METHODS OF ANALYSIS OF

METALLURGICAL SLAGS, LATATERITES, AND ALUMINIUM ALLOY

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BY

JOHN UDE OJONUBA, B.Sc. (Hons.) CHEMISTRY

DEPARTMENT OF CHEMISTRY
AHMADU BELLO UNIVERSITY
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D E D I C A T E D

T O

My parents, for their unique sacrifice, and
Ibaji people, for their interest and encouragement
throughout my education.

A C K N O W L E D G E M E N T S

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D E C L A R A T I O N

I hereby certify that the work herein described
s the result of my own investigation. It is not being
nd has not been submitted in candidature for any
ther degree.

J. U. OJONUBA

U. U. IBOK
(Supervisor)

Ag (HEAD OF DEPARTMENT)

A B S T R A C T

The problems encountered in the dissolution of refractory materials such as metallurgical slags and laterites and methods of estimating the different elements in solution are revealed in a literature survey. On the basis of previously reported work, decomposition by anhydrous sodium carbonate fusion has been chosen as the most feasible method of dissolving the materials.

The decomposition of the samples and the different methods used in determining the concentrations of the elements in solution are described.

The results obtained show that:

(i) The amount of tin decreases from about 17% in the first run slag (No.1 slag) to 0.5% in the final slag and that the Jos tin smelting and reclamation processes are quite efficient.

(ii) The primitive ferrous slags contain significant amount of iron (26 - 34%) compared to (0.3 - 1.0%) in modern iron making slags, suggesting a crude and inefficient practices.

(iii) The laterites in Samaru West are of very low iron (15 - 22%) and aluminium (5 - 7%) contents but high in silica and therefore cannot be economically exploited as sources of iron and aluminium in the foreseeable future.

An aluminium-alloy has also been analysed. From the results obtained, a composite alloy is suspected. Apart from aluminium (88.7%), other major constituents are Fe(5.8%) silicon Fe(5.94), Mg(0.55%), Pb(0.51%) and Cu(0.12%) plus traces of other metals.

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C H A P T E R I

1 I N T R O D U C T I O N

1.1 Preamble

Since the advent of civilization, analysis has continued to be of paramount importance in technological advancement. For example in industry, analysis is often constantly carried out as a check on specifications and control of products. The discovery of new compounds in certain disciplines (Chemistry, Pharmacy, Biology, Medicine, etc.) depends to a greater or lesser extent on the answers provided after analysis. In ferrous production and other metal extraction processes, theoretically if one knew precisely all the reactions taking place at any particular moment during the manufacture of steel (and other metals) we would be able to produce metal to close specifications with a high degree of certainty. In practice however, this ideal cannot be achieved at present. The conditions of the metal and

slag within the furnace are constantly changing and a state of equilibrium is never attained. This means that a sample taken from the furnace can only be representative of the melt at the time of taking that sample. Obviously, therefore, the faster and more accurate one can perform the analysis, the more closely can one control the reactions taking place within the furnace. In recent years, there have been rapid advances in the use of modern instrumental techniques to speed up analysis, with each new development aiming at providing more rapid and accurate results.

The enormous ferrous slag samples excavated by an archeologist (Dr. J. E. G. Sutton) in Samaru and submitted to the Department for analysis, tin slags from tin smelting company in Jos, and the aluminum alloy sample sent to the Department for analysis from the Defence Industries Corporation, Kaduna, prompted the present investigation into methods of analysis of metallurgical slags, laterite, and alluminum alloy. The results obtained from the analysis of ferrous slags could provide not only metal content but also a means of comparison of the primitive and modern methods of iron manufacture. Analysis of tin slags would reveal the efficiency of tin

extraction whilst that of aluminium alloy would supply the much needed information on the composition of the alloy to the Nigerian Defence Council.

Thus, in view of the fact that future research may be devoted to the development of rapid analytical techniques, it would be reasonable to expect continuing interests in different methods of analysis of slags and other desired specimens.

1.2 Slags

Even after intensive ore dressing operations, the resulting concentrates still contain sufficient amount of gangue and other minerals associated with the ore. These minerals react with the fluxes and silica during smelting to produce a molten mass which being lighter than the molten metal floats on the molten metal. This non-metallic molten silicate mass is known as slag. Most metallurgical slags are molten silicates, with aluminates, phosphates, borates, and fluorides as other possible major or minor acid constituents.

Slags formed from the oxides among the gangue minerals as mentioned above are known as extraction slags. Fluxes are carefully chosen so as to produce a slag with low solubility for the oxide of the metal being smelted in

order to ensure maximum recovery. Thus, siliceous gangues are commonly fluxed with CaO and FeO, while Limey gangues might be fluxed with sand (SiO_2). In thermal refining of metals or some other metallurgical processes like steelmaking, special slags are required which would be capable of absorbing, usually as oxides. impurities from the metal. These refining slags, as they are termed, may incorporate chemical reagents for converting these impurities into soluble or volatile forms. Recently the term slag has also been used to refer to molten inorganic salts, mainly halides, which are products of smelting operations involving the reduction of pure metal halides with metals like calcium, magnesium, or sodium. These also are extraction slags.

Slags are believed to be ionic. This view is based on X-ray diffeaction studies of silica, silicates, and glasses, and on the measurement of viscosity, surface tension, and also on electrical conductivity.

1.2.1 Tin Slags

Tin Slags are only produced as by-products during tin smelting operations. The number of slags produced (and hence slag treatment) in one cycle of operation varies from smelter to smelter.

The conventional route by which tin (and hence tin slag) is obtained is by reduction of the stannic oxide ore, cassiterite (which incidentally is the principal source of primary tin) with carbon in modern reverberatory furnaces at about 1250° - 1350°C (Jos practice 1400°C). Difficulty does arise in producing clean slags due to the amphoteric nature of tin oxide. Tin silicates are formed, as it has a high affinity for silica, while stannates of calcium and other metals are produced if basic fluxes are used with the object of minimizing the former tendency. Hence, although reduction with carbon is comparatively easy, the smelting operation is complex because of intensive retreatment of slags.

Of all the tin ores available, cassiterite, (SnO_2) containing when pure, 78.6 per cent tin is the only significantly economic mineral from which tin is produced. Small amounts of the metal occurs in the mineral stannite which is an Fe-Cu-Sn sulphide (SnS_2. Cu_2S. FeS) but little or no tin is produced from this mineral. The smelting of tin ores after preliminary treatment embraces three distinct steps.

(i) primary smelting of the ore

(ii) retreatment of slags (usually the first run slags)

(iii) refining of the metallic tin.

The reduction of tin oxides is comparatively easy, hence pyrometallurgical reduction process remains dorminant for the extraction of tin. The reduction takes place readily when the oxide is heated with carbon to fairly high temperatures (850° - $900^{\circ}C$) (1, 2), but the composition of slags formed determines the temperature required for smelting operations since smelting temperatures should be such as to form fluid slags and allow the reduced tin to separate, settle and collect in the bottom of the furnace.

In practice, the ore premixed with fluxes is first smelted in a furnace (usually reverberatory furnace) usually with carbon, preferably anthracite to produce an impure tin and a tin - rich slag which may contain up to 30 per cent Sn.

The principal reaction takes place according to the equation.

$$SnO_2 + C = Sn + CO_2$$

$$\Delta H^{\circ} = 185 \text{ KJ mole}^{-1}$$

indicating that the reaction is highly endothermic.

Tin melts at $232^{\circ}C$, but a much higher temperature is required for the reduction of cassiterite. As earlier

mentioned. Temperatures in the range 1250° - 1350°C are commonly in use and ensure separation of the liquid tin from slags. The charge to the smelting furnaces consists of concentrates, anthracite fines, limestone, and small amount of dross.

The slag containing 20 - 40 per cent tin is often retreated in a reverberatory furnace with coal and limestone with or without iron to produce metal analysing about 95% Sn compared to that of the primary of 98 - 99% Sn and a second run slag. The resulting slag frequently still contains sufficient metal to necessiate retreatment (because of the high price of tin). The low grade metal from the second slag smelt is often a tin-iron alloy (80% Sn and 20% Fe) known as "hardhead" and is smelted with fresh concentrate and silicous flux,

$$SnO_2 + 2FeSn = 3Sn + 2Fe,$$

the ferrous oxide going into slag as a silicate.

In the Jos practice, the retreatment of first run slags produces "hardhead" and a lean slag (No. 2 slag). The lean slag so produced is further treated for tin recovery by fuming proces i.e. fuming with gypsium ($CaSO_4$) and collecting the fumes in baghouses while the final slag is sold for Nb, Ta, and W content.

The re'ining of the impure metallic tin will not be discussed since no slag is produced in the operation.

1.2.2 Ferrous Slags

Ferrous slags are produced from primary iron smelting process (iron making) as well as the refining of pig iron (steelmaking) produced from the primary blast furnace smelting.

The modern iron making blast furnace has evolved directly from the early shaft furnaces, particularly the tall stack, the bosh, the ring of tuyeres for the air blast and the hearth with its slag and iron tapholes.

The ore is fed into the furnace from the top together with coke and fluxes. Hot air from the bottom at about 600^{o} - $800^{o}C$ burns the coke to CO. This reduces the oxide to metallic iron. Pure iron melts at $1537^{o}C$, although it is possible to reduce the oxide at 700^{o} - $800^{o}C$ by carbon or CO to the solid metal (in the loose granular form called sponge iron at this temperature range). The melting point of iron ($1537^{o}C$) is progressively lowered by the addition of most of the common solute elements. The metal from the blast furnace is always in contact with coke and the melting point of iron saturated with carbon is about $1200^{o}C$.

Also, there exists the final slag consisting principally of lime (CaO), alumina (Al_2O_3), magnesia (MgO), silica (SiO_2), and sulphur and this slag melts at 1400° - 1500°C depending upon the composition. The fusion temperature of the slag thus sets the lower limit of operation temperature of the process. In practice, the actual temperature is somewhat greater than this minimum in order to ensure that the slag is sufficiently free flowing.

