CHAPTER VIII.

MATERIALS AND PRODUCTS OF METALLURGICAL PROCESSES.

Ores.—This term is applied by the metallurgist only to those minerals from which, on a large scale, metals may be obtained with profit. The ores must be supplied to the works in a suitable condition for smelting, the preliminary washing and dressing operations being carried out at the mine. *Gangue*, vein-stuff, or matrix is the extraneous earthy matter associated with the ore.

Ores contain the metals—(1) in the native or metallic state (examples—gold, silver, copper, mercury); (2) in combination with oxygen as oxides (for example, hæmatite, Fe_2O_3); (3) as oxides in combination with water (limonite, $Fe_2H_2O_4$); (4) in combination with halogens (horn silver, $AgCl$); (5) in combination with sulphur, arsenic, and antimony (galena, PbS); (6) in combination with acids as salts (anglesite, $PbSO_4$); ores also occur in nature in a state of mixture; (7) as various combinations of the same metal (for example, azurite, $2CuCO_3 + Cu(HO)_2$); (8) as various combinations of more than one metal in one mineral species (for example, pyrargyrite, $3Ag_2S,Sb_2S_3$); lastly, (9) as several mineral species occurring together in the ore deposit, galena and blende, spathic iron ore and iron pyrites.

The value of an ore depends upon the nature of the metal it contains and the difficulty with which its extraction is attended. Thus, iron ores containing less than 25 per cent. of metal are rarely smelted. Ores of iron are not considered rich unless they contain 50 per cent of metal. Copper ores are rich when they contain 15 per cent. of metal, whilst ores yielding a few ounces of gold per ton are extremely valuable. These relations, however, continually change as new methods of concentration or treatment of poor ores are adopted.

Fluxes.—In order to separate the extraneous matter usually contained in a furnace charge of ore and reducing agent, certain materials must be added to form slag. These materials are known as fluxes.

In the smelting processes, earthy, alkaline, and metallic substances are used as fluxes. The alkaline fluxes are expensive, and are rarely used except in refining processes. The following are the principal earthy fluxes in use:—

1. Lime, which acts as a powerful base for removing silica. Lime is used in a pure state or as carbonate. As a rule, limestone is used, especially if the furnace is large. Limestone is largely used in iron smelting, as most iron ores contain an excess of silica. Dolomite, the carbonate of lime and magnesia, is specially useful, but more expensive.

2. Fluorspar (calcium fluoride), which is a useful flux for ores containing silica, barytes, or gypsum. With the two latter it easily fuses. It is also used in the open-hearth furnace to increase the fluidity of the slags and for the removal of sulphur, but on account of its expense its employment is limited. The greater portion of the fluorspar is found unchanged in the slag; it facilitates the fusion, and increases the fluidity of the mass.

3. Barytes, which acts as a powerful base. It is a good sulphurising agent; for example, in the concentration of nickel speise, the copper present with the speise being removed and a regulus formed.

4. Alumina-bearing rocks, such as clay-slate, are used in smelting ores very rich in lime. As a rule, however, the charge is so mixed that argillaceous and calcareous ores are present in suitable proportions.

5. Siliceous materials, such as quartz, natural silicates, siliceous slags, are used when the ores contain an excess of basic materials that have to be removed.

6. Oxides and carbonates of iron, basic iron slags, etc., are used in the smelting of siliceous ores, especially of lead and copper, and also in the recovery of valuable metals from slags, residues, and waste.

Metallurgical Agents.—The metallurgical agents chiefly used are—1. Metals, either for decomposing the combinations of other metals, or as a means of concentration. Thus iron is used for decomposing galena, zinc for desilverising argentiferous lead, and mercury for concentrating gold.

2. Metallic oxides are used for purifying the raw metal in refining processes. Thus iron ore or hammer-scale is used for refining iron, and as a flux in lead and copper smelting.

3. Slags serve to increase the fluidity of the furnace charge, or mixtures of slags may be used for recovering the metals they contain, and lastly for preventing "scaffolding" or choking of the furnace when pulverised ores are smelted. Their chemical action varies with their composition; basic slags are able to take up a large proportion of silica, while acid slags readily absorb bases. Alkaline slags are rarely used except in crucible processes, as in assaying.

4. Iron pyrites (FeS_2) and magnetic pyrites (Fe_7S_8) exert a reducing action on oxides by giving up sulphur and forming sulphurous anhydride. Certain sulphides, such as zinc sulphides, infusible alone, may be rendered fusible by the addition of iron pyrites.

