ON BLAST FURNACE SLAGS AND THE FUSIBILITY OF SILICATES.

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Blast furnace slags are, with pig iron, the ultimate products of the reduction of the charges, their composition depending on the proportion of the different earthy elements contained in the ashes of coal, in the limestone and the ores, at least, of such elements as can form fusible compounds. As such, they are the real criterion by which a skillful manager will judge of the economical running of his furnace.

In general, other things being equal, the composition of the slags directly affects their fusibility and bears a close relation to the grade of iron obtained. Certain conditions corresponding to a comparatively low temperature in the furnace require also a very fusible slag and a readily fusible iron. Within certain limits, to be mentioned later, such a temperature may be sufficient to melt slags of a somewhat different composition, and that slag which requires the fusion of the least quantity of foreign matters, will be, obviously, the most economical and advantageous. Works on metallurgy contain many analyses of slags, often of little value, because neither the composition of the materials charged, their relative proportion, nor the character of the resulting pig metal are mentioned. There is no way of deducing—from the composition of the slag—its economy under given conditions. A blast furnace is as much a chemical apparatus as any that is used. Chemical laws govern the reactions which take place in it and metallurgists often find in practice that the composition of slags calculated from known charges, agree almost as closely as duplicate analyses. It is very desirable that all analyses of slags published should be accompanied by the data pertaining to each case. The writer has collected the analyses of a great number of slags from European and American furnaces, many made by himself; with most of them he has been able to ascertain the accompanying conditions, and in all the general conditions and the character at least of the pig metal run with them are known. It has seemed to him that some information on a subject so important for iron workers would be of interest.

The works of Berthier, Caron, Ebelmen, Percy and others, on the fusibility of silicates, have been precious contributions to this question, but they are not generally well known to those who would find them most useful, owing perhaps to the preconceived idea that they are too technical. It is intended to quote from them practical data exclusively, showing, by a few examples, that the conclusions which these metallurgists have reached are fully corroborated by blast furnace practice. The present paper will be limited to the subject of fusibility of silicates so far as connected with their composition, with economy of working and character of pig metal. Many circumstances may modify results sometimes foreseen, and to say that a slag of a certain composition and fusibility will invariably correspond to a stated grade of iron is impossible. Still, it will be found that divergences, when well marked and decided, can generally be traced to certain special or abnormal conditions.

The determination of the empirical or rational formula of a silicate presents no difficulty to the technical chemist, but it involves a kind of knowledge which many iron masters, otherwise thoroughly competent, do not always have at command. Slags are complex silicates, principally of alumina, lime and magnesia, but contain also, and normally, notable percentages of ferrous and manganous oxide, potash, soda and baryta, amounting to as much as 7 and 8 per cent. The presence of these elements in quantities which cannot be neglected in ascertaining the type of a silicate, still further complicates the calculations. The composition of a slag, the percentage of its constituents, rarely affords, at first sight, a clear conception of its chemical character. A comparison with others, if it can be easily made, may be of great advantage. Given the percentage of silica and of the different bases, by a simple calculation and a table given below, without the use of any *chemical symbol or formula*, the character of a slag, its approximation to a certain chemical type, can be ascertained at once. The method is given in full.

Blast furnace slag is a combination of silica with various bases, principally alumina, magnesia and lime. The ores of iron contain, as gangue, silica associated with certain earthy or alkaline bases and almost invariably an excess of free silica as quartz. Should such an ore be smelted without any addition of fluxes, the free silica, not finding a base, would combine with a part of the oxide of iron which it would remove as slag. This is what takes place in the Catalan forge, where the slag is obtained at the sacrifice of a certain quantity of iron. Fluxes are then added in the form of limestone or dolomitic limestone, of which as little should be used as is consistent with the proper fusibility of the silicate formed from the silica of the ores and the ash of the coal with the bases found in the latter and in the limestone.

Owing to the complexity of the silicates as compounds, the theory of them is still obscure and, in the following, we do not pretend to deal with theoretical considerations, but only with slags as they appear in books on metallurgy and as they are practically known to ironmasters.

In the composition of slags as given in these works, up to a comparatively recent date, the symbol SiO_3 is used for silica, which was for a long time regarded as a "trioxide." The *equivalent* of silicon was then taken at 22.00 by some, at 21.25 by others ; it is now assumed to be 14.00 ; at. wt. Si = 28.00. The equivalent of silica, SiO_3, was consequently taken as 46.00 or 45.25 as the case might be, that of SiO_2 is now 30, mol. wt. 60. The oxygen of silica calculated from the old formula SiO_3 was then : $\frac{24}{45.25} = 0.530$ or : $\frac{24}{46} = 0.522$. It is now $\frac{8}{15} = 0.533$. In the same manner the *equivalents* of lime, magnesia and alumina, as late as 1865, were slightly different from what they are assumed to be now, that of lime being taken at 28.25, which is now 28.00 ; at. wt. 56. All these differences affect only the hundredths of the composition as given in these books. SiO_2 will be used here for silica, unless otherwise mentioned. All the formulæ of slags are expressed in *equivalents*, (and not in the atomic weights) in all books up to 1886 and even later, and this practice will be followed here. Whatever may be said logically of the consideration of silicates as derivatives of certain hypothetical radicals, the use of the equivalents has, in this case, the advantage of representing clearly to the eye a certain relation of silica to bases, and of the oxygen of the acid to the oxygen of the bases, corresponding, in general, to a certain grade of iron. The different earths not only saturate different quantities of silica according to their equivalents, but, for the same base, the proportions of the basic element to that of the acid may vary. The result of all observations shows that compound as well as simple bodies combine together in a certain number of proportions distinctly determined, which are generally to each other in simple ratio, at least when we deal with natural minerals. For instance, 1, 2, 3 of lime, magnesia or, in general, of such other oxides of symbol RO, will combine with the same quantity 1 of silica or conversely: so also will alumina or isomorphous oxides, R_2O_3, though in different proportions. Blast furnaces slags considered as silicates of protoxide may be: acid, neutral, sesquibasic, bibasic or, occasionally, tribasic. Sesquiacid slags correspond to "types" in which there is respectively: 1 of base to 2 of acid (acid): 1 of base to 1 of acid (neutral); 1½ of base to 1 of acid, or, 3 of base to 2 of acid (sesquibasic); 2 of base to 1 of acid (bibasic); 3 of base to 1 of acid (tribasic): 1 of base to 1½ of acid or 2 of base to 3 of acid (sesquiacid). Their formulæ are

$RO,2SiO_2$ RO,SiO_2 $3RO,2SiO_2$ $2RO,SiO_2$ $3RO,SiO_2$ $2RO,3SiO_2$

Acid, neutral, sesquibasic, bibasic, tribasic and sesquiacid and the ratio of oxygen of the silica to that of the base is respectively for each:

4:1 2:1 4:3 1:1 2:3 6:2 or 3:1

Many other silicates fall between these types and are met with in slags. To form a neutral silicate, that is one in which the oxygen of the acid is double that of the base, the bases of the formula R_2O_3, require 3 atoms of acid. Hence, the neutral silicates in R_2O_3 take the form R_2O_3, $3SiO_2$; the acid silicates, 1 base to 2 of acid, will be represented then by R_2O_3, $6SiO_2$, the sesquibasic, 1½ base to 1 acid, by $1\frac{1}{2}R_2O_3$, $3SiO_2$, or, $3R_2O_3$, $6SiO_2$, or, R_2O_3, $2SiO_2$, and, indeed, oxygen of acid 4, oxygen base 3::4:3. In the same manner the bibasic silicate in R_2O_3 has for its formula: $2R_2O_3$, $3SiO_2$; the tribasic, R_2O_3, SiO_2; the sesquiacid: $2R_2O_3$, $9SiO_2$. If we insist on these points it is because these formulæ are constantly met with in metallurgical books, in which slags are called by the preceding names. As we shall frequently find formulæ in which the silicates are expressed by SiO_3, we must be able readily to transform one formula expressed in SiO_2 into one in which SiO_3 is used, or conversely. For this, the following method will be found convenient:

RULE—To convert the formula in SiO_2 into the older formula in which silica is regarded as a trioxide: Multiply the *entire formula* by 3, correct the silica term by the equation $SiO_2 = \frac{2}{3} SiO_3$ and reduce the whole to its lowest terms. For instance, if to transform the formula, $RO,\ SiO_2 + R_2O_3,\ 3SiO_2$ which represents a neutral silicate of RO and R_2O_3, we multiply by 3, we have:

$$3RO,\ \underbrace{3SiO_2}_{=2SiO_3} + 3R_2O_3,\ \underbrace{9SiO_2}_{=6SiO_3};$$

but since: $1SiO_2 = \frac{2}{3}SiO_3$; $3SiO_2 = 2SiO_3$ $9SiO_2 = 6SiO_3$, and the old formula would be, for the same compound: $3RO,\ 2SiO_3 + 3R_2O_3,\ 6SiO_3$ or, reduced, $3RO,\ 2SiO_3 + R_2O_3,\ 2SiO_3$.