The pig iron produced can contain up to about 4½% carbon since it is in contact with coke in the furnace. Because of this, the pig iron must be refined. Steel-making is thus the process of burning off the carbon by O_2 and reducing the concentrations of other elements present (Mn, P, Si, e.t.c.) to acceptable limits.

The process by which the blast furnace metal and ferrous scrap are converted into steel are conventionally named after the furnace in which the refining operation is performed and the nature of slag (e.g. Acid Bessemer, Basic Bessemer processes) which is employed to absorb the product of oxidation. Hence, during steelmaking, the impurities like Si, P, and Mn are oxidized and enter the slag which floats on the molten steel.

Tylecote (3) has summarized primitive smelting practice throughout the world, while Sassoon (4) has described probable iron-smelting operations used in Sukur, North - Eastern Nigeria. From the reports of these workers (3, 4), the possible chemical constituents of the resulting slags may be listed. For example in Tylecote's review, the iron ore includes magnetite (Fe_3O_4), whilst minerals such as haematite (Fe_2O_3) and limonite ($Fe_2O_3 . 3H_2O$) are essential constituents of laterites. The iron content of some of the ores may be as low as 34 per cent but could be crushed and washed to produce a concentrate analysing over 56 percent iron. The ore is reduced to a spongy metal with charcoal and in almost all cases, no flux is added. Slags produced in these operations are usually very close in chemical composition to that of the ore, and the metallic yield is very low.

1.2.3 Slag Analysis

Slag analysis is very essential in metal manufacture. Any information about the composition of the slags is used in assessing the efficiency of metal winning operations and also in maintaining specifications of metallurgical products such as steel.

The use of fast and accurate instrumental techniques, such as X-ray fluorescence and emission spectrography has enabled the analysis of metal component of steel-making furnace to be so rapid that it can be used for the control of steel products (5). This is possible because of the homogenity of the metal produced which requires no extensive sample preparation. Slags, however, are both complex and heterogeneous and hence considerable sample preparation is necessary to produce a homogeneous sample. This is tedious and time consuming and prevents slag analysis in taking advantage of the rapid means of analysis now available. Thus, analysis of slags has only served to produce "post mortem" results to be used in the adjustment of conditions of operation.

Recently attempts have been made to investigate possible rapid methods of analysing slags by spectrographic means (6). Firstly, the group investigated the usefulness of the solution technique for the analysis of slags. The slag was brought into solution by first fusing it in a mixture of sodium carbonate and borax and then dissolving the fused melt in dilute nitric acid containing a small amount of hydrogen peroxide or sodium nitrite to prevent the precipitation of manganese. Cobalt was

added as an internal reference. Using the rotating disk or 'Retrode' technique and the impregnated electrode technique to excite the solution, early results were not satisfactory due to errors arising from impure chemicals and setting up procedures. Satisfactory results were obtained later after removing these sources of error. Two further methods were introduced; namely the Danielsson Tape technique, and the briquetting technique. In both cases, the slag, after the addition of an internal reference, was fused, the fused melt ground to a fine powder and the analysis performed. These procedures proved faster than the solution method (taking 10 - 15 minutes most of which were consumed by sample preparation). The accuracy was higher than that from routine chemical control methods. Similar results were obtained by the Tubes Division of Bisra Chemical Analysis Committee who used X-ray fluorescence.

Purely chemical techniques were considered for the rapid analysis of iron - and steelmaking slags (6). In this scheme, all the main constituents are determined from one solution of the sample, taking aliquots for each constituent. With a number of improvements suggested, the revised method was shown to be more rapid than classical chemical procedures and suitably accurate for

works analysis but could not however be considered as a means of slag analysis control.

Another attempt made by other workers was aimed at by - passing the long and tedious conventional methods of analysis of slags. In this investigation, a fusion method with anhydrons lithium metaborate followed by dissolution of the melt in dilute nitric acid was compared with a method based on decomposition of the sample by hydrofluoric acid at 110°C. The resulting sample solution in each case was analysed for SiO_2, Al_2O_3, Cu, Zn, and Fe by means of atomic absorption spectroscopy. The accuracy and precision of the two methods were compared by carrying out replicate analyses of standard iron ore sinter and typical copper smelting slags. Bailey and Wood (7) concluded that both methods provide rapid alternative methods for slag analysis and that the lithium metaborate fusion method was more convenient to be used for most samples with the exception of those samples with a high total metal content.

The results of these studies reveal two major problems encountered in slag analysis. These include the decomposition and solution of slags and the determination of the constituent elements present in the slags.

Some of these decomposition procedures and methods of analysis are discussed below.

1.2.3.1 Decomposition Procedures

As refractory materials, slags are generally very resistant to attack by common solvents and can only be dissolved by more intensive treatment. It is seen (1.2) that slags consist of silicates with aluminates, phosphates and borates formed from oxides and gangues associated with the minerals. It is therefore convenient to discuss the decomposition of slags in terms of the procedures adopted for silicates and other constituent refractory compounds such as refractory oxides.

The decomposition of silicates and similar materials has been extensively covered by Maxwell (8) and Jeffery (9). The methods of getting the material into solution can be divided into three distinct groups:

(1) Decomposition by mineral acids (HNO_3, $HClO_4$, hot concentrated H_2HO_4, HCl, HF, H_3PO_4, HBr, dilute H_2SO_4 and dilute $HClO_4$),

(2) Decomposition by fusion with suitable compounds (fluxes), and

(3) Decomposition at high temperatures and pressures (in bombs or sealed tubes) using suitable solvents (e.g. mineral acid).

Acid fluxes include the bisulphates, pyrosulphates and acid fluorides, while the most basic fluxes are hydroxides, peroxides, carbonates, and borates. With these basic fluxes there is probably less tendency of losses by volatilisation during fusion compared to the acid fluxes (e.g. those mentioned above) where losses are usually encountered in acid solution. It is worth noting that the oxidation potential of alkaline peroxides increases with increasing temperature while alkaline carbonate fusion leads to oxidation of some elements owing to more intimate contact between elements and air. This oxidation tendency is less observed in fusion with bisulphates.

The advantage of decomposition of slags by fusion is two-fold. Firstly, the colour of the solidified melt may be indicative of the presence of some of the constituent elements (e.g. transition elements). Additionally, relatively short time is required for fusion of the samples.

Of all the mineral acids, hydrofluoric acid appears to be the most commonly used for the decomposition of most silicates. The use of HF in combination with HNO_3, $HClO_4$, or H_2SO_4 results in a substantial removal of fluorine and silica during evaporation, the residue being

dissolved in water or dilute acid for the determination of other elements present in the slag or silicate materials. HF/perchloric acid mixture has the advantage (compared to HF/sulphoric acid mixture) that almost all the perchlorates are water soluble. On the other hand, evaporation with sulphuric acid is somehow more efficient in the removal of fluorine. However, the use of HF without the addition of other mineral acids has recently been recommended by several workers, (10, 11), although this requires decomposition at high temperatures and presseures in bombs. This procedure, despite associated difficulties would be preferred since silicon is not lost through volatilisation and can be determined photometrically or otherwise.

The decomposition of silicates with HF is suspect because of possible loss of silicon as volatile SiF_4 although Langmyhr and Graff (12) have shown that no appreciable loss of Si occurs when SiO_2 is decomposed by HF even at 100°C. A small amount is said to be lost when the solution of fluorosilicic acid is evaporated to a very small volume (e.g. 0.2 mg SiO_2 is lost from 46 mg SiO_2 present when a 1:3 HF solution is evaporated from 25 to 2ml at 100°C). Decomposition is also long and tedious, for maximum decomposition may take as long as

24hr. using 48% HF (w/w) which is available in most laboratories.

The use of HCl for the chemical dissolution of slags and silicate materials is restricted to samples with low silica content. Any silica present appears as hydrous suspension. The solubility of the samples in HCl is markedly increased by prolonged heating possibly at high temperatures (in sealed tubes). The acid is easily removed by evaporation. Loss of some elements (e.g. Ge, Sb, As, Sn, e.t.c.) may occur because of the volatility of their chlorides especially at high temperatures.

Relatively little use is made of H_2SO_4 as a solvent for silicates and refractory materials such as slags but extensive use is made of the acid as a mixture with HF. This is because of the formation of insoluble sulphates with most metals. Similarly nitric acid can also only be used in conjuction with HF for dissolving such resistant materials.

Perchloric acid is very attractive as a solvent for slags because of the solubility of most perchlorates (except those of K, Rb, Cs). Many silicates can be decomposed with hot concentrated perchloric acid with subsequent dehydration and separation of silica.

As has already been mentioned, it is used sometimes as a mixture with HF to decompose silicates especially when silicon is to be removed as volatile SiF_4.

In most fusion processes, anhydrous sodium carbonate appears to be the most commonly used flux. It fuses silica and slags forming silicates and other compounds which are subsequently leached with suitable solvents such as dilute mineral acids. Fusion may be carried out in crucibles of platinum or platinum-alloy (e.g. platinum-iridium alloy, nickel and even iron) provided none of the metal used in the manufacture of the crucible is to be determined. A flux to sample ratio of about 5:1 and a temperature of 1000° - $1200^{\circ}C$ are used.

Potassium carbonate, which is more hydroscopic than Na_2CO_3, is only used to produce fusion melts likely to be more soluble than corresponding sodium salts, viz niobium. An equimolar intimate mixture of anhydrous Na_2CO_3 and K_2CO_3, called fusion mixture, has an advantage of a lower melting point than either of the single salts, especially for the fusion of samples in which chlorine or fluorine is to be determined.

Potassium or sodium hydroxides, though very powerful alkaline fluxes, cannot be used for fusion in platinum crucible, so other crucibles such as gold, silver,

nickel (for fusion below 500°C), must be used. In addition, these compounds are difficult to obtain pure and tend to froth and spit when heated.