In the roasting of ores in furnaces or in piles the following chemicals are used :—(1) Salt, for the formation of silver chloride in the treatment of silver ores ; (2) Lime, for the absorption or separation of the acids formed on roasting copper regulus, etc. ; (3) Ferrous sulphate, in the treatment of silver ores containing a little iron pyrites.

Selection of Fluxes.—In the choice of fluxes, when the gangue is siliceous, at least two bases must be added in order to form a fusible silicate. When the gangue is argillaceous, a single base is sufficient to form a double silicate. When the gangue is basic, that is, containing lime, magnesia, alumina, or iron, a siliceous flux must be added. Quartz alone is sufficient if the gangue already contains two or more bases, but if there is but one base, clay or some other silicate must be added with the quartz. Siliceous slags may be advantageously used for the purpose.
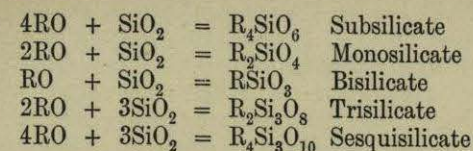
Slags.—The silicates formed in metallurgical processes by the combination of silica with the earths and metallic oxides are termed *slags*. As a rule, slags are smelters' refuse. In the refining of metals, however, slags are frequently formed by the oxidation of the metallic impurities. Such slags consist largely of metallic oxides, and are smelted again in order to recover the large proportion of metals they contain. These slags may be distinguished as cinder or scoria.

The bases that occur in silicate slags, mostly combined with the silica, are—lime, alumina, magnesia, rarely ferric and manganic oxides, ferrous oxide, manganous oxide, zinc oxide, more rarely baryta, and alkalies in slags of all blast furnaces using charcoal as fuel, and, in addition to these, small amounts of the metals that are being smelted are invariably present, partly in chemical combination with the silica, and partly in other combinations mechanically mixed with the slag.
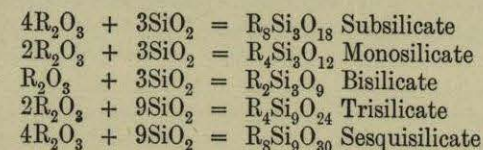
Some oxides and earths, such as zinc oxide and alumina, not only interfere with the fluidity of the slag, but also cause a scum to form which is difficult to separate from the slag. In many slags, calcium fluoride is found. The calcium fluoride melts without decomposition, and is merely in a state of mechanical mixture with the slag. This is also the case with the calcium sulphide frequently met with in blast-furnace slags.

Silica consists of one atom of silicon and two atoms of oxygen, so that the various silicates have the compositions given below. $2RO + SiO_2$ is the monosilicate or neutral silicate of the metallurgist. It contains in acid and base equal amounts of oxygen, whilst the neutral silicate of the chemist, which has the formula

$RO + SiO_2$, is termed a bisilicate by the metallurgist, because the acid contains twice as much oxygen as the base. The series of formulæ for silicates is—

$$4RO + SiO_2 = R_4SiO_6 \quad \text{Subsilicate}$$
$$2RO + SiO_2 = R_2SiO_4 \quad \text{Monosilicate}$$
$$RO + SiO_2 = RSiO_3 \quad \text{Bisilicate}$$
$$2RO + 3SiO_2 = R_2Si_3O_8 \quad \text{Trisilicate}$$
$$4RO + 3SiO_2 = R_4Si_3O_{10} \quad \text{Sesquisilicate}$$

For bases having the composition R_2O_3 the formulæ are—

$$4R_2O_3 + 3SiO_2 = R_8Si_3O_{18} \quad \text{Subsilicate}$$
$$2R_2O_3 + 3SiO_2 = R_4Si_3O_{12} \quad \text{Monosilicate}$$
$$R_2O_3 + 3SiO_2 = R_2Si_3O_9 \quad \text{Bisilicate}$$
$$2R_2O_3 + 9SiO_2 = R_4Si_9O_{24} \quad \text{Trisilicate}$$
$$4R_2O_3 + 9SiO_2 = R_8Si_9O_{30} \quad \text{Sesquisilicate}$$

The quantities of oxygen in the bases bear the following proportions to those in the acids in the various silicates :—

	O in base : O in acid.
Subsilicate	2 : 1
Monosilicate	1 : 1
Bisilicate	1 : 2
Trisilicate	1 : 3
Sesquisilicate	2 : 3

Every sesquisilicate may be resolved into a monosilicate and a bisilicate : thus $R_4Si_3O_{10}$ is equal to $R_2SiO_4 + 2$ ($RSiO_3$), and $R_8Si_9O_{30}$ is equal to $R_4Si_3O_{12} + 2(R_2Si_3O_9)$. If a silicate contains but one base it is termed a monobasic or simple silicate, but if two or more bases are present it is termed a double silicate or a multibasic silicate, and in the formula the silicates of the various bases are united by a plus sign.

