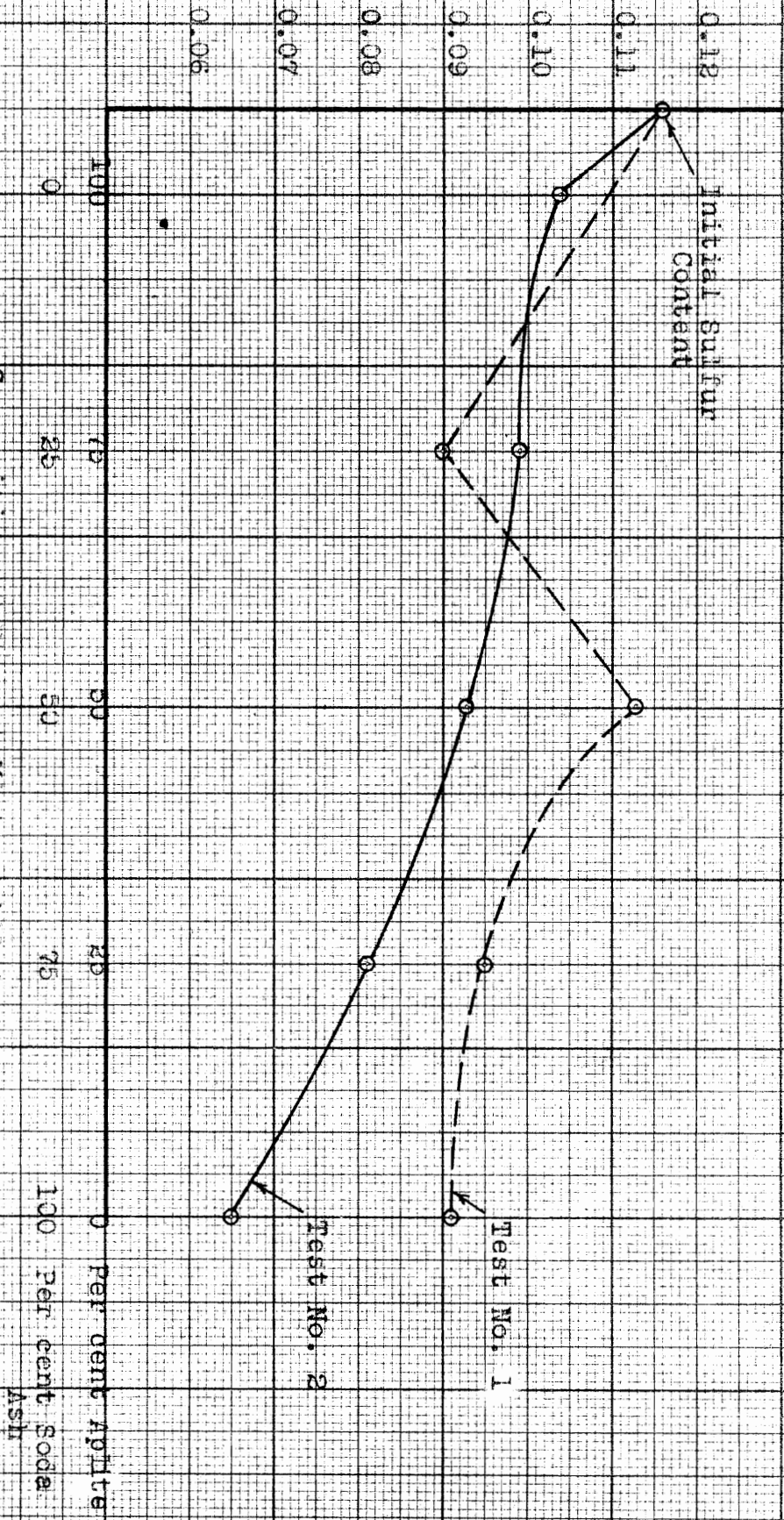


FIG. 5. DESULFURIZING POWER OF SODA ASH - APPLIED MIXTURES OF TOTAL AMOUNTS 10 POUNDS PER TON

Composition of Reagent Mixture Added

Note: In Test No. 1 the slag formed during the melting of the iron (burned-in-slag and iron oxide) was not removed before desulfurization. In Test No. 2 this slag was removed.

4. Test 3

a. Introduction -- The literature has revealed that $\text{Na}_2\text{O} \cdot \text{SiO}_2$ has some desulfurizing power. It has also shown that two patents have been taken out that involve adding Al_2O_3 or SiO_2 to soda ash in desulfurization.

The literature has indicated moreover that a less basic reagent or one that would be less fluid at melting temperature should have less effect on a fireclay refractory. It was noticed in Tests 1 and 2 that the more the aplite in the mixture, the less fluid was the slag. Also aplite-soda ash mixtures are less basic than soda ash alone.

With these facts in mind it was decided to next determine the effect of aplite on the desulfurizing power of soda ash. If it was found that sulfur reduction was not cut down appreciably, the effect on the refractories would then be determined. Ten pounds per ton of soda ash would be used in each mixture.

Test 2 gave some evidence that successful results might be achieved since seven and a half pounds per ton of soda ash plus two and a half pounds per ton of aplite reduced the initial 0.116% sulfur to 0.081% whereas ten pounds of soda ash alone reduced the sulfur to .065%.

b. Procedure -- In Test 3 the medium size "couplings" and plugs were used. These "couplings", in reality unions, were not threaded on the inside and the plugs were forced into

the unions instead of screwing in as before. The rest of the procedure was similar to Test 2.

c. Discussion -- The "coupling" and plug could not be ignored this time as their total weight of one quarter of a pound was one thirteenth of the total melt weight. Therefore a coupling and plug was added to one melt and this was taken to be the original iron.