Sodium peroxide is a very powerful flux; it is the usuall flux used for complete decomposition of cassiterite or chromite (9). It attacks most crucibles thereby seriously contaminating the resulting solution. Silver, gold and zirconium crucibles resist its attack (although these are expensive). Fusion is carried out at 600° - 700°C.

Jeffery (13) has found that refractory oxides are completely fused with borax. Borax fluxes (e.g. alkaline flux and boric acid, an acidic flux) are not often used probably because the resulting melts are viscous and boron must be removed at a later stage of the analysis.

The alkaline fluxes KF, KHF_2, NH_4F, are low-temperature fluxes used chiefly for the opening up of refractory silicates and oxides (e.g., niobium and tantalum minerals, etc.) by formation of soluble fluoride complexes. Fusion can be achieved mostly in platinum crucibles in less time than most other fluxes.

Rafter (14) has proposed a sintering procedure that will, at a comparatively low temperature, easily and

completely decompose those minerals resistant to decomposition by the usual methods, without the slightest attack on a platinum crucible, and very slight attack on iron or nickel vessels. Sodium Carbonate, calcium carbonate and ammonium chloride are some of the sintering substances.

The attack of mineral acids (e.g. HCl) on difficulty soluble minerals can be improved by the use of high pressures and temperatures in sealed glass tubes or bombs. Their relatively less popularity stems mainly from the need for specialised equipment and the hazards involved. The resulting solutions are free from contamination of elements from fluxes.

The procedures for the dissolution of siliceous samples (e.g. slag and silicates) and estimation of constituent elements have been divided into two distinct groups (15). In the first group, the sample is brought into solution with a suitable solvent (e.g. mineral acids) while the second group involves fusion with suitable fluxes. Silicon can be got into solution ($<25\%$) together with other elements and their concentrations estimated using atomic absorption spectrophotometer. Alternatively, the silicon can be completely removed by volatilisation or precipitated as silica when its

content can be determined gravimetrically. Price (15) suggests lithium metaborate as the readily used flux for fusing slags and other similar refractory materials. The fusion is said to be carried out in platinum or graphite crucibles at a temperature of about 900°C for 15 minutes after which the melt is leached with dilute nitric acid. The alternative to Price's view is where the slag is fused with sodium carbonate and leached with hydrochloric - nitric acid mixture (16).

Having discussed the possible methods of getting slag into solution, it will be convenient to review the different ways of estimating the concentration of individual elements present in the slags. Some of these methods are discussed below (section 1. 2. 3. 2).

1.2.3.2 Methods of Analysis

In evaluating analytical techniques with respect to their relative utility for a given problem, the principal factors generally considered are selectivity, sensivity, and speed. Selectivity is the ability to detect and determine one substance in the presence of others which are commonly associated with the desired constituent and which might be expected to interfere with its identification and determination. The sensitivity demanded depends on the concentration of the constituent

present in the sample. The degree of accuracy required depends on the intended use of the analytical data, the availability of relevant facilities and experienced manpower. It is the desire of the analyst to strike a reasonable balance between these factors, which will result in low overall cost in time and material with a minimum of chemical processing and separation of the constituent elements before making the final estimation.

In analytical chemistry, researchers have continued to direct their efforts towards the discovery, development, and improvement of methods for obtaining reliable results. Rapid and accurate instrumental methods are playing important roles in analytical chemistry today. An important progress being made in this direction is the development of atomic absorption spectroscopy.

The conventional methods of analysis include, gravimetry, titrimetry, spectrophotometry and electrochemistry. When the concentration of the constituent of interest lies within the range of 10 - 100% in the sample, gravimetric method is usually capable of giving reasonable degree of accuracy with a precision better than 1 part in 1000. Gravimetry is not selective, it often requires complete separation of the metal or compound of interest, it is time consuming and at the

same time tedious. It is however generally cheap since no complicated equipments are required.

Titrimetry is usually designed to be specific, although in many instances separations may be necessary. It is capable of giving an accuracy of 0.2 - 0.5% and a precision of about 3 parts per 1000. It is not very versatil but is inexpensive.

Atomic absorption covers a concentration range from fractions of a part per million of many cations in solution to tens of percent of metallic constituents in the samples.

Spectrophotometry usually covers a slightly smaller concentration range than atomic absorption but it has the advantage that its calibration curves shift less, and as the contents in the cells are static, its precision and accuracy depend critically upon the sensitivity of the instrument, chemical separation, and the preparation of the sample which may be time - consuming. The chemical separations can be avoided by adequate treatment of the solutions such as, adjustment of pH, formation of complexes, oxidation-reduction, selection of reagent, selection of the wavelength used, e.t.c.

Electrochemical methods may compare favourably with atomic absorption only when preliminary separations are

not required. Generally, the instrumental methods are faster than the classical titrimetric and gravimetric methods, especially as only one soution prepared may be required for the determination of several or all elements present in the original sample. In addition, they are highly sensitive, and therefore find useful application for trace analysis. On the other hand, titrimetric and gravimetric methods are more precise and accurate for major constituent analysis. The high cost of complicated and complex equipments in instrumental methods compared to titrimetric and gravimetric methods is more than offset by the multiple number of estimating a number of elements from one solution prepared and the time and labour saved.

Originally, all chemical analysis were to be carried out using a Unicam SP 1900 Atomic Absorption spectrophotometer newly acquired in the Department. In the event, this technique was not used for all the metals and elements because of the lack of appropriate hollow cathode lamps and nitrous oxide gas which are required for specific elements. Consequently, other methods such as gravimetry, titrimetry and molecular spectroscopy were used when these could have served as a check on the results obtained by atomic absorption technique.

Tin can be separated from various interfering elements in a number of ways (17). For example, tin is separated from iron, aluminum, chromium, etc., by the insolibility of its sulphide in dilute hydrochloric acid. Tin, together with antimony, arsenic, platinum, and gold, is separated from lead, mercury, copper, cadmium, and bismuth, by the solubility of its sulphide in yellow ammonium sulphide. Antimony, arsenic, platinum, and gold are precipitated as metals from a hydrochloric acid solution by the action of metallic iron, leaving tin in solution. Although these methods are available, distillation is very effective in isolating tin from various elements such as arsenic, antimony, etc. which can first be distilled over as the chloride. Tin can then be distilled with a hydrobromic - hydrochloric acid mixture which leaves behind the remaining non-volatile interfering metals.

Gravimetrically, tin can be determined as SnO_2 by first precipitating metastannic acid (H_2SnO_3) when dilute stannic chloride solution is boiled in the presence of aluminum nitrate and finally decomposing the metastannic acid by heating to SnO_2. The reactions

$$SnCl_4 + 4NH_4NO_3 + 3H_2O \rightarrow H_2SnO_3 + 4HNO_3$$

and $H_2SnO_3 \xrightarrow{heat} SnO_2 + H_2O$

take place.

This procedure, though rapid, suffers from interference by the oxides of Bi, Nb, Ta, W, Sb, As, P (Fe, Cu, and Zn) which contaminate the SnO_2.

Tin can also be determined by precipitation of tin as sulphide but this involves some difficulties which can be avoided by using other methods. Another gravimetric method is the precipitation of tin by cupferron which is weighed as the oxide.

In the titrimetric method for the estimation of tin, titration is conventionally carried out with A. iodine or iodate as titrants in the presence of KI and starch as indicator in an atmosphere of CO_2. A full account of the method is given by several authors (18 - 21). The method depends on the oxidation of tin in the stannous to the stannic state by iodine or iodate according to the equations

iodine: $Sn^{2+} + I_2 = Sn^{4+} + 2I^- \quad \ldots\ldots\ldots (1)$

iodate: $3Sn^{2+} + KIO_3 + 6H^+ = 3Sn^{4+} + I^- + 3H_2O \quad \ldots\ldots\ldots (2)$

During dissolution of tin bearing materials, the tin may be in the stannic state. This must first be reduced to stannous ion. Iron, antimony, aluminum or lead can be used as reductants. This method is considerably free of interference from most elements usually found in association with tin ores, and is reasonably accurate. The end-point of the titration is reached when the concentration of I_3^- is sufficient to produce a blue colour with starch.

Dithiol (Toluene -3, 4- dithiol) and phenylfluorone are two reagents commonly employed in the colorimetric determination of tin (22). Dithiol gives a red precipitate with Sn^{2+} and the use of dispersing agents (e.g. gum arabic, sodium lauryl sulphate, santomerse) enables colorimetric estimation to be made. As little as 1 ppm of tin can be estimated, while 0.1 ppm of tin can be detected. However, many ions (e.g. Bi^{3+}, Cu^{2+}, Ni^{2+}, As^{3+}, No_2^-, etc.) interfere with the results, but it is possible to carry out the estimation in the presence of 20 times more Fe and Pb than tin. Any Sn^{4+} present is rapidly reduced to Sn^{2+} by the addition of thioglycollic acid. The coloration given by phenylfluorone with Sn^{4+} becomes selective when Sn^{4+} has been separated by carbomate-chloroform extraction. Interferences are

reported with Ge^{4+}, Zr^{4+}, Ga^{3+}, Fe^{3+}, Ta^{5+}, and P^{5+}, while small amounts of Mo^{4+}, Ti^{4+}, Nb^{5+}, Ta^{5+} can be complexed with hydrogen peroxide. The limit of sensitivity is 0.02 ppm.

A number of problems associated with the estimation of tin using the above mentioned methods may be overcome by the use of atomic absorption technique. However both air-acetylene and hydrogen-acetylene flames are said to be prone to interferences, but these can be lessened by use of nitrons oxide-acetylene flame (15). Hydrogen-acetylene flame gives similar sensitivity to nitrons oxide-acetylene, but the sensitivity with air-acetylene is lower than in either case. 10000 ppm of iron is said to enhance a tin concentration of 20 ppm by 8%.