A classification of the silicates as ortho- and meta-silicates, based upon their analogies to phosphates, was suggested by Odling,[1] but it has not come into use amongst metallurgists.

The fusibility of slags is dependent on the amounts of silica and bases they contain. As a rule, the subsilicates are very fusible, forming a limpid liquid ; they consolidate very rapidly, and split up in so doing. They have usually a dark colour and, on account of the large proportion of bases they contain, a high specific gravity. The monosilicates are less fusible, and do not form so limpid a liquid. The bisilicates are less fusible still ; they form a viscous mass, which may be drawn out into threads. They are usually glassy and consolidate slowly. The trisilicates also flow very slowly, consolidate slowly, and require a very high temperature for their formation.

The most fusible silicates are those of the alkalies, next those

[1] *Phil. Mag.*, vol. xviii. (1859), p. 368.

of lead, iron, manganese, and copper, and last the earthy silicates. The most desirable silicate depends upon the nature of the operation. Blast-furnace slags from iron smelting are mostly monosilicates or bisilicates. Those in lead smelting are generally monosilicates,[1] although a sesquisilicate is, under certain conditions, desirable.

Economic Application of Slags.—The slags obtained in smelting metals other than iron are largely used as fluxes in various metallurgical processes for taking up either the silica or the bases, or, when they are ferruginous, for precipitating purposes. Occasionally the slags are moulded into bricks, and used for walls or other light constructions.

The slags obtained in iron smelting are used, if not too glassy, for macadamising roads. For the ballast of railway lines glassy slags may advantageously be used, as the mass is very permeable and keeps the sleepers dry. In the form of large blocks, they may be used for road-making. They may be moulded into bricks, the best results being obtained when the moulded bricks are kept at a white heat for several hours in a tightly closed space, whereby they are devitrified, and become considerably harder if they are allowed to cool slowly under a cover of coal dust and ashes. Good bricks may be made of granulated slag mixed with lime, the proportions being usually 10 parts of slag sand to 1 part of lime. Blast-furnace slag, if not too acid, may be burnt in a state of powder with lime, and gives an hydraulic cement almost equal to Portland cement.[2]

The manufacture of slag cement has of recent years acquired so considerable a development that it may safely be said that an advantageous method of utilising blast-furnace slag has at length been found. The following are analyses of slags actually used for this purpose :—

	Middles-brough.	Bilbao, Spain.	Saulines, France.	Choindez, Switzer-land.	Harz-burg, Germany.	Belgium.
Lime . . .	32·75	47·30	47·20	45·11	48·59	44·75
Silica . . .	30·00	32·90	31·65	26·88	35·72	32·51
Alumina . . .	28·00	13·25	17·00	24·12	16·40	13·91
Ferrous oxide . .	0·75	0·46	0·65	0·44	0·43	0·48
Magnesia . .	5·25	1·37	1·36	1·09	1·28	2·20
Calcium sulphide .	1·90	3·42	...	1·86	2·16	4·90
Manganese oxide	0·60	1·13	0·85	0·50	traces	0·60
Residue . .	0·75	0·17	1·29	...	0·42	0·65
Totals .	100·00	100·00	100·00	100·00	100·00	100·00

[1] Collins, *Metallurgy of Lead*, p. 113.
[2] *Inst. Mech. Eng.*, 1892, p. 70 ; *Stahl und Eisen*, xxiii. pp. 361–375.

The slag is run into water so as to render it easy to obtain slag sand. This is ground under edge-runners, and the pasty mass is spread on drying plates. The dried slag is then ground under millstones to a fine powder and sifted to exclude coarse particles. Freshly burnt lime is slaked, and then carefully screened, and 25 per cent. of this slaked lime is thoroughly mixed with 75 per cent. of slag sand.