Table V and Fig. 6 show the results of Test 3. It was evident that when five pounds per ton or more of aplite was added to 10 pounds per ton of soda ash, the desulfurizing power of the reagent was cut down considerably. Increase in the amount of aplite did not appear to change this effect.

5. Test 4

a. Introduction -- Upon consideration of Test 3 it appeared that a source of error might have been introduced by not removing the desulfurizing slag before allowing the metal to cool. According to Wood, Barrett, and Holbrook of the Bureau of Mines (25) in soda ash desulfurization the sulfur in the slag will re-enter the metal unless the slag is removed at the proper time. The chief reason given is addition of silica by oxidation of part of the silicon in the metal and by corrosion of the silicate lining of the ladle. Another reason proposed is an increase in the ferrous oxide content of the slag as a result of oxidation. The first reason should not have pertained to the desulfurization with soda ash-aplite mixtures since there was no re-

fractory corrosion during the short period used and since ap-
lite in itself adds silica to soda ash. The latter reason,
however, may have had an effect.

b. Procedure -- Test 3 was repeated, therefore, but this
time the desulfurizing slag was removed after ten minutes of
desulfurization. In addition 10 pounds per ton of soda ash with-
out apelite were introduced into one melt. This was done because
the initial sulfur content in Tests 3 and 4 was different from
that in Tests 1 and 2 because of the heavier coupling and plug
used.

c. Discussion -- There appeared to be not improvement
but the opposite on the effect of apelite on soda ash. An increase
in the apelite content showed an increase in the final sulfur con-
tent of the iron.

The melt that was desulfurized with 10 pounds per ton
 Na_2CO_3 and no apelite showed little sulfur reduction. Somehow
something had gone wrong in that particular test. Therefore the
desulfurization was repeated with another melt. The results
this time were as would be expected.

Table V. EFFECT OF APLITE ON THE DESULFURIZING POWER
OF SODA ASH

Note: Desulfurizing Slag Not Removed

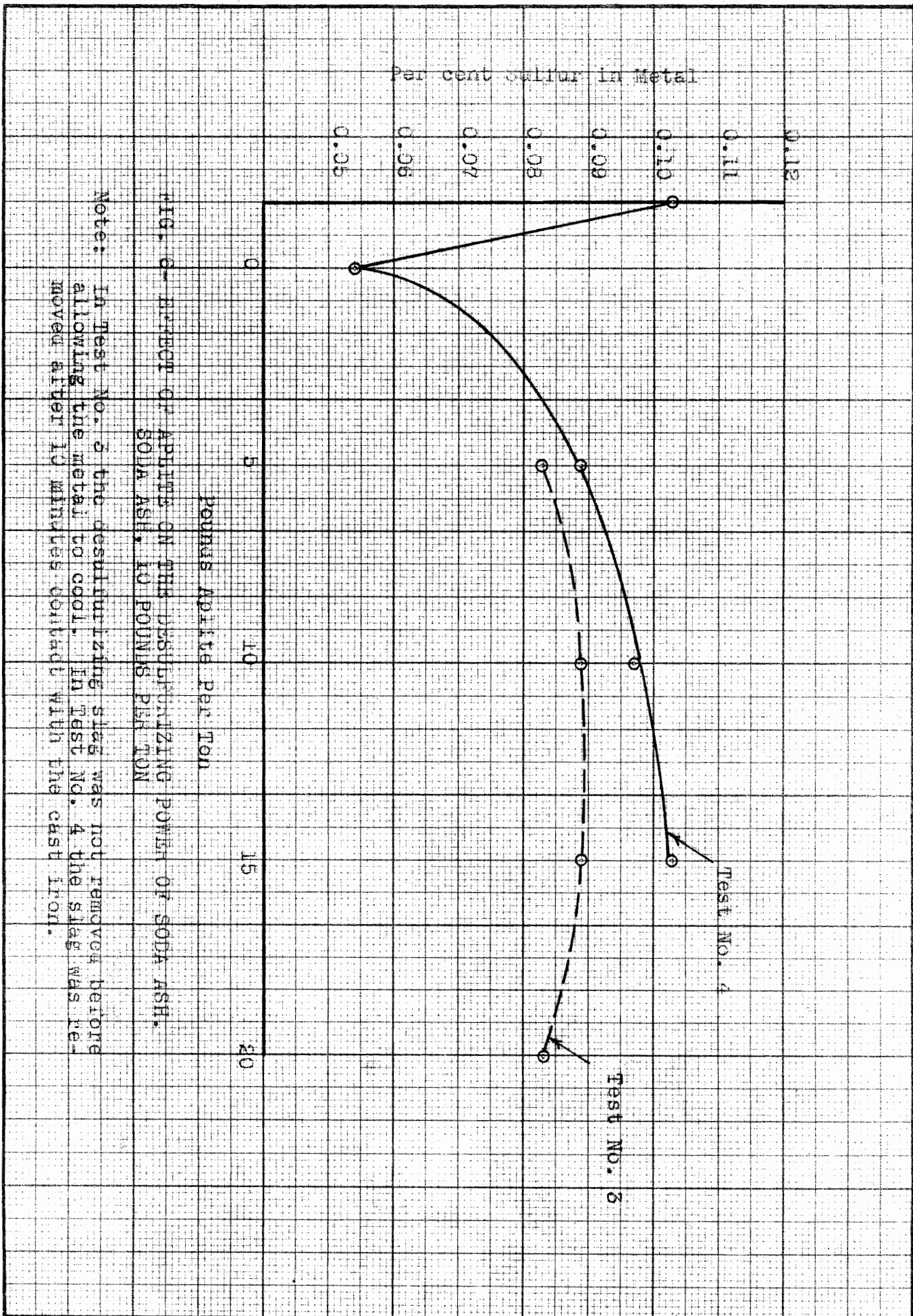
| Melt Number | Pounds Per Ton Soda Ash | Pounds Per Ton Aplite | Grams Soda Ash | Grams Aplite | Percent Sulfur |
|-------------|-------------------------|-----------------------|----------------|--------------|----------------|
| 11 | 0 | 0 | 0 | 0 | 0.103 |
| 12 | 10 | 5 | 6.8 | 3.4 | 0.083 |
| 13 | 10 | 10 | 6.8 | 6.8 | 0.089 |
| 14 | 10 | 15 | 6.8 | 10.2 | 0.089 |
| 15 | 10 | 20 | 6.8 | 13.6 | 0.083 |