Iron can be separated (22 - 23) from interfering ions by precipitation with (i) NaOH, which separates it from such elements as V, W, Mo, As, Al, e.t.c., (ii) H_2S in a weakly acidic solution which separates it from Hg, Pb, Bi, As, etc. (iron is left in solution); or by extraction (i) from concentrated (6 - 8 M) HCl solution into ethyl, dichloroethyl, or isopropyl ether saturated with HCl; (ii) as the 8-quinolinate or cupferrate into chloroform which separates iron from Mn,

Ni, Cr, and Al. Solvent extraction serves as a means of separating large amounts of iron from solution.

Precipitation with ammonia, oxine, and cupferron are some of the gravimetric methods for estimation of iron. The fact that estimations must be carried out from solutions practically free from other metal ions makes these methods less attractive. Iron can also be estimated volumetrically with standard ceric sulphate solution, which is claimed to be one of the most satisfactory reagents for titration of ferrous iron. Other reagents include $KMnO_4$ and K_2CrO_7. Thiocynate and O-phenanthroline methods are two most popular colorimetric methods of estimating iron. The thiocyanate method is simple and allows trace amounts to be estimated. The method is however not selective and special precautions must be taken to enhance its accuracy. O-phenanthroline is selective and, in addition, permits the estimation of trace amounts. The coloration is stable. Both methods suffer from interferences from certain ions.

Silica and concentrated perchloric acid are said to cause depression in the estimation of iron using atomic absorption spectrophotometer (15). Depression caused by silica may be eliminated by the addition of calcium chloride.

The analytical chemistry of aluminium is adequately covered and illustrated by Tikhonov (24). The metal can be estimated gravimetrically by precipitation with oxine (8-hydroxyquinoline), and as hydroxide with ammonia or weak organic bases, for example, pyridine. The gravimetric determination of the element is rarely used since other more accurate methods are available. However, it is useful as a means of separating aluminium from interfering metals provided such metals are not coprecipitated. Iron and several other metals which are precipitated must be removed, prior to the precipitation of aluminium. The precipitate is weighed as Al_2O_3 after ignition.

The photometric estimation of aluminium have been well described by Kassner et al (25). In this method, aluminium oxinate formed in the presence of tartrate, cyanide and hydrogen peroxide is extracted in $CH\ Cl_3$ with selective separation occurring at pH 9. Under these conditions the influences of Fe, Ti, U, V, Sn, Co, Ni, Mn, Cu, Cr, Zn, Cd, Mo, and Zr are eliminated. A concentration as low as $10_{\mu}g$ of aluminium in 25ml of solution can be estimated.

Atomic absorption spectrophotometric method of estimating aluminium requires the use of N_2O-acetylene

flame. Ionization interference can be eliminated by employing lanthanum or potassium as an ionization buffer. Calcium, silicon, and perchloric acid depress results while titanium, iron, fluoroboric acid, and acetic acid enhance results. Magnesium and calcium can be determined titrimetrically using EDTA (26) but these can also be accurately determined using atomic absorption spectrophotometer when available. The usual interferences are eliminated by addition of releasing agents (e.g. strontium or lanthanum).

Silicon is more or less usually determined gravimetrically. This involves the production of silica by dehydration of silicic acid with concentrated mineral acids, such as HCl. The method is somehow long and tedious.

The element (silicon) can also be estimated using colorimetry. The two most important examples using this method include the formation of the yellow silicomolybdate complex and the reduction of this complex and the blue compound formed. Phosphate and arsenate do interfere.

The third method employs atomic absorption spectrophotometer using N_2O-acetylene flame. A number of elements (Al, Ca, Na, V, etc.) interfere.

1.3 Laterites

Laterite is part of the earth crust, which has been derived from a variety of rocks and minerals. Laterites occur mainly in the tropics where they are extensively used in road building and other construction works. The name laterite was derived from the Latin word "Later" which means "brick earth". The material was first observed and described by Buchanan (27) in 1807 during his travel through India where laterite was being quarried from the subsoil stratum, trimmed and used as building blocks for local buildings.

It appears difficult to give a purely morphological, purely physical or purely chemical definition, since it covers a wide variety of tropical soil formation and is too general. However the term is used always in relation to red formations of varied morphology always indurated but rich in sesquioxides of alumina, iron or manganese besides combined or uncombined silica. Numberous attempts have been made to define the term including the definition given by Alexander et al (28): i.e. "Laterite is a highly weathered material rich in secondary oxides of iron, aluminum, or both. It is nearly void of bases and primary silicates, but it may contain large amounts of quartz and kaolinite. It is

either hard or capable of hardening on exposure to wetting and drying".

Some of the older ideas concerning the origin of laterites include suggestions that laterite is a residual alteration product, a detrital, a sedimental product and is of volcanic origin. Each of these theories started from the morphology and occurrences of laterite. From the numerous theories about the origin of laterite that have since been postulated (partly as a result of new analytical methods or progress in determination of soil constituent and the achievement of experimental soil science), it has become clear that the origin of laterite cannot be due to a single process. Several phenomena are involved to varying degrees some of which may not be easily differentiated from others.

The system for the classification of laterite varies from country to country but in many cases is based on certain chemical compositions, especially the silica - alumina ratio.

Maignien (29) has reviewed work on laterites. His review covers the definition, morphological and analytical characteristics, distribution, origin, classification, and utilization of laterites. A monograph by Persons

(30) on the origin, geology, and uses of laterites is based on an engineer's point view

1.3.1 Analysis of Laterites

Laterite analysis is of interest not only to the geologist but also to the soil scientist, hydrologist, mineralogist, and the metallurgist.

Methods of analysis of laterites cannot be much different from those used for rocks and minerals. Some of these can be used or modified for laterite analysis, especially as laterite is derived from rocks and other earth's materials through weathering and chemical alteration of their constituents during erosion.

The main constituents of laterites are silica, iron and aluminium compounds with some other elements or compounds. They may be low in such basic compounds as CaO, MgO, Na_2O and K_2O, and probably due to the ease with which these compounds could be leached out with time by erosion.

Since the major constituents are silica and oxides, the methods used in the decomposition and analysis of silicates, slags, and oxides (sections 1.2.3.1 and 1.2.3.2) may apply for the estimation of constituent elements and compounds in laterites.

1.4 Aluminium Alloys

An alloy is a metallic solid or liquid formed from an intimate combination of two or more elements. Any chemical element may be used for alloying, but the only ones used in high concentrations are metals. Aluminium alloys are formed by melting commercially pure metal and adding other elements, one of the objects being to obtain metal of greater strength. All alloys are appreciably stronger than the pure metal, but only in the case of certain casting alloys does strength depend on composition.

Formation of alloys is a complex subject, beyond the scope of the present investigation, but some broad generalisations can be made. The compositions of the various groups of alloys have been evolved to produce the qualities required for particular purposes. A wrought alloy, for instance, should not only posses the properties needed in the finished article, but should also have hot - and cold working characteristics to enable it to be fabricated economically. For casting alloys, good foundry characteristics are important since pure aluminium is difficult to manage in the foundry. High strength is usually attained at the expense of the ease of fabrication and, in certain wrought alloys,

with some reduction in resistance to corrosion.

The principal elements alloyed with aluminium are copper, magnesium, silicon, manganese, zinc, nickel, and chromium, Iron and silicon are almost always present as impurities (31) while titanium, cadmium, columbium, cerium, tin, lead and other metals are also employed in small amounts.

The majority of aluminium alloys used are covered by standard specifications especially as far as the composition, mechanical properties and tests of the different fabricated forms in which they are supplied are concerned.

1.4.1 Analysis of Aluminium Alloys

It has been revealed above (section 1.4) that aluminium alloys used are covered by standard specification especially as far as composition and other properties are concerned. Analysis will therefore undoubtedly play a very important role during and after alloy manufacture (serving as a check on alloy compositions). It is not surprising that considerable efforts are devoted to the improvement of existing analytical equipments and methods and development of more highly selective and sophiscated techniques.

Methods of analysis of aluminium alloys have been adequately treated by Tikhonov (24) and others (17, 32).

There is not much problem in getting the alloy into solution. For example, aluminium alloy in a fine powder form can be easily dissolved in the mineral acids (e.g. HCl) or a combination of these. Having got the alloy into solution, the determination of the constituent elements can be carried out using atomic absorption spectrophotometer or any of the methods earlier discussed (see section 1.3.2.2).

Spectroscopic method of analysis and atomic absorption spectrophotometric techniques will be discussed in greater detail in the next sections (sections 1.5 and 1.6) below.

1.5 Spectroscopic Method of Analysis

Spectroscopy has been extensively used as an analytical technique in this work, so it would be appropriate to give an outline of some aspects of the technique. Full accounts of the subject are however available elsewhere (33, 34).

Atoms and molecules are capable of undergoing electronic, vibrational or rotational energy transitions by absorption or emission of quanta of the appropriate

elelectromagnetic radiant energy, ΔE, given by the Plank's equation

$$\Delta E = h\nu$$

where h is Plank's constant, and ν is the frequency of the electromagnetic radiation. The value of ΔE (and hence ν) depends on the type of atomic or molecular energy state and the species involved. For example, a transition between electronic energy levels will result in an absorption or emission within the UV-visible region, while that between vibrational or rotational energy levels will correspond to infrared or microwave region, respectively.

Quantitative analytical aspects of molecular absorption spectroscopy are based on the linear relationship between the amount of light absorbed and the number of the absorbing species and also the thickness of the sample solution. This is known as the Beer-Lamberts law and is often represented by the equation

$$A = \epsilon cl$$

where c is the concentration in moles per litre of the absorbing species, A the corresponding absorbance, ϵ the absorption coefficient for the sample in $moles^{-1}\ cm^{-1}$ at a particular wavelength, and l the thickness of the sample in cm. A is given by

$$A = -\log\frac{I}{Io}, \quad \text{or } \log\frac{Io}{I}$$

where Io is the intensity of the incident radiation and I is the intensity of the emergent radiation.