Conversely: to change formula containing SiO_3 into one containing SiO_2, divide *all* terms by 3 and correct the silica term by $SiO_3 = \frac{3}{2} SiO_2$. We have put in Table I. the new and old formulæ for silicates of the same chemical character, giving also for each the oxygen ratio of bases in RO to oxygen of bases in R_2O_3 and the ratio of the total oxygen of the bases to that of the acid.

TABLE I.

NEW FORMULA: SiO_2. Corresponding to:	OLD FORMULA: SiO_3.
Equiv....$SiO_2 = 14 + 16 = 30$ At. wts. ..... $= 28 + 32 = 60$ Oxygen Silica $= \frac{28}{60} = \frac{14}{30} = \frac{7}{15} = 0.533$ of SiO_2	Equiv.............$SiO_3 = 21.25 + 24 = 41.25$ Oxygen...........$SiO_3 = \frac{24}{21.25} = 0.5304$ of SiO_3
(A.)—*Acid Silicate.* 2 Equiv. acid to 1 base RO 6 " to 1 " R_2O_3 Oxygen ratio.....RO...R_2O_3..SiO_2 1 : 3 : 16 Formula..........$RO,\ 2SiO_2 + R_2O_3,\ 6SiO_2$ O of acid : O of bases :: 16 : 4 = 4 : 1 The disilicate of modern nomenclature derived from $H_2Si_2O_5 = H_2O,\ 2SiO_2$; O ratio, 4 : 1.	(A).—*No corresponding name given by Percy.* Oxygen ratio............RO — R_2O_3 SiO_3 3 : 3 24 or 1 : 1 : 8 Formula...........$3RO,\ 4SiO_3 + R_2O_3.\ 4SiO_3$ O of acid : O of bases : 24 : 6 = 4 : 1 In accordance with other names, based upon SiO_3, this would be a *quadrisilicate.*

TABLE I.—*Continued.*

NEW FORMULA : SiO_2. Corresponding to :	OLD FORMULA : SiO_3.
(B.)—*Sesquiacid Silicate.* 1½ Eq. acid to 1 base RO or 3 " to 2 " RO 9 " to 2 " R_2O_3 O. ratio.... ..RO...R_2O_3..SiO_2 2 : 6 : 24 or 1:3:12 Formula.....$2RO, 3SiO_2 + 2R_2O_3, 9SiO_2$ O of acid : O of bases :: 12 : 4 = 3 : 1 Trisilicate derived from $H_4Si_3O_8 = 2H_2O, 3SiO_2$ O ratio = 3 : 1	(B.)—*Neutral or Trisilicate of Percy.* O. ratio.................. RO...R_2O_3.. SiO_3 1 : 3 : 12 Formula............$RO, SiO_3 + R_2O_3, 3SiO_3$ O of acid : O of bases :: 12 : 4 = 3 : 1
(C.)—*Neutral Silicate.* 1 Equiv. acid to 1 base RO 3 " to 1 " R_2O_3 O. ratio..... ....RO...$R_2O_3SiO_2$ 1 : 3 : 8 Formula..............$RO, SiO_2 + R_2O_3, 3SiO_2$ O of acid : O of bases : : 8 : 4 = 2 : 1 The monosilicate of modern type derived from metasilicic acid $H_2SiO_3 = H_2O, SiO_2$ O ratio 2 : 1	(C.)—*Sesquibasic or Bisilicate of Percy.* O. ratio ....RO R_2O_3 SiO_3 3 : 3 : 12 or 1 : 1 : 4 Formula.. ....$3RO, 2SiO_3 + R_2O_3, 2SiO_3$ O of acid : O of bases :: 4 : 2 = 2 : 1
(D.)—*No Special Name.* 3 Eq. acid to 4 of base RO 9 " to 4 " R_2O_3 RO O. ratio ....4 : 12 : 24 or 1 : 3 : 6 Formula..... .....$4RO, 3SiO_2 + 4R_2O_3, 9SiO_2$ O of acid : O of bases = 24 : 16 or 3 : 2 A trisilicate of modern type.	(D.)—*The Bibasic or Sesquisilicate of Percy.* O. ratio......... .. ..2 : 6 : 12 or 1 : 3 : 6 Formula...........$2RO, SiO_3 + 2R_2O_3, 3SiO_3$ O of acid : O of bases :: 6 : 4 = 3 : 2
(E.)—*Sesquibasic Silicate.* 1 acid to 1½ base RO or 2 " to 3 " RO 6 acid to 3 base R_2O_3 O. ratio...3 : 3 : 8 or 2 " to 1 " R_2O_3 Formula...........$3RO, 2SiO_2 + R_2O_3, 2SiO_2$ O of acid : O of bases : 8 : 6 = 4 : 3 A disilicate of modern type derived from $H_6Si_2O_7 = 3(H_2O) 2SiO_2$. O ratio 4 : 3.	(E.)—*No special name by Percy.* O. ratio... ....RO R_2O_3 SiO_3 9 : 9 : 24 or 3 : 3 : 8 Formula.......$9RO, 4SiO_3 + 3R_2O_3, 4SiO_3$ O of acid : O of bases :: 24 : 18 = 8 : 6 = 4 : 3
(F.)—*Bibasic Silicate.* 1 acid to 2 base RO 3 " to 2 " R_2O_3 O. ratio...2 : 6 : 8 = 1 : 3 : 4 Formula..$2RO, SiO_2 + 2R_2O_3, 3SiO_2$ O of acid : O of bases :: 4 : 4 = 1 : 1 The monosilicate, basic, of modern nomenclature, derived from orthosilicic acid $H_4SiO_4 = 2(H_2O) SiO_2$: O ratio 1 : 1	(F.)—*Tribasic or Monosilicate of Percy.* O. ratio....................3 : 3 : 6 or 1 : 1 : 2 Formula ....$3RO, SiO_3 + R_2O_3 SiO_3$ O of acid : O of bases :: 2 : 2 = 1 : 1.
(G.)—*Tribasic Silicate.* 1 acid to 3 base RO 3 " to 3 " R_2O_3 or 1 " to 1 " R_2O_3 O. ratio...3 : 3 : 4 Formula.$3RO, SiO_2 + R_2O_3 SiO_2$ O of acid : O of bases :: 4 : 6 = 2 : 3 The monosilicate, *parasilicate* of modern nomenclature, derived from $H_6SiO_5 = 3(H_2O) SiO_2$, O ratio 2:3.	(G.)- *No special name by Percy.* O. ratio....... . ...9 : 9 : 12 or 3 : 3 : 4 Formula .....$9RO, 2SiO_3 + 3R_2O_3, 2SiO_3$ O of acid : O of bases :: 12 : 18 = 4 : 6 = 2 : 3

It will be seen that the ratio of oxygen of acid to that of bases is *the same* in both formulæ, as it should be, since: $3SiO_2 = 2SiO_3$ as far as oxygen is concerned; and also as to total equivalent; $3SiO_2 = 90$, using present equivalents, or $2 \times 45 = 90$, using the old equivalent assumed for silicon.