Table VI. EFFECT OF APLITE ON THE DESULFURIZING POWER
OF SODA ASH

Note: Desulfurizing Slag Removed

| Melt Number | Pounds Per Ton Soda Ash | Pounds Per Ton Aplite | Grams Soda Ash | Grams Aplite | Percent Sulfur |
|-------------|-------------------------|-----------------------|----------------|--------------|----------------|
| 16 | 10 | 0 | 6.8 | 0 | 0.091 |
| 17 | 10 | 5 | 6.8 | 3.4 | 0.089 |
| 18 | 10 | 10 | 6.8 | 6.8 | 0.097 |
| 19 | 10 | 15 | 6.8 | 10.2 | 0.103 |
| 20* | 10 | 0 | 6.8 | 0 | 0.054 |

* Repeat Desulfurization of Melt 16



6. Test 5

a. Introduction -- It was decided to conclude the investigation by determining if large amounts of apfite had desulfurizing power in a ladle when used alone or with sufficient CaO to neutralize the SiO₂ of the apfite.

Possenti (40) by neutralizing the SiO₂ of a feldspathoid mineral, leucite, with CaO, was able to effect a sulfur reduction of from initial 1.10% sulfur to a final .062%. He used 250 grams of leucite of 17.5% K₂O, 50 grams of CaO, and one kilogram of cast iron. This amount of leucite contained 1.36 times as much K₂O as was necessary to combine stoichiometrically with all the sulfur in the iron. Had the initial sulfur content been 0.11%, 25 grams of leucite and 5 grams of CaO under the same conditions as before should have reduced the sulfur content to even below 0.062%.

This is excellent desulfurization. However, the abstract on Possenti's work did not state the time of contact between metal and slag. The time factor is one of the major differences between furnace desulfurization and ladle desulfurization, which is of comparatively short duration.

Another distinguishing factor is reagent bulk. By the methods used in common desulfurizing practice, a large slag bulk cannot be contained in the desulfurizing ladle.

The apfite mixtures tried are shown in Table VII. Where lime was used, there was just sufficient to neutralize all the SiO₂ of the apfite. Into melt number 23 sufficient apfite was introduced so that half of the sulfur of the metal could be re-

moved stoichiometrically by the Na_2O and K_2O of the aplite. Into melt number 24 was introduced enough aplite to remove three fourths of the sulfur on a stoichiometric basis by the Na_2O and K_2O of the aplite. Larger amounts could not be introduced by means of the coupling used.

The purpose of the soda ash in the above mixtures was to act as a dispersing agent.

b. Procedure -- The procedure was similar to that of Test 4, with the exception that the large size couplings and plugs were used to hold the reagent. Also, a new supply of iron was used in this test as the other had become exhausted.

c. Discussion -- As in Tests 3 and 4 the initial sulfur content was taken to be that of a melt into which a coupling and plug had been introduced. The weight of coupling and plug was five eighths of a pound, which was one-sixth of the weight of the melt. It was not advisable to use a larger coupling; hence the amount of aplite plus CaO added to melt number 24 was the maximum capable of being introduced into a melt by the method used.

Table VII. and Fig. 7, show that although aplite plus CaO gave better sulfur reduction than aplite alone, in all cases the sulfur reduction was poor.

Table VII. DESULFURIZING POWER OF LARGE AMOUNTS
OF APLITE WITH AND WITHOUT LIME

| Melt Number | Pounds Per Ton Aplite | Pounds Per Ton CaO | Pounds Per Ton Soda Ash | Grams Aplite | Grams CaO | Grams Soda Ash | Percent Sulfur |
|-------------|-----------------------|--------------------|-------------------------|--------------|-----------|----------------|----------------|
| 21 | 0 | 0 | 0 | 0 | 0 | 0 | 0.102 |
| 22 | 51.8 | 0 | 2.5 | 35.2 | 0 | 1.7 | 0.092 |
| 23 | 25.9 | 13.1 | 2.5 | 17.6 | 8.9 | 1.7 | 0.086 |
| 24 | 38.9 | 19.7 | 2.5 | 26.4 | 13.4 | 1.7 | 0.087 |