The specific gravity of this cement is very low as compared with Portland cement, whilst the time occupied in setting is comparatively long. For purposes of storage it compares well with Portland cement. By exposure to the air it absorbs carbonic anhydride more rapidly than does Portland cement, but it does not deteriorate greatly by long exposure. Owing to the closeness of the particles, this cement appears to be well adapted for works under water, such as docks or breakwaters.

Blast-furnace slag is also largely used for the production of slag wool or silicate cotton, which is obtained by causing steam to impinge on to a jet of molten slag in such a way that the steam jet encounters only a half of the slag jet. Slag wool is extremely light and fireproof. It is a good non-conductor of heat and of sound, and it is so porous that it will absorb large quantities of water. It is used for covering steam and hot-air pipes. In Silesia and other localities, where ironworks and collieries are in close proximity, blast-furnace slag is largely used for filling the excavations from which the coal has been removed. Finely pulverised blast-furnace slag has been found in Sweden to be an excellent manure for moor land which is deficient in lime, as well as for clay and sandy soils.

The slag obtained in the basic Bessemer process, on account of its high percentage of phosphorus, forms a valuable manure. Many thousands of tons of slag are annually employed for this purpose, it having been found that the phosphorus it contains is in a form that is very readily assimilated by the plants. The utilisation of basic Bessemer slag is referred to in a subsequent chapter.[1]

Calculation of Furnace Charges.—In order to obtain the greatest possible yield of metal with the least consumption of fuel, care must be taken to have a proper mixture of ore and flux. Ores reducible with difficulty should be mixed with fluxes that render the charge pasty, so that the slag-forming constituents do not melt before the metals are reduced from their combinations. When raw coal or coke is used as fuel, the quantity and composition of the ash must be taken into consideration, as this always contains silica. With charcoal as fuel this may be neglected, as the percentage of ash is always low, and the ash itself, which is strongly alkaline, is a useful flux.

As an example of the calculations necessary, a charge of iron ore

[1] Methods of utilising slag are fully described by G. Redgrave, *Journ. Soc. Arts*, vol. xxxviii. (1890), p. 221.

may be selected which is to be smelted with coke to grey pig-iron, and for which the necessary amount of lime as flux is required to be determined. For the example now to be given the author was indebted to Prof. C. A. M. Balling, Director of the School of Mines at Przibram in Bohemia, who has permitted him to borrow it from his valuable treatise on metallurgical chemistry.[1]

Let it be assumed that there are to be smelted four varieties of ore having the following compositions :—

	Fe.	Al₂O₃.	CaO.	MgO.	SiO₂.	S.
A.	54	7	2	...	12	...
B.	47	8	1	1	15	...
C.	38	10	2	1	24	1
D.	40	9	2	1	20	...

In order to simplify the calculations whole numbers are taken, and the percentages of water and carbonic anhydride are disregarded. The ore to be used as flux (I.) and the 10 per cent. of ash (II.) in the coke have the following percentage compositions :—

	Fe.	Al₂O₃.	CaO.	MgO.	SiO₂.	S.
I.	25	4	25	4	6	...
II.	12	35	1	1	44	0·5

For the production of 100 parts by weight of iron, 190 parts by weight of coke are necessary.

In view of the large proportion of silica in the ores C and D, high percentages of these ores are inadmissible in the charge. The ore A, on the other hand, is the best, and must therefore form the greater portion of the charge, which is to be mixed so as to contain on an average 45 per cent. of iron. Taking into account the important constituents of the ores, the following weights would be selected for the charge :—

Ore B.	Ore C.	Ore D.	Flux.	Total.
25	10	15	15	65

It must now be calculated how much iron and slag-giving constituents this mixture contains in order to determine the quantity of ore A that must be added to give an average of 45 per cent. of iron. In this way, by proportion, the following amounts of the various constituents are calculated to be present :—

	Fe.	Al₂O₃.	CaO.	MgO.	SiO₂.	S.
25 parts of B contain .	11·75	2·00	0·25	0·25	3·75	...
10 ,, C ,, .	3·80	1·00	0·20	0·10	2·40	0·10
15 ,, D ,, .	6·00	1·35	0·30	0·15	3·00	...
15 ,, flux ,, .	3·75	0·60	3·75	0·60	0·90	...
65 Totals .	25·30	4·95	4·50	1·10	10·05	0·10

[1] *Compendium der metallurgischen Chemie*, Bonn, 1882.