This ratio of oxygen of acid to oxygen of base is the most *characteristic feature of a type of silicates,* whatever may be said of their exact molecular composition. When it is found to be *the same* in two silicates containing different bases in different proportions it corresponds to the same calculated empirical formula for each, to the same saturation of bases and acid and the same fusibility, the conditions of temperature determining the production of such slags in a blast furnace are similar, in other words, they are likely to accompany the same grade of iron.

In a question of such importance as this, involving references to works in which notations and nomenclature are different from those now used, it is necessary to establish a clear basis of understanding.

Using the symbol SiO_3 for silica, Percy and others have called a *neutral silicate or trisilicate* a silicate in which the O of base: O of acid ∷ 1:3. Hence, RO, SiO_3 represented for him a trisilicate. Now such silicate, with SiO_2, corresponds to a *sesquiacid* silicate $2RO, 3SiO_2$; O of silica, 6: O of RO, 2 ∷ 3:1: the neutral silicate of our days being one in which O of acid $= 2 \times$ O of bases or $RO\ SiO_2$, silica being a *dioxide,* not a *trioxide.* In R_2O_3 this neutral silicate of Percy has the formula R_2O_3, $3SiO_3$ (O of silica, $9 = 3 \times 3$ times O of base). Now: $2R_2O_3$, $9SiO_2$ (O acid $18 =$ O base, 6×3).

In the same manner he called a *sesquibasic or bisilicate* a silicate in which O of acid $= 2 \times$ O of bases, $3RO, 2SiO_3$; $R_2O_3, 2SiO_3$; now: $RO, SiO_2 + R_2O_3$, $3SiO_2$ (neutral).

He called a *bibasic or sesquisilicate* a silicate in which O acid: O bases ∷ 3:2; $2RO, SiO_3, 2R_2O_3, 3SiO_3$; O ratio; 3:2; $9:6 = 3:2$. Now: $4RO, 3SiO_2 + 4R_2O_3, 9SiO_2$: O ratio; $6:4 = 3:2$; $18:12 = 3:2$, and does not correspond to any of the types under SiO_2 mentioned in the table I.

He called a *tribasic or monosilicate* a silicate in which O of acid $=$ O of base, now called bibasic: $3RO, SiO_3 + R_2O_3$, SiO_3; now: $2RO, SiO_2 + 2R_2O_3$, $3SiO_2$.

In all that follows when the terms *acid*, *neutral*, etc., silicate are used, reference is made to silica expressed by the symbol SiO_2, and not by SiO_3, unless otherwise mentioned.

In the modern conception of the composition of the silicates, normal hydrated silicic acid has the formula H_4 $SiO_4(=2H_2O, SiO_2)$, a tetrabasic acid containing 4 atoms of hydrogen which can be replaced by metals. It has not been isolated, but it is probable that it exists in the pseudo-solutions coming from the dialysis of liquids containing alkaline silicates. The metasilicic hydrate is formed when solutions of dialyzed silicic hydrate are evaporated. It is probable that metasilicic acid can be condensed in the same way as metaphosphoric acid to form complex molecules of polysilicic acids. There are known: orthosilicates, $2RO$. SiO_2. corresponding to the normal hydrates (bibasic silicates of table 1); monobasic silicates, RO, SiO_2 (neutral), which seems to be derived from metasilicic acid. The real molecular constitution of the polysilicates is ignored. In most of the formulæ one is satisfied to express the ratio of oxygen of silica to oxygen of bases. In the orthosilicates (bibasic) it is 1:1 in the metasilicates (neutral) 2:1; in the trisilicates (sesquiacid) 3:1, *e. g.*, or those, $2RO$, $3SiO_2$. In basic silicates (serpentine type) 4:3 (sesquibasic). There are other basic silicates in which it is 3: 2 (dysthene).*

Although no solid hydrate of silicic acid possessing a constant composition is known, we are acquainted with a large number of silicates forming many natural mineral species. "The hypothetical acids or hydrogen salts from which they are supposed to be derived are here given." "Molecular weights have been ascertained only for the volatile organic silicates or silicic ethers, the molecular weight of the other compounds is therefore doubtful: the oxygen ratio being the best criterion to classify them; their formulæ are represented by the simplest form possible." (Roscoe & Schorlemmer's Chemistry.)

Also, from another authority. "But scarcely any of the silicates are represented by formulæ which express their derivation from the acid. H_4SiO_4; or other hypothetical radicals. They are generally represented as combinations of metallic oxides with

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* Frémy.

SiO_2" (Bloxam's chemistry). It is this mode of representation that we have adopted, using the equivalents and the formula SiO_2, for silica. In this manner the slag of composition, $6Ca_2SiO_4$, $Al_4(SiO_4)_3$, using atomic weights and derivation from hypothetical radicals, would be represented by the formula, $12CaO$; $2Al_2O_3$, $9SiO_2 = 6(2CaO,SiO_2) + 2Al_2O_3$, $3SiO_2$ (O of acid = O of bases), which, referring to Table I, represents what we may call a *bibasic silicate* with RO and R_2O_3, derived from the orthosilicic acid; $H_4SiO_4 = 2H_2O_3$, SiO_2. A monosilicate; orthosilicate according to modern nomenclature, (Table II). O of acid = O of bases. The tribasic or *monosilicate* of Percy, $3RO$, $SiO_3 + R_2O_3, SiO_3$ (O of acid = O of bases) (Table I).

TABLE II.

MONOSILICATES.

1° *Metasilicic acid:* $H_2SiO_3 = H_2O,SiO_2$, forming monosilicates (monobasic) O ratio 2:1 corresponding to RO,SiO_2 (neutral), Ex. Enstatite $Mg, SiO_3 = MgO, SiO_2$. Augite $(Ca, Mg) SiO_3 = O,2SiO_3$—Beryl. $\begin{matrix}Al_2\\Be_2\end{matrix}(SiO_3)3 = \left.\begin{matrix}Al_2\\Be_2\end{matrix}\right\} O_3 \quad 3SiO_2 \left.\begin{matrix}Be_2\\Al_2\end{matrix}\right\} O_3,2SiO_3$

O ratio 2:1.

2° *Orthosilicic acid* $H_4SiO_4 = 2(H_2O)SiO_2$ forming bibasic monosilicates. O ratio 1:1 corresponding to $2RO,SiO_2$ (bibasic); $2R_2O_3,3SiO_2$—Ex: Olivine, $Mg_2,SiO_4 = 2MgO,SiO_2$; Phenakite, $Be_2SiO_4 = 2BeO, SiO_2$.

3° *Parasilicic acid* = $H_6SiO_5 = 3H_2O,SiO_2$; Oxygen ratio 2:3 forming monosilicates corresponding to: $3RO,SiO_2$ (tribasic, O ratio 2:3). Ex: Chondrodite $Mg_3,SiO_5 = 3MgO,SiO_2$; Andalusite, $Al_2SiO_5 = Al_2O_3,SiO_2$ (tribasic silicate) $= Al_2O_3\frac{2}{3}SiO_33Al_2,O_3$ $2SiO_3$ O ratio = 6:9 or 2:3 as before.

DISILICATES.

$H_2Si_2O_5 = H_2O,2SiO_2$ O ratio : 4 : 1 corresponding to RO, $2SiO_2$ (acid silicate) O ratio 4 : 1, Ex : Petalite

$$(Na,Li)Si_2O_5 = \left.\begin{matrix}Na\\Li\end{matrix}\right\} O,2SiO_2$$

$$= \underbrace{3RO,4SiO_3}_{\text{acid silicate,}} + \underbrace{4Al_2O_34SiO_3}$$

an acid silicate in SiO_3; O ratio 12 : 3 = 4 : 1.