Per Cent Sulfur in Metal

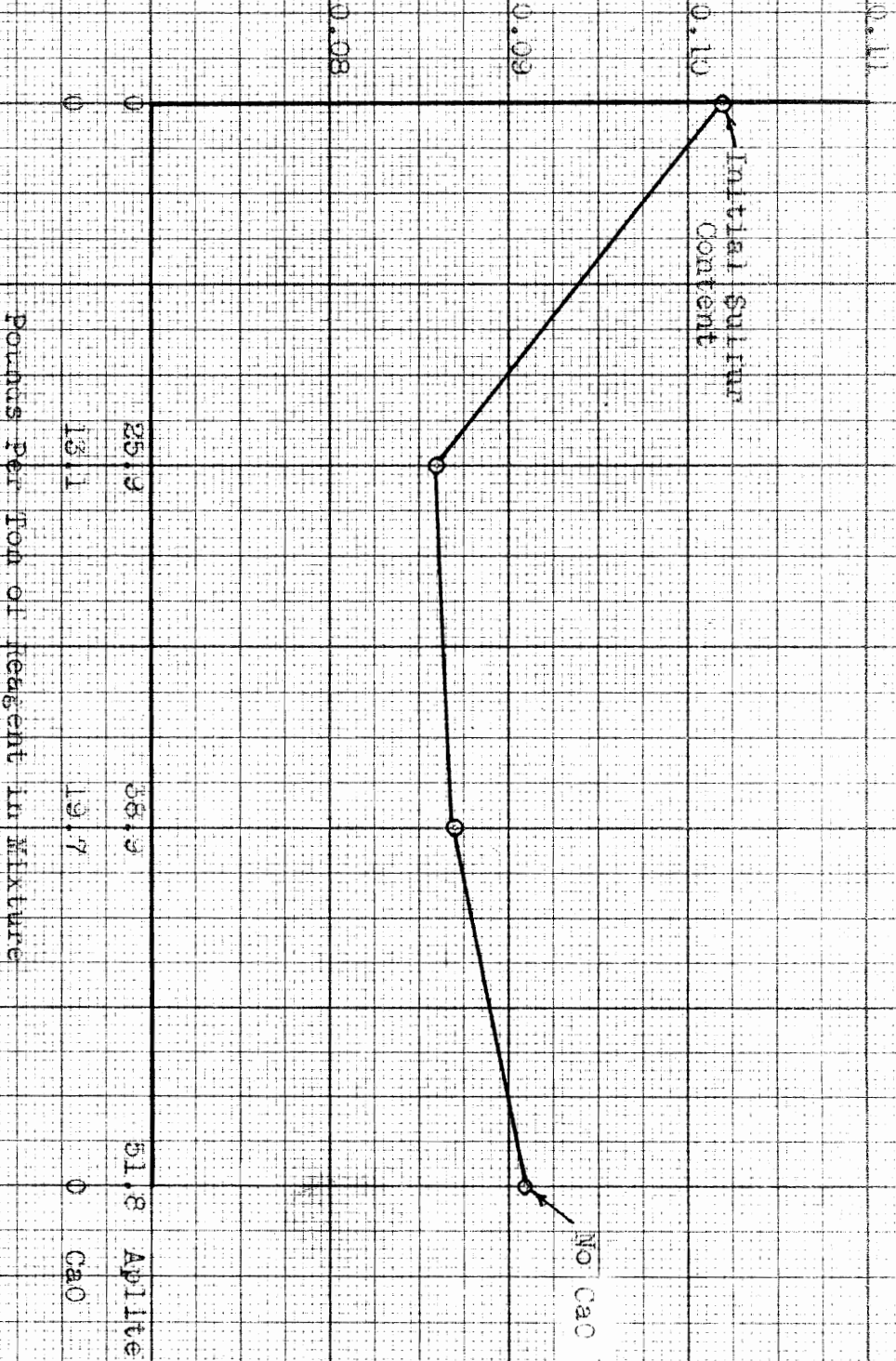


FIG. 7 - DESULFURIZING POINTS ON LARGE AMOUNTS OF APHITE WITH AND WITHOUT LIME

Note: The desulfurizing slag was removed after 10 minutes contact with the cast iron.

IV. DISCUSSION

A. General Discussion

One of the most important factors controlling the degree of desulfurization is the time and degree of contact between reagent and metal. In Tests 1, 2, 3, and 4 the ap-
lite was well dispersed by the evolution of gases from and
melting of the soda ash. The only exception was melt^{ten} where
no soda ash was in the reagent charge. Because of this ex-
cellent dispersion, the data secured should be accurate and
applicable to the drawing of correct conclusions.

On the other hand, in Test 5 the amount of soda
ash in the reagent charges was insufficient to provide dis-
persion except to a small extent. It was because this sit-
uation had been foreseen that fusible reagent holders had
been used in the whole investigation. By the melting of
the coupling and plug, the reagent mixture was introduced
into the metal to some degree, whereas had a steel or gra-
phite holder been used, the ap-
lite-CaO slag would have re-
mained in the holder.

It is recognized that Test 5 may therefore not show
the desulfurizing power of ap-
lite and lime and ap-
lite alone
under certain conditions, such as during longer and more in-
timate contact with the metal. But in the methods ordinarily
used to introduce a desulfurizing reagent into a ladle, the

conditions would have been about the same as those existing during Test 5 or perhaps even less favorable.

To determine the desulfurizing power of apelite and apelite plus CaO under optimum conditions, the mixtures could have been kept in contact with the melt for a long period of time, such as three hours, or dispersed throughout the metal by some good method. In the first case, the results would not apply to ladle sulfur reduction, where the time of contact between slag and metal is comparatively short.