To determinate A light from appropriate source is resolved by means of a dispersing agent such as prism or grating and a suitable beam of light of narrow wavelength range is then selected by means of a narrow slit. This is then passed through the solution of the sample held in a glass or quartz cell. The intensity of the light emerging from the solution and that of the incident light are measured and compared.

The determination of A is carried out using a spectrophotometer. In practice the pure solvent is placed in the path of the beam; the cell with the solution is placed in the path of the beam, and the intensities or the two emergent beams are compared. The "Io" that is used in the Bear-Lamber law is actually the intensity of light transmitted by the cell that contains pure solvent. In this way light lost by reflection at the surfaces of the cell walls is compensated for .

1.6 An Outline of Atomic Absorption Spectroscopic Technique

Another major analytical technique used extensively in this work is atomic absorption spectroscopy. This is a relatively new technique in chemical analysis having been introduced for the first time in 1955 by A. Wash (35).

Atomic absorption spectroscopy is a method for detecting and measuring chemical elements, particularly metallic elements, and is based on the absorption of radiation by free atoms.

1.6.1 Some Theoretical Considerations

The atomic absorption method involves the spraying of a solution into a flame, in which a portion of the solute is reduced to free atoms of its constituent elements. These free atoms can be raised to an excited state by the absorption of hight but only light of the energy corresponding to the difference in energy between the ground and excited states (that is by incident energy at certain discrete wavelengths known as "resonant wavelengths"). Thus if light of a resonant wavelength of a particular element is passed through a flame into which a solution of a compound of that element is being sprayed, a fraction of that light will be

absorbed by the ground-state atoms of the element and the extent of absorption (or degree to which the incident light is diminished on passage through the flame) is a measure of the concentration of the species of the absorbing atom.

In atomic absorption spectroscopy, the source of the incident light is usually a "hollow cathode" lamp designed to emit characteristic spectrum lines, including the resonant wavelengths of the element in question. The wavelength, reduced in intensity after passage through the flame, are isolated by means of a grating or prism monochramator, and their intensities measured by a photomultiplier tube, as done in both molecular absorption spectroscopy and flame (emission) photometry.

In atomic absorption spectroscopy, selectivity is achieved by the narrowness of the band of incident energy provided by the hollow cathode lamp, the effect of continuous radiation from the flame being eliminated by means of a mechanical interupter, or pulsed power supply in the source which is tuned to an alternating current delector circuit in the receiver. In molecular absorption spectroscopy selectivity is achieved by ensuring the absence of other absorbing species through

preliminary treatment which may involve isolation of the desired species.

Atomic absorption spectroscopy, the technique and applications which are the subject of continuous research (15, 36, 37, 38), has several attractive advantages over the other techniques. For example, it has a high selectivity, low limits of detection, and many elements can be determined from one solution.

The few interferences that are at times encountered arise mainly from ionization of free atoms of the elements analysed and the formation of involatile compounds in the atomizer. These can be suppressed by use of ionization buffers and releasing agents.

C H A P T E R II

2 E X P E R I M E N T A L

2.1 Experimental Approach

Much of the previous work has involved the use of procedures which could be used for rapid analysis of typical slags and other samples, with a minimum loss in accuracy and precission. This might enable slags taken at any particular time from smelting furnaces to be rapidly analysed and may subsequently lead to the control of products to desired specifications. These procedures may perhaps be the aims of commercial practices which require maximum possible immediate use of these analytical data. In laboratory experiments however, the methods and techniques used though slow, may invariably result in the production of better and more reliable results. Correlation of analytical methods and results with actual commercial requirements are therefore bound to be a difficult exercise although it is to be envisaged

that any result produced can in the end be of considerable interest to the industrialists.

The experimental technique first involved preliminary qualitative tests on sample in solution using atomic absorption and spot tests to detect elements present and getting a known weight of the sample into solution and determining the amount of some of the elements by an atomic absorption spectrophotometer together with any other available method. Some of the elements were also estimated by gravimetric method (e.g. tin), e.t.c. Sampling was by coning and quartering (8).

2.2 Materials

The tin slags and hardhead used for part of this work were supplied by Amalgamated Tin Mines of Nigeria Ltd., Jos, Nigeria. The No.1 slag is a first run slag from primary smelting and is tin rich, while that produced from first slag smelt is No.2 slag. The fuming with gypsium to recover tin from No.2 slag produces the third and final slag.

Ferrous slags are hard to come by in this country since the Nigerian Iron and Steel plants are not yet in operation. The ferrous slags used were therefore those from iron-working (primitive practice) around Samaru.

The samples were excavated and supplied by Dr. J. E. G. Sutton (an Archeologists in the Department of History, Ahmadu Bello University, Zaria). The sites are generally situated close to outcrops of the ore in the Upper Kubanni Valley and Samaru West, and the slags kept in heaps were numbered 1 to 4 (hence slag heaps 1 to 4).

The 'Older and Younger Laterites' were picked in the same surroundings as the ferrous slags.

The aluminium alloy was supplied by the Defence Industries Corporation of Nigeria, Kaduna.

2.3 Sample Preparation

Initial efforts to prepare samples were directed towards easy and fast means of dissolving the samples particularly the refractory and resistant slags and laterites. laterites. Straight forward fusion of slags and laterites with anhydrous sodium carbonate in a platinum crucible showed that after evaporation to almost dryness and leaching with aqua regia, silica precipitated and could be determined. The filtrate and washings collected in a volumetric flask and made up to specified volumes therefore formed the stock solutions for the estimation of the other constituents present in the slags and laterites.

All the experiments on the analysis of slags, laterites and hardhead were therefore carried out by fusion of powdered samples with anhydrous sodium carbonate. The samples were dried to constant weight (e.g. at 110°C for 24 hours) and when necessary samples were ground until all of the samples had very fine particles. The weight of the samples used for each decomposition procedure was small (1.00g), so that leaching after fusion could be relatively easy.

The dissolution of aluminum alloy presented no problem. A small weight (0.500g) tended to dissolve easily in 50 per cent hydrochloric acid, the residue being treated for the estimation of silica and the solution used for estimating other elements present in the alloy.

2.4 Dissolution of Samples

Although fusion with anhydrous sodium carbonate is one of several alternatives suggested for the decomposition of slags and other refractory materials, the use of this flux now forms part of the popular technique for such materials. Not surprisingly, the experimental conditions are of critical importance, and several materials may be found to exhibit undersirable properties as test conditions vary.

The several dissolution procedures had already been discussed and the wet analysis technique supplemented by gravimetric method was used. Experiments were carried out using analytical grade reagents when available. As previously indicated, 1.0g of sample such as slags, laterites ~~and~~ or hardhead (which had been finely crushed, dried to constant weight and stored in a dessicator) was thoroughly mixed with anhydrous sodium carbonate (5g) in a platinum crucible and the mixture covered with additional flux (1g). This was fused in an electric muffle furnace at 1000^{o}C for 30 minutes. The solidified melt was allowed to cool to about 30^{o}C and loosened from the crucible with hot water in a 400 ml beaker. The resulting solution was evaporated to dryness and the residue digested and leached on a hot plate with aqua regia. The precipitated silica was filtered off, ignited to constant weight at 1100^{o}C in a muffle furnace and the silicon content determined as silica. The filtrate and washings were transfered to a 100-ml. volumetric flask and made upto the mark. After preliminary qualitative analysis, aliquots were taken from this stock sample solution for the estimation of the different constituent elements.

The aluminum alloy (0.5g) was dissolved in 50 per cent hydrochloric acid. The residue was treated for the estimation of silica as earlier mentioned. The filtrate was also treated as above and the elements determined by different techniques.

2.5 Determination of Elements

2.5.1 Introduction

It may be of interest to explain how the several data concerning the determinations were obtained. The amount of element of interest present in the solution was compared with the amount of sample initially used in order to evaluate the percentage composition of the material. In each case, the data may be the average of two or more determinations while the results obtained by a particular method were compared with those obtained from other techniques.

2.5.2 Apparatus

The apparatus used in most of the determination of elements is very simple. For iodimetric titration of tin, a 300-ml Erlenmeyer flask (fitted with a stopper having provisions to lead in the titrant and sodium bicarbonate solution for generation of CO_2) was used

Spectronic 20 photometer was used for photometric dterminations and a Unicam SP1900 Atomic Absorption Spectrophotometer was also used for determination of several elements whose lamps and flame system were available.

2.5.3 Determination of Tin

The amount of tin in the samples was determined by titrimetric and photometric methods. In the first, 50ml aliquot of the stock sample solution (see section 2.4) and 2ml of concentrated H_2SO_4 were evaporated to a moist residue on a water bath in the flask and allowed to cool. About 100ml of water was added followed by 50ml of concentrated hydrochloric acid and the mixture gently warmed until the solution was clear.

The apparatus was then assembled, about 2g of test lead put in the flask followed by 10ml of saturated sodium bicarbonate solution and the stopper immediately replaced. After the removal of any air in the flask by suction of the bicarbonate solution into the flask (which generated CO_2), about 5ml of starch solution was added and the tin solution immediately titrated with standardized iodine solution. The solution was constantly agitated by swirling and the end point indicated by blue coloration. The tin content was calculated from the relation that

1ml 0.1N Iodine solution ≡ 0.005935g Sn.

In the photometric determination of tin with dithiol (Toluene -3, 4- dithiol), tin was first separated from iron in the test solution. To achieve this, 25 ml of the stock sample solution was evaporated to a moist residue on a water bath and 25 ml of acid solution containing 2.4 ml concentrated HCl per 100 ml of water added. Tin was precipitated as a sulphide by passing in H_2S gas. The precipitated sulphide, separated from the supernatant liquid containing iron and aluminium was redissolved in a minimum amount of aqua regia and made upto 50 ml with water. Exactly 5ml of this solution was neutralised with ammonia, 0.5 ml of concentrated hydrochloric acid was added followed by 0.5 ml dithiol solution. The mixture was boiled for 1 minute and after cooling shaken with 2 ml of gum arabic (10% in water). The absorbance of the resulting solution was read at 530 mμ in Spectromic 20 photometer.