$H_6Si_2O_7 = 3H_2O,2SiO_2$; O ratio 4 : 3 corresponding to $3RO, 2SiO_2$ (sesquibasic) Ex.: Serpentine, $Mg_3,Si_2O_7 = 3MgO, 2SiO_2$ $9MgO,4SiO_3$ (sesquibasic) O ratio 12 : 9 = 4 : 3.

$H_{10}Si_2O_9 = 5H_2O,2SiO_2$; O ratio 4 : 5 corresponding to $5RO, 2SiO_2$, Ex. Enclase $Al_2,Be_2,Si_2O_9 = \left.\begin{matrix}Al_2O_3\\2BeO\end{matrix}\right\} 2SiO_2$ or $\left.\begin{matrix}Al_2\\Be_2\end{matrix}\right\} O_5$. $2SiO_2$ O ratio 4 : 5.

TRISILICATES.

$H_4Si_3O_8 = 2(H_2O),3SiO_2$: O ratio 6 : 2 = 3 : 1 corresponding to $2RO, 3SiO_2$ (sesquiacid) Ex.: Orthoclase $Al_2K_2(S_3O_8)2 = (Al_2K_2)O_4,6SiO_2$ or $(Al_2K_2)O_8,12SiO_2 = 2(K_2O),3SiO_2 + 2R_2O_3,9SiO_2$: O ratio 6 : 2 = 18 : 6 = 3 : 1 = $KO,SiO_3 + Al_2O_3 3SiO_3$ O ratio 9 : 3 = 3 : 1 (sesquiacid).

$H_{15}Si_3O_{11} = 5(H_2O)3SiO_2$; O ratio 6 : 5 Ex.: Prehnite, $Al_2Ca_2Si_3O_{11} = \left.\begin{matrix}Al_2O_3\\2CaO\end{matrix}\right\} 3\ SiO_2$: O ratio 6 : 5.

$H_{14}Si_2O_{13} = 7(H_2O)3SiO_2$: O ratio 6 : 7 Ex.: Epidote, $Al_6Ca_4H_2(Si_2O_{13})_2$.

This mode of representation has the great advantage of showing at once the oxygen ratio which, certainly, the formulæ : $6Ca_2SiO_4$, $Al_4(SiO_4)_3$, and especially $Ca_{12}Al_4(SiO_4)_9$! ! ! do not *clearly* indicate as compared with : $6(2CaO,SiO_2) + 2Al_2O_3, 3SiO_2$ or even with $12CaO,2Al_2O_3,9SiO_2$.

The atomic weights of silicon, oxygen, aluminum, calcium, magnesium, iron, manganese, barium, the oxides of which are always present in variable quantities in a slag, entering into its composition wholly or in part, being *all double the equivalents* of these elements, the formulæ of silicates, considered as "combinations of metallic oxides with SiO_2," expressed either by using the *atomic weights or the equivalents, are then, in fact, exactly the same.* The terms monobasic or neutral, bibasic, tribasic of Table I. are based on the amount of *base* 1, 2, 3 as compared to *1 of acid ;* these silicates are really monosilicates, as in the more modern conception of Table II., in which, for 1 of silica, SiO_2, there may be 1, 2, 3 of base replacing 1, 2, 3 of H_2O of the hypothetical radical. The acid silicate of Table I., containing *2 of acid* for 1 of base, is, in the same manner, a "disilicate" of modern nomenclature (Table II.);

and, for the same amount of acid, *2*, there may be 1, 3, 5 of base. Likewise, the sesquiacid silicate of Table I., containing 3 of acid for 2 of base, is the modern trisilicate of Table II.; and, for this quantity, 3 of SiO_2, there may be 2, 5 or 7 of base.

In the names used in Table I. the proportion of the *basic element* has been taken as a guide in giving the name to the compound; in Table II. it is the amount of the *acid element* which has given its name to the type of silicate. In both denominations the oxygen ratio remains the same as well as the proportion of silica to bases. The whole difference lies in considerations of a certain order which may satisfy the mind as implying the idea of logical derivations from hypothetical radicals, but practically there is none, as there should not be.

The ground being thus cleared of all possible confusion in the notation we have followed and shall follow, as best conforming with data furnished by books on metallurgy and best known amongst technical blast furnace managers, let us proceed with the subject proper.

Berthier and, after him, many others (Percy, Ebelmen, Caron), have designated respectively as

Very Fusible = Silicates melting completely to a liquid glass at the temperature of a porcelain kiln, no blast.

Little Fusible = Silicates melting at the temperature of fusion of wrought iron.

Fusible = Silicates melting at a white heat or above in a furnace having a forced blast.

Refractory = Silicates not fusible or melting imperfectly at a temperature above that of fusion of wrought iron.

It is not enough that a slag should melt when it reaches the zone of the tuyeres, in the blast furnace; it must not run pasty nor thicken; it must preserve a certain fluidity when it comes in contact with the air or the sides of the forepart of the crucible. The word "fusible" indicates then a limit which it is possible to reach, but beyond which it would not be safe to go except in extraordinary cases of pressure and temperature of blast. All the silicates intermediate between "very fusible" and up to "fusible," constitute really the admissible slags.

Fusibility of Silicates = The *silicates* of potash and soda are very fusible in almost all proportions.

Aluminium Silicate = This compound, the basis of all clays, is absolutely infusible at the highest temperature of a blast furnace. The silicate containing $73SiO_2$, 27Al, softens a little. 3% of potash or soda is enough to cause the aluminium silicate to soften considerably; such quantities are frequently met with in iron ores.

Calcium Silicates = Simple calcium silicates are not generally fusible; practically only *one* of them is really fusible in the blast furnace.

LIME.	SILICA.	
88.5%	11.5%	Refractory: nearly 25 RO, $3SiO_2$ or 8RO, SiO_2 O of acid = $\frac{2}{8}$ = $\frac{1}{4}$ O of base........Hectobasic.
78.0	22.0	Refractory: nearly 24 RO, $6SiO_2$ or 4RO, SiO_2 O of acid = $\frac{2}{4}$ = $\frac{1}{2}$ O of base.........Quadribasic
70.3	29.7	Refractory: nearly 20 RO, $8SiO_2$ 5RO, $2SiO_2$ O of acid = $\frac{4}{5}$ O of base...............(Disilicate Table II.)
64.2	35.8	Little Fusible: 18 RO, $9SiO_2$ or 2 RO, SiO_2 O of acid = $\frac{2}{2}$ = O of base. Bibasic (Table I.), Monosilicate Orthosilicic (Table II.)
47.2	52.8	Fusible: 14 RO, $14SiO_2$ or RO,SiO_2 O of acid = $\frac{2}{1}$ = 2 × O of base.................Neutral (Table I.)
37.8	62.2	Fusible: 10 RO, $8Sio_2$ or 5RO, $4SiO_2$ O of acid = $\frac{8}{5}$ O of base..................Metasilicate (Table II.)
24.4	75.6	Little fusible: 6.8RO, $20SiO_2$ or RO, $3SiO_2$ O of acid = $\frac{6}{1}$ = 6 O of base..Triacid (Trisilicates, Table II.)

And we see from these experiments of Berthier, that the more *basic* the silicate becomes the *less* fusible it is, the neutral silicates being more fusible than the bibasic, and the latter more fusible than the quadri—and hectobasic. We see also that *beyond a certain limit of acidity* the refractory properties increase.

Magnesium Silicates.

MAGNESIA.	SILICA.	
72.2%	27.8%	Refractory: 28.80 MgO, $7.40SiO_2$, nearly 4 RO, SiO_2; O of acid = $\frac{2}{4}$ = $\frac{1}{2}$ O of base. Quadribasic (Table I.)
56.5	43.5	Refractory: 22.60 MgO, 11.50 SiO_2, nearly 2RO SiO_2; O of acid = $\frac{2}{2}$ = O of base. Bibasic (Table I.)