Regarding this ore-mixture as a single ore the percentage composition will be as follows :—

Fe.	Al₂O₃.	CaO.	MgO.	SiO₂.	S.
38·92	7·61	6·92	1·69	15·46	0·15

With this ore, or rather mixture containing 38·92 per cent. of iron, it is required to mix the ore A so as to bring the charge to 45 per cent. of iron. If the ore mixture is represented by x we have the following equation :—

$$x + A = 100$$
$$38·92\,x + 54\,A = 100 \times 45$$

On solving this equation, A is found to be 40·5, and $x = 100 - A = 59·5$ parts by weight. The equation thus requires that 40·5 parts of the ore A should be mixed with 59·5 parts of the ore-mixture chosen, and consequently the 65 parts must be reduced by proportion to 59·5, giving the following percentages as the definite composition of the charge :—

Ore A.	Ore B.	Ore C.	Ore D.	Flux.	Total.
40	23	10	13	14	100

In this charge the percentages of the various constituents are found by proportion to be as follows :—

	Fe.	Al₂O₃.	CaO.	MgO.	SiO₂.	S.
In 40 parts of A . . .	21·60	2·80	0·80	...	4·80	...
23 ,, B . . .	10·80	1·84	0·23	0·23	3·45	...
10 ,, C . . .	3·80	1·00	0·20	0·10	2·40	0·10
13 ,, D . . .	5·20	1·17	0·26	0·13	2·60	...
14 ,, flux . . .	3·50	0·56	3·50	0·56	0·84	...
100 Totals .	44·90	7·37	4·99	1·02	14·09	0·10

For the production of 100 parts of iron,

$$100 : 45 = x : 100.$$

$x = 222·2$ parts of this charge are required, and in this are contained the following weights of iron and slag-giving constituents :—

Fe.	Al₂O₃.	CaO.	MgO.	SiO₂.	S.
99·77	16·40	11·09	2·26	31·30	0·22

For its production, 190 parts of coke are required, the ash of which, according to the analysis, contains—

Fe.	Al₂O₃.	CaO.	MgO.	SiO₂.	S.
2·28	6·65	0·19	0·19	8·36	0·95

It is therefore necessary to remove as slag: Al_2O_3 23.05; CaO 11.28; MgO 2.45; SiO_2 39.66; S 1.17.

For the formula $Al_4Si_3O_{12} + Ca_2SiO_4 + Mg_2SiO_4$, representing a monosilicate, the amount of silica slagged by the bases may be found by proportion with the aid of the atomic weights, thus:—

$$2Al_2O_3 : 3SiO_2 = 205.6 : 180 = 23.05 : x \; ; x = 20.18$$
$$2CaO \; : SiO_2 \; = 112 \quad : \; 60 = 11.28 : y \; ; y = \;\; 6.04$$
$$2MgO \; : SiO_2 \; = \;\; 80 \quad : \; 60 = \;\; 2.45 : z \; ; z = \;\; 1.83$$

—giving a total $(x + y + z)$ of 28.05 parts by weight of silica, so that $39.66 - 28.05 = 11.61$ parts of silica remain to be converted into slag. According to the same proportion—

$$SiO_2 : 2CaO = 60 : 112 = 11.61 : a.$$

From which a is found to be 21.7 parts by weight of lime base, which, as calcium carbonate contains but 56 per cent. of CaO, is contained in 38.7 parts of calcium carbonate.

Similarly, for removal as calcium sulphide, the sulphate requires, according to the proportion $S : CaO = 32 : 56 = 1.17 : \beta$, $\beta = 2.05$ parts of lime, which amount is contained in 3.65 parts of calcium carbonate. Consequently, altogether there is required $38.7 + 3.65 = 42.35$ parts of calcium carbonate. But as this is added in the form of impure limestone containing only some 95 per cent. of calcium carbonate, the quantity to be added will be 44.58 parts. As this amount, however, is required for 222 parts of charge, 100 parts will require 20.1 parts of limestone as flux. In this example, the small quantity of limestone required is explained by the fact that 14 parts of fluxing ore, containing 25 per cent. of lime, have already been added.

The following is an example of South Wales practice, prepared for the author by Mr H. Raleigh. Four ores, all of which are siliceous, have been taken, namely:—

	Iron.	Alumina.	Lime.	Magnesia.	Silica.	Sulphur.
A.	57	3	...	...	8	...
B.	49	6	1	1	14	...
C.	48	2	1	2	18	...
D.	47	3	2	...	12	...