The mechanical dispersing unit devised by the Bureau of Mines (25) to disperse calcium carbide in pig and cast irons could have been used, or one of the several methods listed in the literature in connection with desulfurization with slags (See Section II, 5, b), such as pouring the metal through the molten reagent mixture.

It is conceded, therefore, that the possible desulfurizing power of apelite and apelite-CaO mixtures may not have been determined.

The reactions indicating resulfurization of the metal whenever there is an introduction of silica or ferrous oxide (See Section II. A, 1) were verified in Test 1.

Tests 2 and 3 in addition to indicating that apelite cuts down the desulfurizing power of soda ash appreciably also seemed to verify that decreasing the contact time between metal and slag decreases the amount of sulfur removal. In test 3,

this decrease in time was about 10 minutes, since the iron solidified in that time after the burner was cut off.

B. Recommendations

Although the desulfurizing power of apelite and apelite plus lime was not determined at optimum conditions, it is felt that no further work on apelite is necessary or advisable. Even if an apelite-CaO mixture was found to have good desulfurizing power, the large amount of bulk necessary to accomplish what a small amount of soda ash or other reagent can do would make its use inadvisable. The usual desulfurizing ladle could not readily handle such a large bulk as 60 pounds or more per ton. Moreover, the addition of such a large amount of cold material to the iron would tend to chill the iron.

It seems advisable to seek a solution to refractory corrosion by either the use of a better brick, the development of a non-corrosive reagent, or a modification of the reagent in widespread use now, soda ash. As there appears to be a difference of opinion concerning the merit of plastic linings and Offutt's special brick, and since the usual foundry hesitates to put forth the initial outlay necessary for the purchase of super-duty hard fired brick, modification of the reagent seems to be the best line of attack, other than using a different reagent such as calcium carbide. Colclough (4) has already proposed (and patented) a good modification of the reagent.

V. CONCLUSIONS

1. Aplite cannot be substituted for soda ash on an equal weight basis.
2. Aplite reduces the desulfurizing power of soda ash to an appreciable extent. No mixture of soda ash and aplite was found that had almost the same desulfurizing power of soda ash and hence could be tested to determine its effect on refractory corrosion.
3. Aplite alone, in small amounts or in quantity such that the Na_2O , K_2O content could stoichiometrically combine with all the sulfur in a cast iron, has little sulfur reducing power when added to a ladle by ordinary methods.
4. Mixtures of aplite and dehydrated lime, wherein enough lime is present to neutralize all the silica of the aplite, have little desulfurizing power when added to a ladle by ordinary methods. The Na_2O , K_2O contents of mixtures tested were sufficient to remove half in one case and three-fourths in another of the sulfur in the iron.

VI. LITERATURE CITED

1. Evans, G. S. Refining Cast Iron. Foundry Trade J. 60, 99-101 (1939). Original Not Seen. Chem. Abst. 33, 2858 (1939)
2. Leomoine, R. P. Cupola High Test Cast Iron. Reprint of French Exchange Paper, Am. Foundrymen's Ass. Paris, France.
3. Voronin, S. D. The Use of Calcined Soda In The Foundry of Cast Iron. Linternoe Delo. 8, No. 5-6 (1938). Original Not Seen. Chem. Abst. 33, 9224 (1939)
4. Colclough, T. P. Desulfurization of Pig Iron and Steel. Iron Age. 140, Nov. 18, 34 (1937)
5. Girardet, L. F. C. Cast Iron and the Reactive Slags. Bull. Assoc. Tech. Fonderie. 10, 203-7 (1936). Original Not Seen. Chem. Abst. 30, 6681 (1936)
6. Joseph, T. L., Scott, F. W., and Tenenbaum, M. Effect of Treating Cast Iron with Caustic Soda. Metals and Alloys. 9, No. 12, 330 (1938)
7. Evans, G. S. Desulfurizing Pig Iron By Ladle Treatment With Soda Ash or Caustic Soda, and a Nontechnical Discussion of the Reactions of Alkali Slags. Metals Technology. A. I. M. E. 5, No. 6, 7 (1938)
8. Same as (4)
9. Girardet, L. F. and Lelievre, R. Desulfurization of Cast Iron and the Action of Sodium Carbonate on Molten Cast Iron. Bull. Assoc. Tech. Fonderie. 6, 467-75 (1932). Original Not Seen. Chem. Abst. 27, 1303 (1933)
10. Refining Iron With Purite. Bulletin No 285, 3. The Mathieson Alkali Works (Inc.). 250 Park Avenue, New York City. 1928
11. Purite In Malleable. Bulletin No. a86, p. 4. The Mathieson Alkali Works (Inc). 250 Park Avenue, New York City. 1929
12. Evans, G. S. Desulfurizing With Fused Soda Ash. Reprint From The Foundry. 5 (1934) P. 2