MAGNESIA.	SILICA.	
40.1	59.9	Little fusible: 16MgO, $16SiO_2$, nearly RO, SiO_2 O of acid = $\frac{2}{1}$ = 2 O of base. Neutral (Table I.)
30.0	70.0	Little fusible: 12 MgO, $18SiO_2$, nearly 2RO, SiO_2; O of acid = $\frac{6}{2}$ = 4 O base. Sequibasic (Table I.)

And again, though none are "fusible" the *less* basic the silicate the *less* infusible it is.

Double and Multiple Silicates.

The compound silicates are enormously more fusible than any single silicate, not even excepting the alkaline silicates. They melt at a temperature much inferior to the average of the temperatures of fusion of the simple silicates composing them, this temperature being frequently *lower* than that corresponding to the fusion point of *the most fusible,* as in certain alloys, indicating, in a multiple silicate, a normal chemical combination. Lime, which forms with silica, alumina, and magnesia, but one refractory or practically infusible compound of which the simple silicates are absolutely refractory, furnish double silicates which fuse readily.

LIME.	MAGNESIA.	SILICA.	
17.3%	25.0%	57.5%	Very fusible: 5 (CaO, SiO_2) × 10 (MgO, SiO_2) Neutral Silicate; O of acid : O of bases : : 2 : 1
33.5	12.1	54.4	Very fusible : 4.84 (MgO,SiO_2) × 9.60 (RO, SiO_2) Neutral Silicate; O of acid : O of bases : : 2 : 1
25.0	30.0	45.0	Very fusible : 12 MgO, 7.50 SiO_2, approximating $3RO,2SiO_2$ (Sesquibasic); O of acid, O of bases 4 : 3
19.8	14.0	06.2	Fusible : approximating $2RO,3SiO_2$ (Sesquiacid); O of acid : O of bases 3 : 1
9.3	20.3	70.4	Fusible : approximating $4RO,7SiO_2$; O of acid : O of bases 2 : 2 3½ : 1
21.2	7.7	71.1	Fusible : nearly $RO,2SiO_2$ (Acid); O of acid O of bases 37 : 9.15 4 : 1
20.9	15.8	73.3	Fusible : approx. $2RO,3Sio_2$....$2RO,3SiO_2$ (Sesquiacid); O of acid : O of base 39 : 12.50 nearly 3 : 1

Moreover we see that the *Sesquibasic* silicates are less fusible than the *Neutral*, and again, when the silicate goes beyond a certain "acidity" it becomes less fusible.

LIME.	ALUMINA.	SILICA.	
26.1%	15.7%	58.2%,	Very Fusible : 7.50 CaO,7.50SiO_2 + 2.50 R_2O_3, 7.50SiO_2 = RO,SiO_2 + R_2O_3, 3SiO_2, (Neutral) 2 : 1.
34.0	16.0	50.0	Very fusible : 2.13R_2O_3, 6.15SiO_2 + 7,45RO, 7.20SiC_2, nearly RO,SiO_2 + R_2O_3,3SiO_2, (Neutral) 2 : 1.
26,0	31.3	43.7	Very fusible : 7.40RO, 3.70SiO_2 + 4.86R_2, O_3 7.95SiO_2, nearly 2RO, SiO_2 + 2R_3O_2 3SiO_2, (Bibasic) 1 : 1.
36.8	22.0	41.0	Very fusible : approximating 2RO,SiO_2 + 2R_2O_3, 3SiO_2 (Bibasic) 1 : 1.
47.3	14.2	38.4	Fusible : Exactly..2RO SiO_2 + 2R_2O_3 3SiO_2, (Bibasic) 1 : 1.
46.3	27.8	25.9	Fusible: 13.23RO, 3.35SiO_2 + 441R_2O_3, 3.45 SiO_2, approximating 4RO, SiO_2 + 4 R_2O_3, 3SiO_2, (Quadribasic) 1 : 2.
20.2	12.1	67.7	Fusible: 5.77RO, 8.65SiO_2 approxim. 6RO, 9SiO_2 or 2RO, 3SiO_2 + 2R_2O_3 9SiO_2, (Sesqui acid), 36.10 : 11.42 = 3 : 1.
10.5	19.0	70.5	Fusible: 5.77RO, 8.65SiO_2 approxim. 6RO, 9SiO_2 or 2RO, 3SiO_2 + 2R_2O_3 8SiO_2 (Sesqui acid), 37.60 : 11.80 = 3 : 1.

And again, the *Neutral* slags and slags approximating the *bibasic* are more fusible than the exactly *basic or quadribasic slags* or those in which the acidity is beyond a certain limit, as the silicates are less basic the more fusible they become.

In certain cases, however, silica is not alone sufficient to saturate the oxides; according to ordinary laws, it has been observed that certain slags were *fusible*. It has been admitted that alumina in those circumstances can perform the functions of an acid. This is corroborated by the experiments of Berthier, who found that in the proportions given below some aluminates were fusible.

ALUMINA.	LIME.	MAGNESIA.	
19.9%	56.5%	23.6%,	Little fusible : 6 $CaO, 3MgO, Al_2O_3$.
49.9	32.3	14.8	Fusible : $6CaO, 3MgO, 4Al_2O_3$.
47.0	33.8	19.2	Fusible : $4CaO, 3MgO, 3Al_2O_3$.

We find such compounds in nature : Spinel, MgO,Al_2O_3 is fusible in the blast furnace, and certain slags containing only from 23 to 25% of silica and a large quantity of alumina have been run in English furnaces.

MAGNESIA.	ALUMINA.	SILICA.		OX. RATIO.
29.3%	24.8%	45.9%,	Very fusible: $4RO,3SiO_2 + 4R_2O_3, SiO_2$ (Bibasic of *Percy*)	24 : 16 3 : 2.
20.0	17.0	63.0	Very fusible : 8RO, 8.40 SiO_2 or approxim. $RO,SiO_2 + R_2O_3\ 3SiO_2$ (Neutral)	33.6 : 16, or nearly 2 : 1.

Looking over these tables, the results of many experiments by Percy, Caron, Berthier, etc.,* we find that of the compounds which SiO_2 can form with lime and alumina, or alumina and magnesia, or magnesia and lime, as a general rule, the *less basic they are the more fusible they become* until a certain *limit of acidity* is reached, and that amongst them, when the quantity of silica is *above 40% and not above 60%,* the compound becomes as much more fusible as the percentage of silica is above the first figure, varying between 40 and 60, beyond which last limit the silicate appears to fuse again with more difficulty.

In replacing in a double silicate any weight whatsoever of one of the bases by an equivalent weight of a third, a still more fusible compound is *invariably* obtained. The more complex the silicate, the more fusible and more fluid it becomes. If we consider that oxide of manganese, ferrous oxide and alkalies are always met with in slags in proportions which may reach 5 to 7%, that the alkalies, in very small quantities, increase considerably the fusibility of even the most refractory silicates, it can be better understood why unjudicious charges in limestone do not necessarily produce injurious ef-

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* Quoted in Vathaire *Les Haus Foarneaux.*

fects. A slag, for instance, which, if based upon a certain per cent. of alumina and lime would have been somewhat refractory and might have become the cause of serious trouble, acquires a greater *fusibility* and *fluidity* owing to the presence of manganous and ferrous oxides, alkalies and magnesia, derived from the limestone. Magnesia was for many years considered as a detrimental element, tending to produce infusibility! Had the iron master been aware of the conditions of fusibility of his slag and of the influence of the elements entering into its composition, affecting the said fusibility, he might have been able to reduce notably the charges in limestone, thus saving on first cost, on burden of furnace and on coal consumed, and gained at the same time in fluidity.