Calibration standard tin solutions (different concentrations) were prepared making sure that all the reagents present in the test solution were added. Their absorbance were noted and a calibration curve plotted. From the calibration curve, and the absorbance read with the test solution, the tin content was deduced.

2.5.4 Determination of Iron

Two methods were used for the determination of iron- Colorimetric determination with potassium thiocyanate and atomic absorption spectrophotometer. In colorimeteric determination, 25 ml of sample stock solution was evaporated to moist residue and then dissolved in 25 ml of 6MHCl. The iron was extracted from the solution with three 25 ml portions of ether. The iron was later removed from the combined extracts by extraction with another three 25 ml portions of water. Any traces of ether in the aqueous extract was boiled off on a water bath and the final solution made upto 100 ml.

To 5 ml. of this test solution in a 50-ml volumetric flask, 5 ml of conc. HCl, 5ml of acetone and 12ml of thiocyanate solutions were added and made upto the mark. Colorimetry was carried out at 480 m_{μ} and the iron content determined from a calibration curve plotted using standard iron solutions.

Chemical analyses of iron (and some other metals, Ca, Mg, e.t.c.) were also carried out using a Pye Unicam SP1900 Atomic Absorption Spectrophotometer (A.A.S.) (15). Samples for analyses were crushed and ground and 1.0g of the powdered samples were fused and leachedin acid according to standard procedures. 1000 ppm stock iron solution was prepared using analytical grade reagents.

On the Unican SP1900 Atomic Absorption Spectrophotometer, which has continuous scale expansion and curve correction facilities, the sample concentration can be displayed directly. Thus two standards prepared from the 1000ppm stock solution (by appropriate dilution) were required - the higher standard containing a concentration of the test element above the estimated maximum concentration in the sample and the lower standard containing exactly half the concentration of the test element in the higher standard. Care was taken so that standards were compensated by the addition of all reagents present in the test solutions.

2.5.5 Determination of Aluminium

This was carried out using gravimetric and photometric methods.

Gravimetrically, after separation of iron from 25ml of sample stock solution by extraction with ether (section 2.5.4) from 6 M-HCl solution, the water extract was made up to 100ml and neutralized with ammonia until a faint turbidity was observed. The turbidity was cleared by redissolving. this with 2 drops of HCl; 10 g of NH_4Cl was added and the mixture heated to boiling. Pyridine solution (20%) was carefully added drop by drop to the boiling solution (while stirring)

until methyl red indicator changed colour and then 15ml excess added. After boiling the mixture for 30 minutes, the precipitate which coagulated and settled was filtered and washed with 3% ammonium chloride solution containing a few drops of pyridine. The precipitate was ignited to constant weight at 1200°C and the amount of aluminum estimated (Al = 0.5291 Al_2O_3).

In the photometric determination of aluminum with oxine, 2ml of tartaric acid (10%) and 1ml of hydrogen peroxide (10 volume) were added to 25ml of weakly acidic test solution (obtained by appropriate dilution of the stock solution). The mixture was allowed to stand for 5 minutes before 5ml of sodium sulphite (20%) was added and after a further 3 minutes, 10ml of potassium ~~thio~~cyanide (13%) was added. The solution was heated to 70 - 80°C and later cooled to 25 - 30°C. Finally, 2g of ammonium nitrate was added and the pH adjusted to 8.9 ± 0.3. The solution extracted with four 5ml portions of oxine solution (2g in 100 ml chloroform) was collected in a 50 ml volumetric flask and made to the mark with chloroform.

A colorimetric estimation of aluminum was carried out at 389 mμ comparing with a blank containing identical

reagents as the test solutions. A calibration curve was plotted using standard aluminium solutions and the amount of aluminium in the test solutions determined from the calibration curve.

2.5.6 Determination of Calcium, Magnesium and Other Elements (Pb, Zn, Cu, Ni, Co, and Cr)

The amounts of these elements were determined using atomic absorption spectrometer. As already described (section 2.5.4), samples for analyses were crushed and ground and 1.0g of the powdered samples fused and dissolved in acid according to standard procedures. Standard solutions were prepared using analytical grade reagents. Calibration graphs of the percentages of the required elements in the standard solutions versus optical density were plotted and the percentage of the elements in the dissolved samples obtained from the graphs.

On the Unicam SP1900 Atomic Absorption Spectrophotometer, the graphical method of calibration may be eliminated depending upon the concentrations of the elements in solution. This is because of the scale expansion and curve correction facilities, while the digital read out and autozero systems enable element concentration to be displayed directly (section 2.5.4).

This method was applied to metals with reasonably low concentrations. In this method, only two standards were required - the one with a concentration of the element of interest significantly above the estimated maximum concentration (higher standard) in the sample and the second (lower standard) containing exactly half the concentration of the element of interest in the standard with high concentration.

Ionization interference during the estimation of calcium and magnesium was eliminated by the use of 0.1% lanthanum (as chloride) in both sample and standard solutions.

2.5.7 Determination of Manganese

This was carried out colorimetrically by the periodate method. Exactly 25 ml of the aluminum alloy stock solution was evaporated to dryness and the residue redissolved with 50ml 0.5M H_2SO_4 in a 100ml volumetric flask plus 10ml of concentrated H_2SO_4 followed by 10 ml of concentrated phosphoric acid. About 0.4g of potassium periodate was added the solution heated for 10 minutes at about 90°C. After cooling, the solution was made up to 100ml and a colorimetric estimation carried out at 552 mμ using a Spectronic 20 photometer.

The concentration of manganese in the sample was determined from a calibration curve.

C H A P T E R III

3 RESULTS AND DISCUSSION

3.1 Introduction

In this Chapter, the results of the chemical analyses of all the materials provided are given and discussed. They are divided into four sections; results obtained using tin slags and hardhead, which will provide data on the metal composition of tin smelting slags; results from experiments on primitive iron slags for comparison with modern iron making practices; and a few results on aluminum alloy which may indicate the probable approximate composition of the alloy.

In order to facilitate discussion of the efficiency of the primitive iron smelting operations, analyses were carried out on laterites picked on areas surrounding the sites of the excavations. Additionally, the results obtained by other workers on similar materials have been considered and the few results of their tests are presented

for comparison.

The analytical data for the different samples are given in Tables I (Tin slags and hardhead), 2(Ferrous slags), 3(laterites), and 4(aluminum alloy). The results of other workers on a few similar samples have been tabulated in Appendices I - IV.

3.2 Tin Slags and "Hardhead"

Table I lists the chemical analyses of all the tin samples (No.1, No.2 and final tin slags and "hardhead") investigated, as determined by means of atomic absorption spectrophotometer in this department and other techniques as indicated. A critical appraisal of these results reveals that each slag retreatment leads to a diminishing amount of tin in the resultant slag. This is not unexpected since the smelter aims at maximum recovery of tin present in slags. Of more interest is the actual amount of tin in each slag. It can be seen from Table I that in the No.1 slag, the approximate amount of tin is 17 percent, No.2 slag about 3 percent and the final slag about 0.5 percent. This indicates an efficient smelting practice because conventional smelting operations aim at about 20 - 40 percent Sn in the primary slag (No.1 slag), 3 - 7 percent Sn in No.2 slag and less than

1 percent Sn in the final slag. These relatively low concentrations of tin in the slags (compared to other major world tin smelters) are obtained because of the nature of the cassiterite concentrates treated. Whereas other plants may handle very complex low grade and "dirty" lode ores, the Jos smelters treat relatively high grade and clean alluvial concentrates. The processing of the low grade lode concentrate together with the other minerals associated with it results in the production of larger slag volumes and accompanying loss of tin into the resultant slags. Appendix I lists the chemical composition ofthe final slags from different plants in the world (30) and it can be seen that even the most efficient of these plants, Maurer and Straits plants, still produce slags containing about 2.6% Sn (3% SnO). It must however be stressed that the slag compositions from these plants cannot be compared with that in Jos since the final slag from the latter is obtained from a fuming process. Secondly some of these smelters migh not have gone through the two stages of slag retreatment since these processes depend to a large extent on the price of tin in the world market at the time of operation.

Apart from silicon, the only other element of significant amount in the slags is iron. Initially, the amount of iron is about 21% in the No.1 slag and is reduced to 17% in the No.2 slag. This would be expected since the iron combines with tin during the slag retreatment to produce "hardhead", a tin-iron alloy.

The progressive increase in the silica content is also not surprising because silica and other fluxes including fresh concentrates (when necessary) are often added during the resmelting of slags. Hence, as more tin and probably iron are removed from the slags, the concentrations of the slagging materials such as silicon as silica, calcium as CaO from $CaCO_3$ and aluminum as alumina (Table I) are bound to increase. The amount of magnesium has remained almost constant since this probably arises from its presence in the original concentrate.

The product of the second slag retreatment in most plants (first slag retreatment in Jos) is a tin-iron-alloy known as "hardhead". Analysis of this material has produced about 74% Sn and 18% Fe. The composition of "hardhead" is often assumed to be about 80% Sn and 20% Fe. However, hardheads with variable compositions have been reported e.g., 20% Sn, 60% Fe (19) and 95% Sn,

5% Fe (39). The result produced (Table I) though not exactly as assumed by most authors, is in agreement with that produced in the Makeri Smelting Company's Laboratory in Jos. The source of silica in the "hard-head" should be pretty obvious realising that siliceous flux is a usual constituent of the feed.

The reclamation of tin from slags is beyond the scope of the present work. However, suffice is to say that the Jos final slag is not discarded but is sold for its tantalum, tungsten and niobium contents. It is also possible that this slag might be the future source of the metal when conditions are likely to favour economic processing of the material.