And of these A is a "rich" red hematite, B is "soft" red hematite, C a "hard" red hematite, D is "rubio" (S) ore.

For the production of 100 parts by weight of pig-iron, 100 parts by weight of coke are found to be necessary; this coke contains 10 per cent. of ash, and its composition is as follows:—

	Iron.	Alumina.	Lime.	Magnesia.	Silica.	Sulphur.	Carbon and Moisture.
I.	0.2	4.4	0.2	0.1	4.8	1.0	90

A more or less arbitrary mixture of the ore on the principles already explained will be—

Ore A	.	. 20 parts		Ore B	.	. 20 parts
Ore C	.	. 40 parts		Ore D	.	. 20 parts

	Iron.	Alumina.	Lime.	Magnesia.	Silica.
20 parts of A contain	11.4	0.6	...	...	1.6
20 ,, B ,,	9.8	1.2	0.2	0.2	2.8
40 ,, C ,,	19.2	0.8	0.4	0.8	7.2
20 ,, D ,,	9.4	0.6	0.4	...	2.4
Totals	49.8	3.2	1.0	1.0	14.0

—and as the total number of weights of ore taken happens to be 100, the total contents are percentages.

The pig-iron produced has a percentage composition—

Iron.	Graphite.	Combined Carbon.	Silicon.	Sulphur.	Phosphorus.
93	3.9	0.22	2.8	0.03	0.05

For the production of 100 parts of pig-iron containing 93 per cent. of iron, 186.7 parts of ore are necessary:—

$$49.8 : 100 : : 93 : x \qquad x = 186.7.$$

In 186.7 parts of ore the following weights of iron and slag-giving constituents are contained:—

Iron.	Alumina.	Lime.	Magnesia.	Silica.
93	6.0	1.87	1.87	26.13

For its production, 100 parts of coke are required, containing—

Iron.	Alumina.	Lime.	Magnesia.	Silica.	Sulphur.
0.2	4.4	0.2	0.1	4.8	1.0

The pig-iron contains 2.8 parts of silicon, reduced from 6 parts of silica, so that it is necessary to remove as slag $30.93 - 6 = 24.93$ silica, 10.4 alumina, 2.07 lime, 1.97 magnesia, and 1.0 sulphur. The slag invariably contains a little iron which may be brought as low as 0.2 per cent. $= 0.26$ ferrous oxide, and, putting p, x, y, z as the amount of silica required to flux off the alumina, lime, magnesia, and iron respectively,—

$$2\,Al_2O_3 : 3\,SiO_2 = 205.6 : 180 = 10.4 : p \; ; p = 9.1$$
$$2\,CaO \; : SiO_2 = 112.0 : 60 = 2.07 : x \; ; x = 1.1$$
$$2\,MgO \; : SiO_2 = \;\; 80.0 : 60 = 1.97 : y \; ; y = 1.5$$
$$2\,FeO \; : SiO_2 = 144.0 : 60 = 0.26 : z \; ; z = 0.1$$

$(p + x + y + z) = 11.8$ parts by weight of silica, so $24.93 - 11.8 = 13.13$ parts of silica, besides 1.0 sulphur, remain to be converted into slag by the addition of limestone, according to the following ratios—

$$SiO_2 : 2CaO = 60 : 112 = 13.13 : a \; ; a = 24.5 \text{ parts of lime}$$
$$S : CaO = 32 : 56 = 1.0 : b \; ; b = 1.75 \text{ parts of lime}$$

—and putting a, b, as the amounts of lime required to satisfy the silica and sulphur respectively, the total lime required will be 26·25 parts, and these are contained in 46·87 parts of calcium carbonate. The limestone used contains 97 parts of calcium carbonate, 1·0 part alumina, and 1·5 part silica. The 1 part of alumina slags off 0·88 part of the silica, leaving 0·62 part silica to consume 2·07 parts of calcium carbonate. The available calcium carbonate then is $97 - 2·07 = 94·93$ per cent. of the limestone added,

$$\text{and } \frac{100}{94·93} \times 46·87 = 49·37 \text{ parts of limestone.}$$

The slag obtained in the production of 100 parts of pig-iron would be 68·2 parts, made up as follows:—

	Parts.			Per cent.
Silica	25·67		Silica	37·6
Alumina	10·90		Alumina	16·0
Magnesia	1·97		Magnesia	2·9
Ferrous oxide	0·26	=	Ferrous oxide	0·4
Lime	27·15		Lime	39·8
Calcium sulph.	2·25 (1 pt. sulphur)		Calcium sulphide	3·3
	68·20			100·0