Within certain limits, the *more basic* the silicate *the less fusible* it is as a rule, meaning by basic not only the *number of bases* but also the *total quantity* of the basic element as compared with that of silica. The pig metal will also have more tendency to be gray as the slag is less fusible and to be white if the latter melts readily. The reason of this is found in the fact that the pig metal separates from the gangue which surrounds it only when the latter melts. If the gangue melts in the boshes at a comparatively low temperature the pig metal will pass to the hearth without stopping, reaching the crucible without having been exposed to the high temperature of the zone around the tuyeres and without having charged itself with carbon or silicon ; carbon being more soluble in cast iron as the temperature of the latter is higher, and silicon being produced only by the contact of silica and iron carbides at high temperatures.

The same observations regarding the fusibility of the silicates as connected with the proportion of silica to bases apply to triple and multiple silicates as well as to double. Berthier has even remarked that, in the triple silicates of alumina, magnesia and lime, these compounds are much more fusible, as the ratio of the quantity of lime and magnesia to that of alumina approximates 3 : 1.

As an example of the fusibility of multiple silicates, according to their composition, many analyses of slags that the writer has had occasion to make in the course of his practice might be quoted. Three are here given :

1° Slag run with *white iron and a little mottled;* furnace, 40 ft. high; hot blast at 650° to 700° F.; pressure of blast, $3\frac{1}{2}$ lbs. per square inch; ores, magnetites; temperature, comparatively low in the furnace.

SiO^2	48.35	
Al_2O_3	12.74	
MgO	10.71	38.76
CaO	24.83	
Alkalies	1.01	
MnO	0.63	
FeO	1.58	

Silica is above 40%, nearly 50%. Bases in RO, 38.76% = nearly three times the alumina. 12.74%×3 = 37.22%. Oxygen of silica : 25.98 : 18.49 oxygen of bases : : 24 : 18, nearly or 4 : 3. A sesquibasic silicate but a little *less basic.*

Exact ratio: 4.49 : 3.08. A good corroboration of the remarks of Berthier. Formula: $3RO, 2SiO_2+R_2O_3SiO_2$, approximately.

2° Slag run with *gray iron No. 2;* furnace, 60 feet high; blast, 850° to 900° Fahr.; pressure, $7\frac{1}{2}$ lbs. per square inch; temperature in furnace much higher; slag *less fusible:*

SiO_2	= 40.45	
Al_2O_3	= 8.90	
MgO	= 15.65	49.61
CaO	28.80	
MnO	3.01	
FeO	1.00	
Alkalies	1.15	

Silica is about at the limit, 40%; bases RO = nearly 6 times bases R_2O_3. O of acid, 21.57 : O of bases, 19.80 : : 1.09 : 1 : approximating a bibasic slag. $2RO, SiO_2 + 2R_2O_3, 3SiO_2O$, ratio 1 : 1. The pig iron was gray No. 2. Slag *bibasic, less fusible,* according to the observation of Berthier, than the preceding.

3° *Slag run in the same furnace* with a change in the charges. Ores, magnetites and hematites containing 7 to 8% manganese oxide, fuel, coke and anthracite.

SiO_2	= 32.65	
Al^2O^3	= 23.00	
CaO	31.00	37.20
MgO	0.00	
FeO	2.00	
MnO	4.20	

Silica much below 40%. Bases in RO = $1\frac{1}{2}$ times bases in R_2O_3. O of acid, 17.41 : O of bases 20.94 : : 1 : 1.20 : more basic than a bibasic silicate, 1 : 1.

Formula of slag : $10.23RO, 4.35SiO_2 = 4.35\ (2.35RO, SiO_2)$ *less* basic than a tribasic slag, $3RO, SiO_2$, but *more basic* than a *bibasic* : $2RO, SiO_2$. Slag more basic than the preceding, consequently *less* fusible. Iron, Scotch gray No. 1, graphitic iron, kish cinder.

It seems, at least, to be established from the direct experiments of metallurgists, corroborated by blast furnace practice, that, whatever may be the relation between the fusibility of slags and the grades of iron for simple, double or multiple silicates, the more *basic the type of* the slag the less fusible it is, as a rule.

In calculating a silicate, the saturation of the different bases for silica to produce the same type has to be taken in consideration. Considering only the principal constituents of a slag, lime, magnesia and alumina, it will readily be seen that to form an *acid slag* (Table I.) RO, $2SiO_2 + R_2O_36SiO_2$:

$$\text{Acid Slag}\begin{cases}\text{1 Alumina will saturate } 3.495\ SiO_2.\\ \text{1 CaO} \quad \text{"} \quad 3.000 \quad \text{"}\\ \text{1 MgO} \quad \text{"} \quad 2.143 \quad \text{"}\end{cases}$$

And in the same manner it can be calculated that to form a neutral or a sesquibasic slag, the saturations will be as follows :

TABLE III.

ACID SLAG.	SESQUIACID SLAG.	NEUTRAL (MONOBASIC).
RO, $2SiO_2 + R_2O_3$. $6SiO_2$ 1 Al_3O_2 will take.....3.495 SiO_2 1MgO " .3.000 " 1CaO " .2.143 "	2RO, $3SiO_2 + 2R_2O_3$. $9SiO_2$ 1Al_2O_3 will take.....2.6213 SiO_2 1MgO " .....2.2222 " 1CaO " .....1.6071 "	RO, $SiO_2 + R_2O_3$. $3SiO_2$ 1Al_2O_3 will take... 1.7475 SiO_2 1MgO " ....1.5000 " 1CaO " ....1.0714 "
SESQUIBASIC SLAG.	BIBASIC SLAG.	TRIBASIC SLAG.
3RO, $2SiO_2 + R_2O_3$. $2SiO_2$ 1Al_2O_3 will take....1.165 SiO_2 1MgO " ....1.000 " 1CaO " ...0.714 "	2RO, $SiO_2 + 2R_2O_3$. $3SiO_2$ 1Al_2O_3 will take.....0.8738 SiO_2 1MgO " ....0.7500 " 1CaO " .....0.5378 "	3RO, $SiO_2 + R_2O_3$. SiO_2 1Al_2O_3 will take....0.5825 SiO_2 1MgO " ....0.5000 " 1CaO " ...0.3571 "

Hence, 1 lb. of alumina, as far as saturation for silica is concerned, is equivalent, respectively, to

$$\frac{3.495}{3.143} = \frac{2.6213}{1.6071} = \frac{1.7475}{1.0714} = \frac{1.165}{0.714} = \frac{0.8738}{0.5378} = \frac{0.5825}{0.3571}$$

or to 1.631 lbs. CaO, *whatever may be the type of the silicate ;* and for the bases in R_2O_3, in general, in proportion to 1.631, as is the equivalent of one particular base of this formula to the equivalent of Al_2O_3. As to the bases in RO, requiring 1 equiv. of silica, for 1 equivalent of base to form a neutral silicate, *their equivalence* in lime is directly proportional to *their chemical equivalents.*

Hence we can calculate the following table, and say, *as far as saturation of base for silica is concerned and whatever be the type or the character of a silicate:*

TABLE III (A).

1 lb. Al_2O_3 = 1.631 CaO
1 lb. MgO = 1.400 "
1 lb. FeO = 0.780 "
1 lb. MnO = 0.780 "
1 lb. KO = 0.590 "
1 lb. NaO = 0.900 "
1 lb. Fe_2O_3 = 1.125 "
1 lb. BaO = 0.365 "

A glance at the above figures show *a priori*, and apart from the question of the beneficial effect that lime may have in a blast furnace in eliminating certain injurious elements of the ores, the inconsistency of using lime in excess as flux. It is, of all the principal fluxing bases of the rocks and ores, the most expensive as to cost, and the one of which the greatest quantity is required.

More of it is necessary than of magnesia or alumina to saturate, to a certain type, a given amount of SiO_2. The table shows why a *dolomite* is preferable to a *calcite*, each pound of magnesia contained in it being really equivalent to 1.40 lbs. lime, and, moreover, the double or triple silicate into which magnesia enters is much more fusible ; and yet for years dolomitic limestones have been systematically rejected or sparingly used for fear "of inducing infusibility of the slag."