13. Same as (7), P. 7-10
14. Lefebure, G. The Soda Ash Process In Iron Metallurgy. Rev. universelle mines. 15, 263-90 (1939). Original Not Seen. Chem. Abst. 33, 6205 (1939)
15. Oelsen, w. and Middel, w. Desulfurization of Crude Iron By Alkalies. I. The Reactions of Sulfur-Containing, Silicon-and Manganese-Poor Crude Iron Melts With Soda and Sodium Silicates. Mitt. Kaiser Wilhelm Inst. Ersenforsch. Dusseldorf. 21, 27-55 (1939). Original Not Seen. Chem. Abst. 33, 4562 (1939)
16. Oelsen, w. and Korber, G. The Fundamentals of the Dephosphorization of Pig Iron With Sodium Carbonate and Sodium Silicates. Stahl M. Ersen. 58, 905-14, 943-9 (1938). Original Not Seen. Chem. Abst. 33, 103 (1939)
17. Kraus, E. H., Hunt, W. F., and Ramsdell, L. S. Mineralogy. P. 179. McGraw-Hill Book Co., New York 1936
18. Holbrook, W. F. Relative Desulfurizing Powers of Blast-furnace Slags, II. Metals Technology. A. I. M. E. 5, No. 1, 12 (1938)
19. Holbrook, W. F. and Joseph, T. L. Relative Desulfurizing Powers of Blast Furnace Slags. Trans. A. I. M. E. 120, 99 (1936) P. 114
20. Ibid. P. 116
21. Didkowski, W. Desulfurization of Cast Iron With Sodium Bicarbonate. Przeglod Tech. 77, 128-30 (1938) Original Not Seen. Chem. Abst. 32, 8326 (1938)
22. Same as (7), P. 1
23. Purite's Place In Foundry Practice. Bulletin of the Mathieson Alkali Works (Inc). 60 East 42nd Street New York City. 1935
24. Same as 10, P. 4
25. Wood, C. E., Barrett, E. P., and Holbrook, W. F. Desulfurization of Pig Iron With Calcium Carbide. Metals Technology, A. I. M. E. 6, No. 8, 8 (1939)

26. Soc. d'electrochemie, d'electrometallurgie et des acieries electriques d'Ugine. Patent. Dephosphorization and Desulfurization of Steel. Brit. 495, 868. Chem. Abst. 33, 2875 (1939)
27. Soc. d'electrochemie, d'electrometallurgie et des acieries electriques d'Ugine. Patent. Refining Steel. Fr. 815, 227. July, 1937. Chem. Abst. 32, 906 (1938)
28. Hardy, C. Patent. Refining Iron and Other Metals. Brit. 461, 115. Feb. 10, 1937. Chem. Abst. 31, 4639 (1937)
29. Bardenheuer, P. and Osterman, H. The Influence of Alkalies On Iron Baths. Mitt. Kaiser-Wilhelm-Inst. Eisenforsch. Dusseldorf. 9, 129-40 (1927) Original Not Seen. Chem. Abst. 21, 1951 (1927)
30. Metallfrax, A. G. Patent. Desulfurizing Iron. Brit. 477,083. Dec. 20, 1937. Chem. Abst. 32, 4135 (1938)
31. Bardenheuer, P. and Geller, W. The Basis of Desulfurization of Pig Iron and Steel. Mitt. Kaiser-Wilhelm-Inst. Eisenforschung. Dusseldorf. 16, No. 7, 77-91 (1934) Original Not Seen. Chem. Abst. 28, 3037 (1934)
32. Joseph, T. L. and Holbrook, W. F. Silica and Alumina In Iron Ores. Blast Furnace and Steel Plant. 23, 313-16 (1935). Original Not Seen. Chem. Abst. 29, 4302 (1935)
33. Same as 19 p. 115
34. Mikulinsku, A. S. and Umova, M. A. The Reaction of Alumina With Iron Sulfide in the Presence of Carbon. Metallurg. 9, No. 10. 34-42 (1934). Original Not Seen. Chem. Abst. 29, 7894 (1935)
35. Same as 25, P. 1
36. Ibid, P. 2
37. Tamman, G. and Samson-Himmelstjerna, H. O. v. Desulfurizing the Steel Bath, Z. anorg. allgem. Chem. 20, 329-36 (1931). Original Not Seen. Chem. Abst. 26, 1554 (1932)

38. "Equil. Conditions In Desulfurizing Reactions."
Annual Report of the Met. Division, Fiscal Year
1937-38. U. S. B. M. Rept. Investigations.
3419 80 pp. (1938)
39. Girod, P. Patent. Refining Metals or Alloys. Fr.
765,183. June 4, 1934. Chem. Abst. 28, 6693
(1934)
40. Possenti, A. Desulfurization of Iron and Steel by
Acid and Basic Slags. Congres. intern. mines.
met. geol. appliquee. Sect. met. 6th session.
Liege, June, 1930. pp 815-18. Original Not
seen. Chem. Abst. 25, 3760 (1932)
41. Guedras, M. Desulfurization of Steel. Metaux (Aciers
speciaux) 9, 627-8 (1934) Original Not Seen.
Chem. Abst. 29, 4312 (1935)
42. Jenicek, L. The Perrin Procedure In Metallurgy. Chem.
Listy. 31, 213-15 (1937) Original Not Seen.
Chem. Abst. 31, 7371 (1937)
43. Viandon, P. F. The Use of Ferro Alloys In The Foundry.
Bull. Assoc. Tech. fondene. 10, 324-32 (1936).
Original Not Seen. Chem. Abst. 31, 347 (1937)
44. Rochling'sche Eisen und Stohwerke. G, m. b. H. Patent.
Fr. 825,908. Mar. 17, 1938. Chem. Abst. 32,
6222 (1938)
45. Rochling'sche Eisen und Stohlwerke. G, m. b. H. Patent.
Brit. 504,930. April 28, 1939. Chem. Abst. 33,
7721 (1939)
46. Hennig. C. T. Patent. Desulfurizing and Purifying
Iron. U. S. 1,963,a69. June 19, 1934. Chem.
Abst. 28, 5033 (1934)
47. Levi, W. The Effect of Soda Ash Desulfurization On
Fluidity of Cast Iron. Radford, Virginia.
Private Communication
48. Schulz, H. B. Patent. Refining Iron and Steel. W. S.
a,120,298. June 14, 1938. Chem. Abst. 32, 5769
(1938)
49. Lusifer Products Co. Patent. Steel Purification.
Brit. 332,890. Jan 21, 1929. Chem. Abst. 25,
48a (1931)