3.3 Iron making Slags

The slags produced by the primitive iron smelters around Samaru were analysed and the results are tabulated in Table 2. These slags (slag heaps 1 - 4) were analysed with the hope of supplying some form of information on their chemical compositions to the archeologists. Such data would make the comparison of the primitive methods with modern techniques possible.

The metal of interests are iron, aluminum and calcium. As can be seen from Table 2, the amount of iron

in the slags (Heaps 1 - 4) appears to be constant (about 29%). This trend is also observed for magnesium (about 0.2%), calcium (about 0.08% except for slag Heap 2) and aluminum (about 8.0% except Heaps 3 and 4). The almost constant amount of these elements in all the slags should be expected since the smelting operations were probably carried out on identical iron ore deposits and since the addition of fluxes were not known to these primitive smelters. This conclusion is in agreement with Sutton's (40) and Tylecote's (3) views.

It is postulated that since the sites are generally close to the outcrops of laterite, that these were doubtless the source of the ore (40). This association is very clear in the Upper Kubani valley and Samaru West. In both areas, the furnaces are situated close to if not actually right against exposures of the "Older Laterite". This leads one to presuppose that the Older Laterite must have provided a much richer iron-ore than the more ubiquitous "Younger Laterite" which constitutes a sheet covering over so much of the land either side of the Kubani. This suggestion is confirmed by the results of the analysis of the Laterites (Table 3) where the "Older Laterite" is richer in iron content than the Younger Laterite". At Samaru West, the furnaces are

actually built on this Younger Laterite, but their propinquity to exposures of the Older Laterite suggests that the latter was the preferred ore, even though its mining and crushing would have required much more labour.

Interestingly, the slags still contain a rather high concentration of iron, whereas the sources of the ore appear to contain less amount of iron. This is understandable realising that the primitive smelters used no fluxes to produce slags likely to dissolve most of the impurities associated with the ore. Secondly, the method of smelting was crude and heat was generated by means of tuyeres which consisted of clay pipes which attached the furnace to bellows. This type of heating device did not produce reasonably high temperatures to ensure that the metal and slags were molten. Since no molten and free flowing slags were produced, there was likely no effective separation of the sponge iron so produced from the slag. This perhaps resulted in a "concentration process" instead i.e. concentration of the metallic iron into the slags. The output was bound to be small and the yield poor-in the circumstance. One other possible explanation is the fact that since the flux was derived from the ore, the metal produced might have been very close in chemical composition to the ore and

the amount of slags produced might have been very small. Because of the poor quality of the metal produced, it might have been further treated to obtain a purer metal resulting in the production of greater amount of slags. It is just possible that the latter slags are what have been excavated and used for this work.

The low contents of the base metals (e.g. Ca) as already mentioned is indicative of the fact that no fluxes were added during the smelting operation.

The high content of silica is not surprising considering the probable source of the ore. The frequency of quartz ball, which were presumably hammers or pounders, as well as granite and quartz "anvils", on the Older Laterite exposures is probably of significance here.

The composition of these slags (Table 2) may be compared with that obtained from modern blast furnaces (41) (Appendix II). It can be seen that whereas the slag in modern blast furnace contains less than 1% Fe, the primitive slags contain significant amount of iron. It is at once evident that modern techniques are by far superior to the olden methods. There are however no data available on the chemical composition of these slags, so it is difficult to compare results.

3.4 Laterites

The analysis on the laterites suggests some informative results (Table 3). These may be followed up in future samples from other sites in Samaru (and Zaria in general) for comparison. A glance at the results at once reveals that the amount of iron present in the laterites in not of economic value.

The fact that the "Older Laterite" has a higher amount of iron (21% Fe) than the "Younger Laterite (16%) goes to prove our earlier claim (section 3.3) that the latter was probably the source of ore for the primitive iron smelters. It is therefore conceivable that the "Older Laterite" remains the source of the "Younger Laterite", the latter being the products of weather transformation and erosion of the former. Evidence of severe weathering and erosion is still abundant in the area.

The high concentration of silicon (silica) in the laterites is probably caused by the rock type present in the vicinity. For example intensive gulleying has revealed unweathered gnesis with quartz veins visible in parts of the gulley bottom and in the bed of Kubani:. The higher amount of silica in the "Younger Laterite" is probably due to the removal of the resistant sand and quartz from the Older Laterite and subsequent deposition,

the siliceous materials being unaffected by the weathering and erosion agents.

The results obtained may be compared with that obtained by other workers (30) on laterites from different parts of the world (Appendix III). Although there is no basis for comparison, it can only be concluded that the amount of iron in laterite varies from locality to locality.

Generally, at present the two major metals in laterites (Fe and Al) are not in sufficient quantity to warrant their utilization as possible sources of the metals. This is because presently, the average metal content of an iron ore (for economic processing) is 40 - 60% Fe and aluminium 27 - 29%. The laterites would therefore required extensive pretreatment in order to upgrade their iron and aluminium contents. The procedures for such processes are sometimes complex and expensive and therefore uneconomical. The laterites might however serve as future ore deposits when known rich iron (and aluminium) ore reserves have been depleted.

3.6 Aluminium Alloy

Table 4 lists the approximate constituents of the alloy. The amount of Al (89%) which forms the major constituent of the alloy was at first considered too high.

The result was nevertheless confirmed by several experiments using different sample stock solutions and an alternative method. The amount of iron (about 6%) was rather disturbing in view of the fact that iron is said to be almost always present as impurity (31). If this is so, then the amount of iron in the alloy would be dependent upon the source of the aluminum ore and the extent of purification of the finished metal. It is therefore doubtful that Fe is present as an impurity.

From the analytical data (Table 4), it is difficult to categorically predict the type of alloy because of the numerous other metals detected. It may possibly be an aluminum - magnesium - silicon alloy. The two most widely used alloys in this group contain just over ½% magnesium, one of these having about ½% silicon and the other 1% silicon. The presence of lead (0.55%) and iron in significant amounts makes this suggestion doubtful. It is a quarternary alloy with Fe or Pb appearing as impurity. Alternatively, it could be a composite alloy with all the elements as deliberate additions to improve the mechanical properties of the finished product. The majority of the metals (Ca,Cr,Ni,Mn,Zn, etc,) which were detected are traces and may be of no significance.

Only about 96.8% of the constituent elements of the alloy has been accounted for. The balance (3.2%) may be

attributed to other undetected alloying elements which may be present in various aluminum alloys. Because of the difficulty in accounting for the balance, the author can only conclude that the results obtained reveal informative and approximate percentage composition of the alloy. It would have been desirable to know the composition of the rest (3.2%) but insufficient alloy sample was available for this.

3.6 General Discussion

The analyses of the samples (Tables 1 - 3) summate in some cases to figures far below 100 per cent and they refer to dried samples. It is obvious that various amounts of other elements are present in the various slags and laterites in addition to much (chemically combined) oxygen. It is suspected that apart from silicon (which was determined as silica), the other metals in the slags may be present as oxides (e.g. FeO, CaO, Al_2O_3, SiO_2, etc.) and silicates which are infact the usual constituents of slags. Similarly, the laterites are likely to have the elements present as compounds. For example, the iron may have existed as the oxide (Fe_2O_3) or the hydroxide and the aluminum as alumina (Al_2O_3). In most slag works, determinations of CaO, SiO_2, and P_2O_5 are usually made for the adjustment of the slag basicity.

In a few laboratories, more comprehensive analyses are often carried out to provide statistical data with a view to improving metal making practice in future.

These results were obtained from a number of the usual classical and instrumental analytical methods such as titrimetric, gravimetric, atomic absorption spectrophotometric and colorimetric methods. Reference had been made to the accuracies of some of these methods. For example, gravimetric methods are capable of an accuracy and precision of the order of 0.1 percent with any element whose concentration lies within the range 10 - 100 percent. The lack of selectivity necessiates complete chemical separation. Titrimetric methods are selective and generally produce accuracies of 0.3 percent. The accuracies and precisions obtained with atomic absorption and colorimetric methods depend critically on the quality and response of the instruments when accuracies of 0.2 - 0.5% are obtainable.

The accuracy and precision of each method were found to be good, the errors and relative mean deviations rarely exceeding 2 percent. The accuracy and reproducibility of methods were obtained by carrying out three or more replicate analyses on the samples. Again, the methods exhibit an acceptable degree of accuracy.

On the decomposition procedures, a number of workers (8, 9, 15) have pointed out the high efficiency of anhydrous sodium carbonate fusion for slags and similar materials. Any error which could have arisen from incomplete dissolution may be deemed minimal.

It would appear that the decomposition procedure adapted - fusion with anhydrons sodium carbonate for slags and laterites, provides a rapid means of getting the materials into solution. Analyses for the metals such as tin, iron, calcium, etc, can be carried out by making dilutions of the original stock solution. For the aluminium alloy, the hydrochloric acid decomposition method on fine powdered sample is preferred.

3.7 Conclusions

The following conclusions have been drawn from the results of this investigation.

3.7.1. Tin slags and "hardhead" (Jos), primitive iron slags (Samaru), Laterites (Samaru) and an aluminium alloy (Defence Industries Corporation of Nigeria, Kaduna) are analysed using common classical and instrumental analytical methods. The decomposition of slags and later laterites by fusion with anhydrous sodium carbonate is rapid, relatively easy and gives accurate results while the use of hydrochloric acid is sufficient for dissolving fine powdered aluminium alloy.

3.7.2. The tin (metal of interest) content of the slags shows a progressive decrease from 17 percent in the primary slag to 0.5 percent in the final slag. This indicates a very efficient tin smelting and recovery processes compared to major world tin smelters. The iron content, which is initially high in the first run (primary) slag also shows a progressive decrease.

3.7.3. "Hardhead" has a composition within the expected range - 74% Sn and 18% Fe in the present case.