Suppose certain charges to have been so calculated that alumina, lime and magnesia were in proportion to silica within the figures given above : that is, 1 lb. of alumina for every 3.495 lbs. SiO_2, 1 lb. MgO for every 3 lbs. of SiO_2, 1 lb. CaO for every 2.143 lbs. of SiO_2, etc. (acid silicate, Table III.). We arrive then at the following composition for slags of the different types :

TABLE IV.

COMPOSITION.	Acid.	Sesquiacid.	Neutral.	Sesquibasic.	Bibasic.	Tribasic.
SiO_2	73.45	67.36	58.04	47.95	40.85	31.52
Al_2O_3	7.00	8.56	10.98	13.71	15.58	18.04
MgO	8.15	10.10	12.89	15.97	18.15	21.01
CaO	11.40	13.97	18.08	22.37	25.41	29.42
	100.00	100.00	100.00	100.00	100.00	100.00

Or, taking slag of the neutral type, its composition, as taken from the preceding (Table III.) will be :

SiO_2	58.04
MgO	12.89
CaO	18.08
Al_2O_3	10.97
	99.98

Such a slag, according to what has been seen above, and to the remarks of Berthier, ought to be a very fusible slag. First: It is a *neutral* slag, not very basic, consequently, silica is above 40 per cent., nearing the limit of 60 per cent. Bases in RO = 30.97 = nearly 3 × 10.97, the bases in R_2O_3. Its formula is $RO, SiO_2 + R_2O_3 3 SiO_2$. The iron run with it ought to be white or at least of a very light grade of gray. These deductions made, *a priori*, from its composition, from a study of the fusibility of silicates, find their verification in the actual results obtained in a blast furnace in England. This hypothetical slag is identical, as far *as type* is concerned, with one actually run in conditions indicating plainly a low temperature in the furnace, *i. e.*, a very fusible silicate. If, by proportioning properly the charges so as to obtain it, it were found to be more economical in use than those of the English slag, the two types being alike, all the probabilities would be—the conditions of running of the furnace being the same—that the same grade of iron would be obtained, but, in one case, much more economically than in the other.

Percy gives the following analysis of the slag of a charcoal furnace. Working as *white pig* with a little of *light mottled*—consequently of a slag run at a low temperature.

SiO_2 = 54.00
MgO ... 0.57
CaO ... 25.67
Al_2O_3 .. 13.04
FeO 2.44
MnO ... 2.20

If the formula of this slag were calculated it would be found to represent exactly, to the second decimal, a *typical neutral slag.*

Its formula is: 2.02 R_2O_3, 5.97 SiO_2 + 8.60 RO, 8.50 SiO_2 or (R_2O_3, 2.96 SiO_2) 2.02 + 8.00 (1.01 RO, SiO_2) *i. e.*, nearly as possible R_2O_3, 3 SiO_2 + RO SiO_2 :

O of acid : O of bases : : 2 : 1; type neutral, and of the two slags, the typical one would have been obtained *at the least expense*, since, while containing about the same amount of alumina, 10.97 per cent against 13.04, and silica 54 against 58.04, it contains only 18 per cent of lime, as against nearly 26 per cent. in the other, or 50 per cent. less. A *dolomitic* limestone would have readily furnished the 13.04 per cent. MgO without using the *excess* of *pure calcite* with only 0.57 MgO which were necessary to obtain the 25.67, CaO required to make up for the deficiency of bases.

The formula gives of course, the means of comparing these two slags but for the determination of the oxygen of the compound a knowledge of the symbols and equivalents is absolutely necessary, a glance at the two analyses not furnishing sufficient indication as to the similitude in chemical type of the two compounds. We see in this case that silica is about the same: 54 and 58%, that *the total* proportion of bases is 42.00 in one case, against 43.92% in the English slag ; but, in the typical slag, we find 18% of lime and nearly 13% of magnesia, while the English slag contains more lime, nearly 50% more, and *no* magnesia, and the apparant coinsidence of quantity of silica and *total* quantity of basic elements cannot be taken as a criterion owing to the different saturation of the bases for SiO_2. It can hardly be said that the two compounds are of *somewhat* the same nature, certainly they do not seem to be *identical* in type as they really are, nor could it be said that one had been obtained with a much greater economy than the other. No deductions can be drawn from their composition except through a study of their formulæ. Suppose that in the hypothetical slag a certain quantity of magnesia (8%) were replaced by a *proportionate quantity of lime* according to the equivalents of these two bases, which express also, in this case, their *saturation for* SiO_2 ; also that a quantity of 10% of alumina were replaced by the equivalent proportion of lime according to saturation of this latter base for SiO_2, as explained above : that is, at the rate of 1.631 lime for 1 of alumina and 1.40 lime for 1 of magnesia. It is clear that the silicate has preserved its character, its type, the *saturation of* SiO_2 *by the bases remaining the same,* but its composition is considerably changed.

We have left 4.89% of magnesia, 0.97 alumina and 18.08 lime, and then making the calculation we have :

			Hypothetical Slag.	English Slag.
SiO_2...58.04	SiO_2 58.0		SiO_2 53.01..	54.00
MgO... 4.89	MgO 4.89	or reducing	MgO 4.47..	0.57
Al_2O_3.. 0.97	or Al_2O_3 0.97	to per ct.	Al_2O_3 0.88..	13.04
8MgO = 8×1.40 = 11.20CaO	CaO 45.97		CaO 41.66..	25.67
$10Al_2O_3$ = 1.631×10 = 16,31CaO				
	109.49		100.00	...

If we compare this composition with that of the English slag we find that the two analyses are quite different, and still they represent two silicates of the same type, likely to be found in a furnace under the same conditions of temperature and iron.

If, for the sake of illustration, we replace in the original typical slag, 8% of magnesia and 18 of lime by their equivalents in *alumina for saturation of silica* we have the composition :

			Hypothetical Slag.		English Slag.	
SiO_2	58.04		SiO_2	63.16	SiO_2	54.00
MgO	4.89	or reducing	MgO	5.32	MgO	0.57
CaO	0.08	to	CaO	0.09	CaO	25.07
Al_2O_3	28.87	per ct.	Al_2O_3	31.45	Al_2O_3	13.05
	91.88			100.02		

This is a perfectly *neutral silicate,* and certainly this composition does not correspond to that of the English slag.

Neither magnesia, lime, alumina, or silica correspond, nor does the sum of the bases, 38.86, in one case, 49.28 in the other, offer any bases for a comparison. Still they are *both exactly neutral slags* and to all purposes, judging from the type, would have the same fusibility, and would accompany the same grade of iron. This is going to extremes, of course, in order to show how far the differences may be characteristic. *Hence, the apparent composition of a slag does not afford any means of comparison in certain cases and no sure one in any cases.*

It has occurred to the writer, and he has used this method extensively in practice, that, instead of calculating the formulæ, slags could be readily compared in the following manner. Admitting that slags are regular compounds, multiple silicates of the bases in RO and R_2O_3 of the same type, or even taking their empirical formula without any hypothesis or admission on this point, it is evident that, taking the saturation of the different bases for SiO_2, as given in the preceding table for the different types, if we calculate the proportional quantities of all the other earthy elements as *lime*, and then reduce the composition thus found to per. ct. we can show all slags to be composed simply of *silica and lime* in various proportions for each, as the case may be. If we compare the numbers thus obtained with the typical slags transformed in the same manner, we can ascertain at a glance not only to what type a given slag corresponds or between which types it falls, but also *how close* to a given type it comes ; the percentage of *its "basicity,"* so to speak, and this, whatever may be the number or the nature of the bases entering into the composition of the silicate, since what has been said above regarding MgO and CaO will apply, with equal truth, to all the bases of the class RO, and, as regards Al_2O_3, to all bases of the class R_2O_3.