50. Arnovich, M. S. and Lyubarskii, I. M. Determination of Nonmetallic Inclusions In Steel With A Microscope. *Metallurg.* 11, No. 9, 89-95 (1936) Original Not Seen. *Chem. Abst.* 31, 7017 (1937)
51. Scott, F. W. Extraction of Oxide Inclusions In High Carbon Iron-Electrolytic Iodine Method. *Metals and Alloys.* 9, 171-174, July (1938)
52. Frevert, H. L. Patent. Desulfurizing Ferrous Metal. U. S. 1,770,395. July 15, 1930. *Chem. Abst.* 24, 5401 (1930)
53. Robinson, R. Patent. Refining Molten Iron. U. S. 1,997,602. April 16, 1935. *Chem. Abst.* 29, 3643 (1935)
54. Andrews, C. W. (to H. A. Brassert and Co.). Patent. Purifying Molten Iron Containing "Manganese of Sulfur" and Other Inclusions. U. S. 2,085,565. June 29, 1937. *Chem. Abst.* 31, 5743 (1937)
55. Fraser, J. S. and H. A. Brassert Co. Patent. Desulfurizing Iron. Brit. 482,820. April 1, 1938. *Chem. Abst.* 32, 7402 (1938)
56. Andrews, C. W. (to H. A. Brassert and Co.). Patent. Removal of Sulfur From Molten Ferrous Metals. U. S. 2,146,926. Feb. 14, 1939. *Chem. Abst.* 33, 3746 (1939)
57. Colbeck, E. W. and Evans, N. L. The Sodium-Carbonate Process for Treating Cast Iron. *Foundry Trade J.* 49, 191-2 (1933). Original Not Seen. *Chem. Abst.* 28, 81, (1934)
58. Imperial Chem. Industries, Ltd. Desulfurization of Cast Iron By Means of Soda Ash. Harmful Effects of Sulfur As An Impurity In Cast Iron. 1931. 12 pp. Original Not Seen. *Chem. Abst.* 26, 2402 (1932)
59. Siczawinski, S. and Miernik, E. Desulfurization of Iron By Means of Granulated Sodium Carbonate. *Przeglad Tech.* 75, 484-7 (1936). Original Not Seen. *Chem. Abst.* 32, 2064 (1938)
60. Thyssen, A. Patent. Refining Iron. Fr. 832,562. Sept. 29, 1938. *Chem. Abst.* 33, 2470 (1939)

61. Jakova-Merturi, G. (to Societe generale d'explortation des carbones). Steel or Iron From Cast Iron. U. S. 1,779,744. Oct. 28, 1931. Chem. Abst. 25, 66 (1931)
62. Serebrier, J. I. and Shternberg, A. M. Patent. Desulfurizing Cast Iron. Russ. 38,658. Sept. 30, 1934. Chem. Abst. 30, 3396 (1936)
63. Pacz, A. Patent. Refining Metals. Can. 285,291. Dec. 4, 1928. Chem. Abst. 23, 589 (1929)
64. Davies, E. V. Patent. Refining Iron and Steel. Brit. 400,593. Oct. 16, 1933. Chem. Abst. 28, 1979 (1934)
65. Walter, R. Patent. Refining Metals. Ger. 589,256. Dec. 4, 1933. Chem. Abst. 28, 1316 (1934)
66. Harvis, H. (to A. O. Smith Corp.). Patent. Refining Ferrous Metals. U. S. 1,920,465. Aug. 1, 1933. Chem. Abst. 27, 4765 (1933)
67. Heinrich Koppers Industrie-ele Moatschoppij N. V. Patent. Desulfurizing Crude Iron. Fr. 831,381. Sept. 1, 1938. Chem. Abst. 33, 2470 (1939)
68. Pacz, A. Patent. Compositions For Refining Metals. Can. 285,290. Dec. 4, 1928. Chem. Abst. 23, 589 (1929)
69. Osborg, H. Patent. Refining Metals and Alloys. Ger. 602,279. Sept. 5, 1934. Chem. Abst. 29, 440 (1935)
70. Hardy, C. (to Hardy Met. Co.). Patent. Treating Metallic Calcium For Refining Iron, etc. U. S. 1,922,037. Aug. 15, 1933. Chem. Abst. 27, 5048 (1933)
71. Farrel Jr., W. J. Calcium Carbide as an agent For Removing Sulfur and Phosphorus From Iron and Steel. J. Western Soc. Eng. 32, 206-18 (1927). Original Not Seen. Chem. Abst. 21, 3178 (1927)
72. Kroll, W. Desulfurizing Iron With Beryllium. Metallwirtschaft. 13, 21-3 (1934). Original Not Seen. Chem. Abst. 28, 1967 (1934)