3.7.4. Primitive iron smelting slags in Samaru area contain appreciable amounts of iron (26 - 34 percent), compared to 0.3 - 1.0 percent in modern practices, indicating that the smelting operations were crude and highly inefficient. The low calcium contents of these slags may be taken as a confirmation of the fact that primitive iron smelting was characterized by the absence of external fluxes. The silica contents of the slags are high throughout.

3.7.5. The laterites analysed are of very low iron content, but high in silica content. Obviously, these may not serve as economic source of iron ores in the nearest future but might be profitably worked when known high grade ore reserves have been depleted.

The "Older Laterite" is however richer in iron content than the "Younger Laterite".

3.7.6. Results of the analysis of the aluminium alloy show that it is possibly a composite alloy containing apart from aluminium (about 89%), Fe(5.91%), Si(0.84%), Mg(0.55%), Pb(0.51%) and Cu(0.12%) as major constituents and other elements in more or less trace amounts.

3.8 Suggestions for Future Work

Some aspects of the analyses of some of the samples merit further work.

3.8.1. There is no analytical data on the amount of niobium, tantalum and tungsten in the tin slags in Jos, although these elements which are usually left in the final slags are sold abroad for their contents. As a result a more detailed analyses could be carried out when it is hoped the actual percentages of these metals in the slag would be provided. The analysis could be carried out using atomic absorption spectrophotometer supplemented by other available methods.

3.8.2. Further work is desirable on other primitive slag samples from other localities and sites in Zaria and Nigeria in general. The analysis should not be restricted to

metals alone but could be extented to include the non-metallic elements like phosphorus and even carbon which was found to be present in the slags

3.8.3. The analytical data of the laterites can be extended to include phosphorus and sulphur contents which are important in deciding the suitability of a particular iron ore to specific iron and steelmaking processes. Additionally, the iron content in the laterites is the total Fe, and it would be desirable to determine what percentages of FeO, Fe_2O_3 and possibly limonite ($Fe_2O_3.3H_2O$) are present in the laterites. Laterite samples from Samaru farms and other parts of Zaria could be determined for comparison.

3.8.4. A more detailed analysis of the aluminium alloy should be carried out if sufficient quantity of the alloy is supplied. The balance (3.2%) should be accounted for by qualitative and quantitative determination of other elements which may have been present in the alloy. The accuracy and reproducibility of all the methods used could be ascertained by carrying out five or more replicate analyses of the alloy.

3.8.5. Finally, investigation of the different methods of decomposing slags, laterites and other such refractory materials could prove useful exercise. Such methods should aim at getting all the samples including silica (which could be determined by A.A.S.) into solution.

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Table I: Chemical Analysis of Tin Slags and "Hardhead"

Sample	Compound or Element	WEIGHT PERCENT				
		Method 1		Method 2		Mean
No. 1 Slag	Sn	Iodine	16.71	Dithiol	17.01	16.86
	Fe	A.A.S.	21.55	Thiocyanate	20.25	20.90
	Al	Pyridine	4.40	Oxine	4.34	4.37
	Ca	A.A.S.	3.93	A.A.S.	3.79	3.86
	Mg	A.A.S.	0.37	A.A.S.	0.38	0.38
	SiO_2	Gravimetric	33.58	Gravimetric	33.40	33.49
No. 2 Slag		(Methods as for No. 1 Slag)				
	Sn		2.81		2.91	2.87
	Fe		17.15		17.50	17.33
	Al		6.10		5.89	6.00
	Ca		5.04		5.05	5.05
	Mg		0.76		0.76	0.76
	SiO_2		38.33		37.22	37.78
Final Slag		(Methods as for No. 1 Slag)				
	Sn		0.50		0.46	0.48
	Fe		12.00		11.52	11.76
	Al		13.24		13.02	13.13
	Ca		10.71		11.71	11.21
	Mg		0.67		0.72	0.70
	SiO_2		41.23		40.01	40.62
Hardhead		(Methods as for No. 1 Slag)				
	Sn		72.51		75.38	73.95
	Fe		17.31		18.15	17.73
	Al		0.026		0.021	0.024
	Ca		0.008		0.007	0.008
	Mg		0.004		0.005	0.005
	SiO_2		7.02		6.48	6.75
	Pb	A.A.S.	0.13	A.A.S.	0.12	0.13

Table II: Chemical Analysis of Primitive iron making Slags around Samaru.

Sample	Compound or Element	WEIGHT PERCENT		
		Method I	Method 2	Mean
Slag Heap 1	Fe	30.83	28.20	29.52
	Al	8.33	8.20	8.27
	Ca	0.081	0.079	0.080
	Mg	0.21	0.24	0.23
	SiO_2	47.48	47.34	47.41
Slag Heap 2	Fe	26.12	24.74	25.43
	Al	7.87	7.66	7.77
	Ca	0.025	0.026	0.026
	Mg	0.19	0.22	0.21
	SiO_2	53.68	53.65	53.67
Slag Heap 3	Fe	33.70	31.88	32.79
	Al	9.37	9.42	9.40
	Ca	0.088	0.084	0.086
	Mg	0.20	0.24	0.22
	SiO_2	40.75	40.36	40.56
Slag Heap 4	Fe	30.00	28.49	29.25
	Al	10.81	10.70	10.76
	Ca	0.080	0.078	0.080
	Mg	0.20	0.23	0.22
	SiO_2	41.00	40.93	40.97

Table III: Chemical Analysis of Local 'Younger and Older Laterites'

(Methods as for Table I)

Sample	Compound or Element	WEIGHT PERCENT		
		Method 1	Method 2	Mean
Younger Laterite				
	Fe	16.61	15.39	15.70
	Al	5.55	5.64	5.60
	Ca	0.008	0.005	0.007
	Mg	0.054	0.048	0.051
	SiO_2	63.50	63.12	63.31
Older Laterite				
	Fe	21.66	20.20	20.93
	Al	6.83	6.80	6.82
	Ca	0.004	0.003	0.004
	Mg	0.022	0.021	0.022
	SiO_2	48.80	48.60	48.70

Table IV: Analysis of Aluminium Alloy

(Methods as for Table 1)

WEIGHT PERCENT			
Element	Method 1	Method 2	Mean
Al	88.57	88.79	88.68
Fe	5.76	5.97	5.94
Mg	0.55	0.55	0.55
Ca	0.025	0.025	0.025
Si	0.84	0.87	0.86
Pb	0.51(A.A.S.)	0.52(A.A.S.)	0.52
Cu	0.12 "	0.12 "	0.12
Zn	0.073 "	0.074 "	0.074
Ni	0.039 "	0.040 "	0.040
Cr	0.007 "	0.007 "	0.007
Mn	0.022(Periodate)	0.021(Periodate)	0.022
Co	0.016(A.A.S.)	0.014(A.A.S.)	0.015
Total	96.68	96.96	96.82

Appendix I: Tin-Smelting Slags and Their Compositions (Ref. 19)

Plant	Composition (Wt. %)					Remainder (Wt. %)
	SnO	CaO	FeO	SiO_2	Al_2O_3	
Maurer	3	28	18	35		$MgO + Al_2O_3$ 16
Capper Pass	5	13	32	25	10	15
U.S.S.R.(Belyayev)	7	10	20	34	22	19
Swlivan	4	9.5	22	22	22	$W_2O_3 + TiO_2$ 20
German	10.5	5.5	27.5	35		ZnO 12
U.S.S.R. I	13	14.5	35.0	28.2		11
U.S.S.R. II	6.2	6.7	25.8	36.1		25
U.S.S.R. III	17	1.6	37.0	27.0		18
U.S.S.R. IV	12.6	6.1	39.1	27.9		15
U.S.S.R. V	7.5	14.5	20	22.3		46
China A	17		51	19		13
China B	7-20	2-5	20-30	15-26		
China E	21-30	5-6	3-5	23-27		Na_2WO_4
China F	20	20	18-24	30-34		7

Appendix I Continued: Tin-Smelting Slags and Their Compositions

Plant	Composition (Wt. %)					Remainder (wt. %)
	SnO	CaO	FeO	SiO_2	Al_2O_3	
Japan, Watanabe	9.5	1.7	43.4	21.5	8.7	MgO 1.9, 13.3
Straits, Mantell	3	15	32	29	32	
W.		25	16	37-39	10	MgO_2

Appendix II: A Modern Blast Furnace Slag Composition (Ref. 41)

Constituent	Percent	% Metal
SiO_2	30 - 38	
CaO	34 - 45	24 - 32 Ca
Al_2O_3	10 - 20	5 - 10.5 Al
MgO	2 - 10	1.2- 6 Mg
S	1 - 2	
Fe	0.3 - 1.0	

Appendix III: Chemical Analysis of Laterites from Various Locations (Ref. 30).

Sample Location	Percent by Weight		
	Iron Oxide, Fe_2O_3, Fe	Silica, SiO_2	Aluminium Oxide, Al_2O_3
Andersonville PrK, Sumter Co., Ga	27	16	0.1
Appling Co., Ga.	11	27	4.1
Kumba Division, Cameroon	9	31	8.0
Mamfe Division, Cameroon	32	11	0.4
Ellaville, Schley Co., Ga.	10	2.9	7.5
Thailand	59.5	47.3	10.2
Bombay, India	29.5	43.3	12.0
Cape of Good Hope, South Africa	34.5	25.7	19.0
El Salvador	11.6	34.9	26.1
Johannesburg, South Africa	37.9	31.8	15.0
Kumba, West Cameroon	29.2	25.2	24.8
Libreville, Gabon	46.3	10.0	27.1
Nairobi, Kenya	25.3	11.4	14.6
Average	25.6	24.4	13.00

Appendix IV: Chemical Composition of Laterites (Ref. 30)

Chemical Composition	Average, %*	Extreme, %	
		Low	High
SiO_2	16.6	0.6	49.8
Al_2O_3	20.1	2.7	38.7
Fe_2O_3	47.5	20.7	81.9

* 54 Samples