Referring to Table III. and transforming *all* of the bases into their equivalent in lime, and reducing to per. ct.; or, calculating directly from the formulæ RO, $2SiO_2$ . . . CaO, $2SiO_2$ (Table I.), we have :

TABLE V.

COMPOSITION.	Acid.	Sesquiacid.	Neutral.	Sesqui-basic.	Bibasic.	Tri-basic.	Quadri-basic.
SiO_2%	68.19	61.65	51.72	41.66	34.88	26.30	21.13
CaO%	31.81	38.35	48.28	58.34	65.12	73.70	78.87
O of SiO_2 : O of bases	4 : 1	3 : 1	2 : 1	4 : 3	1 : 1	2 : 3	1 : 2
1CaO saturates SiO_2*	2.143	1.6071	1.0714	0.714	0.538	0.357	0.268
$1SiO_2$ " CaO	0.466	0.622	0.932	1.400	1.858	2.829	3.732

NOTE A.—It must be noted here that if the corresponding formulæ, in which SiO_3 is taken as the symbol for silica instead of SiO_2, had been transformed in the same way we should have found exactly the same results as in Table V. or, at least, figures as near to the above as the differences in the numbers expressing the old and new equivalents of the same substance would have permitted; in fact, the hundredths only are affected, as previously remarked.

For instance, the formula 2RO, SiO_2 (Bibasic) corresponds to SiO_3 to 3RO, SiO_3: the equivalent of lime was formerly taken as = 28.25, that of silica at 45.25. We should have had then for the silicate 3CaO, SiO_3:

$$\begin{array}{lr} 3CaO = & 84.75 \\ SiO_3 = & 45.25 \\ \hline & 130.00 \end{array} \qquad \text{Reducing to per. ct.:} \qquad \begin{array}{lr} \text{Lime,} & 65.19 \\ \text{Silica,} & 34.81 \\ \hline & 100.00 \end{array}$$

With the corrected equivalent, 28.00, and the new formula, 2RO, SiO_2, we have found:

$$\left.\begin{array}{lr} \text{Lime,} & 65.13 \\ \text{Silica,} & 34.87 \end{array}\right\} \text{the difference being only in hundredths.}$$

$$\overline{100.00}$$

Having a table of the equivalence in lime of the different bases as far as saturation for silica is concerned (Table III. (a)) the calculations are very simple. Using this method, let us compare the typical neutral slag with the English slag of Percy mentioned above.

The neutral slag corresponds to SiO_2 51.72%, CaO 48.28 (Table V.) the English slag to and the composition of the slag is equivalent to

$$\begin{array}{lr} SiO_2 & 54.00 \\ CaO & 51.33 \\ \hline & 105.33 \end{array} \quad \text{or} \quad \begin{array}{lr} SiO_2 & 51.27 \\ CaO & 48.73 \\ \hline & 100.00 \end{array}$$

$$\begin{array}{rl} SiO_2 = 54 \ldots\ldots\ldots\ldots\ldots\ldots\ldots & 54.00 \\ Al_2O_3 = \ .13 \times 1.631 \ldots\ldots\ldots & \left.\begin{array}{l} 21.25 \text{ CaO} \\ 0.80 \text{ ``} \\ 1.90 \text{ ``} \\ 1.71 \text{ ``} \\ 25.67 \text{ ``} \end{array}\right\} 51.33 \text{ CaO.} \\ MgO = 0.57 \times 1.40 \ldots\ldots\ldots & \\ FeO = 2.44 \times 0.78 \ldots\ldots\ldots & \\ MnO = 2.20 \times 0.78 \ldots\ldots\ldots & \\ CaO = 25.67 \ldots\ldots\ldots\ldots\ldots & \end{array}$$

Compared with the type

$$\begin{array}{lr} SiO_2 & 51.71 \\ CaO & 48.28, \end{array}$$

the differences are as close as we can come, using two places of decimals in analyses. Both slags are neutral; O of acid : O of bases :: 2 : 1. The English slag actually run from a charcoal furnace was exactly the chemical compound having the formula

$$RO, SiO_2 + R_2O_3, 3SiO_2 = (RO, R_2O_3, 4SiO_2),$$

the latter being the empirical formula. The first form supposes that the silicates in, RO and R_2O_3, are of the same type, and it is difficult to conceive how it can be otherwise in a slag A slag is a multiple silicate having a certain fusibility quite different from that of the simple silicates which enter into its composition; it must be then that silica is *so* combined with *all* the bases as to form a compound; having a definite constitution, which can be reproduced each time that the different bases may be taken in the same proportion to each other and to the silica, each base saturating silica, according to its possible saturation in *presence of the others*, in these conditions and this presence itself modifying the type. Any change in the quanitity of one of them—replacing a *given weight* of one by an *equal weight* of another—(not an equivalent weight as regards saturation for SiO_2)—must necessarily give rise to another saturation, since the ratio of the quantity of oxygen of the SiO_2, which has remained the same to the total amount of oxygen of the bases, which has been changed, is thereby modified.

There exists, indeed, in relation to these combinations of oxygen compounds a law by which one can readily reach the comparison of their analyses. The quantity of oxygen of one of the constituents, silica, is, in most minerals, a multiple or a sub-multiple of that of the others. The determination of these numbers furnishes ratios which can be reduced to their simplest expression. By so doing there is no hypothesis made as to the constitution of the substance, the results are furnished by the analysis itself, and if the quantity of oxgen of the acid element, silica, is divided proportionately to the quantity of oxygen found to exist in the bases in RO and to these in R_2O_3, and a rational formula deduced from the numbers thus calculated, it will be found invariably that the types of the silicates in RO and R_2O_3 are the same and the same as that of the compound itself, regarded as a multiple compound in RO and R_2O_3.

When in the analysis of a mineral the ratio of the quantities of oxygen can not be simplified, it is almost always to be attributed to the fact that these minerals have rarely crystalized alone, and that in these conditions one of them may have carried with it a certain quantity of other substances, as, when several salts are found together in the same solution; these foreign substances hide, so to speak, the real proportions, modifying to some extent the characteristic properties of the mineral. Nothing of the kind at any rate can happen with a slag, considering that its type as silicate is determined beforehand in the charges of a blast furnace, by furnishing to the silica of ores, stone, and ash of coal, perfectly definite basic elements, in certain proportions primarily calculated, which necessarily determine a composition which the ultimate analysis of the slag, as run from the furnace, corroborates very closely in the great majority of cases. When it does not happen, it has also to be attributed to disturbing factors, and they can be found, for instance, in this fact that calcium, combined with sulphur, which the slags often contain in very serious quantities, has been calculated as oxide of calcium or *lime*. The same can be said of magnesium and manganese. 5% of sulphur in a slag is by no means an exceptional circumstance; 8% of manganese sulphide is frequently met with in Scotch slags. In other cases alumina, owing to certain condition of the furnace, or the proportions of fluxes, will play the part of an acid, and, in these conditions, ought not to figure in the determinations of the type as saturating silica.

(*To be continued.*)

DETERMINATION OF LITHIA IN MINERAL WATERS.

BY E. WALLER, PH. D.

Practically, three methods are now available. 1. The phosphate method (Mayer's modification) (*Ann. Chem. u. Pharm.* **98**, 193). 2. The amylalcohol method (*Gooch, Am. Chem. Jour.*, **9**, 33). 3. The fluoride method (*Carnot, Bull. Soc. Chim.* [3] **1**, 280).

Rammelsberg's method (*Pogg. Ann.*, **66**, 79) somewhat similar in principle to that of Gooch, in that it depends upon the comparatively greater solubility of lithium chloride in an organic solvent, has been comparatively little used, on account of the difficulty and expense involved in obtaining the pure anhydrous alcohol and ether necessary for the process. Moreover the experiments of J. L. Smith (*Am. Jour. Sci.* [2] **16**, 56), rearranged in convenient form for reference by Gooch (*loc. cit.*) do not indicate that it is