73. Forbenud, I. G. Patent Steel and Iron. Fr. 664,458.
Nov. 22, 1928. Chem. Abst. 29, 819 (1930)
74. Meehan, A. F. (to Meehanite Metal Corp). Patent.
Purifying Cast Iron. Brit. 292,164. June 16,
1927. Chem. Abst. 23, 1382 (1929)
75. Osborg, H. (to Maywood Chemical Works). Patent.
Purification of Metals and Alloys. Can. 340,603.
April 3, 1934. Chem. Abst. 28, 4028 (1934)
76. Heuer, R. P. Patent. Desulfurizing Pig Iron. Brit.
499,302. Jan. 17, 1939. Chem. Abst. 33, 4952
(1939)
77. Paschke, M. and Peitz, E. A New Process of Smelting
Foundry Pig-Iron. Foundry Trade J. 55, 454-7
(1937). Original Not Seen. Chem. Abst. 31,
640 (1937)
78. Frankl, M. Patent. Refining Iron and Steel. Ger.
669,500. Dec. 28, 1938. Chem. Abst. 33, 2475
(1939)
79. Genesis, A. Desulfurization of Cast Iron. Novosti
Tekhniki. 1936 No. 32-3, 13-14. Original
Not Seen. Chem. Abst. 31, 2145 (1937)
80. Gilbert, H. N. (to E. I. duPont de Nemours and Co.).
Patent. U. S. 1,931,144. Oct. 17, 1934.
Chem. Abst. 28, 89 (1934)
81. Brassert, H. A. and Colclough, T. P. (H. A. Brassert
and Co; Ltd). Patent. Iron Manufacture.
Brit. 460,138. Jan 18, 1937. Chem. Abst. 31,
4639 (1937)
82. Laissus, J. The Alloys of Iron and Beryllium. Bull.
assoc. tech. fondene. 11, 124-32 (1937). Original
not Seen. Chem. Abst. 32, 97 (1938).
83. Soc. d'electrochimie, d'electrometallurgie et des acieres
electriques d'Ugine (Fonderia Milanese de acciaio
Vantriques, applicant in Italy). Patent. Dephos-
phorization and desulfurization of Steel. Fr. 803,
491. Oct. 1, 1936. Chem. Abst. 31, 2575 (1937)

84. Lemoine, R. P. (to Soc. d'electrochimie, d'electrometallurgie et des acieries electriques d'Ugine. Patent. Simultaneous Dephosphorization and Desulfurization of Steel. U. S. 2,147,205. Feb. 14, 1939. Chem. Abst. 33, 3799 (1939)
85. The Titanium Alloy Manufacturing Co. Patent. Alloy For Use In Degasifying and Purifying Molten Steel. Brit. 452,092. Aug. 17, 1936. Chem. Abst. 31, 996 (1937)
86. Bettendorf, C. and Nicholas, J. The Desulfurization of Steel and Pig Iron. Stahl u Eisen. 52, 577-82 (1922). Original Not Seen. Chem. Abst. 27, 252 (1933)
87. Oelsen, W. Desulfurization of Pig Iron. Stahl u. Eisen. 58, 1212-17 (1938). Original Not Seen. Chem. Abst. 33, 951 (1939)
88. Joseph, T. L. and Holbrook, W. F. Desulfurization Studies. Progress Reports. Met. Division. 6 Bureau of Mines. Report of Investigations No. 3240 (1934)
89. Kelley, K. K. Data On Theoretical Metallurgy VII. The Thermodynamic Properties of Sulfur and Its Inorganic Compounds. U. S. Bureau of Mines. Bull. No. 406, 154 pp. (1937)
90. Grigsby, C. E. Effect of Typical Slags On Fire Brick. Jour. Am. Ceram. Soc. 12 (4) 241-63 (1929)
91. Hoff, Jr., R. S., Dear, P. S., and Whittemore, J. W. Corrosion of Refractories By Soda Ash Foundry V. P. I. Eng. Exp. Sta. Bull. 38, 9 (1939)
92. Dear, P. S. Study of Soda-Ash Foundry-Slag Attack On the Refractory Lining of a Teapot-Type, Reservoir Ladle. Reprint from Bull. Am. Ceram. Soc. 18, 1 (1939)
93. Parker, O. A Dynamic Test For the Attack of Soda Ash Slag On Ladle Refractories. Unpublished Thesis. Library, Virginia Polytechnic Institute. Blacksburg, Virginia. 1940
94. Boles, C. E. and Blackburn, A. R. Refractories for Foundry Ladles. Paper Presented at Am. Foundrymen's Association Convention, Cleveland, Ohio, May 16, 1938

95. Kinney, C. L. Symposium On "Steel Mill Pouring Pit Refractories." IV. Memoir About Steel Pouring Refractories. Bull. Am. Ceram. Soc. 18, No. 3, 87-92 (1939)
96. Offutt, J. J. Lining For Reservoirs and Ladles Suitable For Soda Ash Treatment. Bull. 71. American Refractories Institute. August, 1938.
97. Dear, P. S., Mathews, A. A. L., and Whittemore, J. W. On Investigation of Some Virginia Feldspars. V. P. I. Eng. Exp. Bull. 35, 2 (1938) p.23
98. Lundell, G. E. F.; Hoffman, J. I., and Bright, H. A. Chemical Analysis of Iron and Steel. p. 239. John Wiley and Sons, Inc. New York. 1931
99. Desulfurizing Pig Iron With Sodium Carbonate. Stahl u. Eisen. 58, 773-9 (1938) Original Not Seen. Chem. Abst. 32, 8324 (1938)
100. Voronin, D. Use of Soda Ash In Iron Casting. Litalnal Delo 8, No. 5-6, 37-9 (1937). Original Not Seen. Chem. Abst. 32, 4497 (1938)