Composition of slag obtained by analysis:—

	Per cent.			Per cent.
Silica	37·2		Silica	37·2
Alumina	15·4		Alumina	15·4
Magnesia	2·3		Ferrous oxide	0·8
Ferrous oxide	0·8	or expressed thus	Lime	41·0
Lime	43·3		Magnesia	2·3
Sulphur	1·32		Calcium sulph.	2·97
	100·32			99·67

All these tedious calculations may be reduced to a few multiplications and additions by employing the accompanying table (p. 305) that has been computed by Prof. Balling.

In order to show the simplicity of the use of this table, the same problem may be solved with its aid. For ascertaining the amount of silica converted into slag by the bases in the charge Table B is used. In the section for monosilicates, the corresponding figures are found for the bases present, and these figures multiplied together give the following products:—

Al_2O_3	.	.	.	.	$23·05 \times 0·873$	=	20·12
CaO	.	.	.	.	$11·28 \times 0·535$	=	6·04
MgO	.	.	.	.	$2·45 \times 0·750$	=	1·84
				Total	.	=	28·00

Thus 28·00 parts of silica (28·05 in the previous calculation) are converted into slag; and of the total amount, 39·66 parts of silica present, there remain $39·66 - 28·00 = 11·66$ parts to be converted into slag by the addition of lime. On referring to Table A, it will be seen that the corresponding amount of lime is 1·86, the product being $11·66 \times 1·86 = 21·69$. Lastly, for the formation of calcium sulphide, 1 part of sulphur requires $\frac{56}{32} = 1·75$ of lime, and there is 1·17 part of sulphur to be passed into the slag. This requires $1·17 \times 1·75 = 2·047$ parts of lime. Thus, altogether $21·69 + 2·047 = 23·737$ parts of lime are required. One part of lime is contained in $\frac{100}{56} = 1·785$ of calcium carbonate; the required addition of limestone as flux is therefore $23·737 \times 1·785 = 42·37$ parts (as compared with 42·35 in the previous solution).

TABLE A. For ascertaining the necessary amounts of Bases to convert given amounts of Silica into slag.		TABLE B. For ascertaining the necessary amounts of Silica to convert given amounts of Bases into slag.	
One part by Weight of Silica requires—	Parts by Weight of Bases.	One part by Weight of Base requires—	Parts by Weight of Silica.
For Monosilicates—		For Monosilicates—	
Lime . . .	1·86	Lime . . .	0·535
Magnesia . .	1·33	Magnesia . .	0·750
Alumina . .	1·14	Alumina . .	0·873
Ferrous oxide .	2·40	Ferrous oxide .	0·416
Manganous oxide .	2·36	Manganous oxide .	0·422
For Bisilicates—		For Bisilicates—	
Lime . . .	0·93	Lime . . .	1·070
Magnesia . .	0·66	Magnesia . .	1·500
Alumina . .	0·57	Alumina . .	1·747
Ferrous oxide .	1·20	Ferrous oxide .	0·833
Manganous oxide .	1·18	Manganous oxide .	0·845
For Sesquisilicates—		For Sesquisilicates—	
Lime . . .	1·24	Lime . . .	0·803
Magnesia . .	0·88	Magnesia . .	1·125
Alumina . .	0·76	Alumina . .	1·310
Ferrous oxide .	1·60	Ferrous oxide .	0·625
Manganous oxide .	1·57	Manganous oxide .	0·633

In order to entirely obviate the necessity for any calculation whatever, Prof. Balling has devised a method of solving the problem graphically. The method is based on the similarity of triangles. From any point a (fig. 146) two lines are drawn at right angles, and these form two sides of a right-angled triangle. The co-ordinate lines are divided into equal parts. If as many parts of one line are taken as there are equivalents of acid in the

slag to be formed, and, similarly, as many parts of the other line as there are equivalents of base, and if the end points of the two sides of the triangle are joined by the hypotenuse, then it is merely necessary to draw from any given point in one side a line parallel to the hypotenuse in order to find on the two sides the equivalent amounts of base and acid in the given silicate.

Fig. 146 is a reduced sketch of the triangles for the monosilicates of the earths that are usually required. For practical purposes the best unit of length to adopt is the centimetre, so that tenths (millimetres) and half-tenths may be read. As, however,
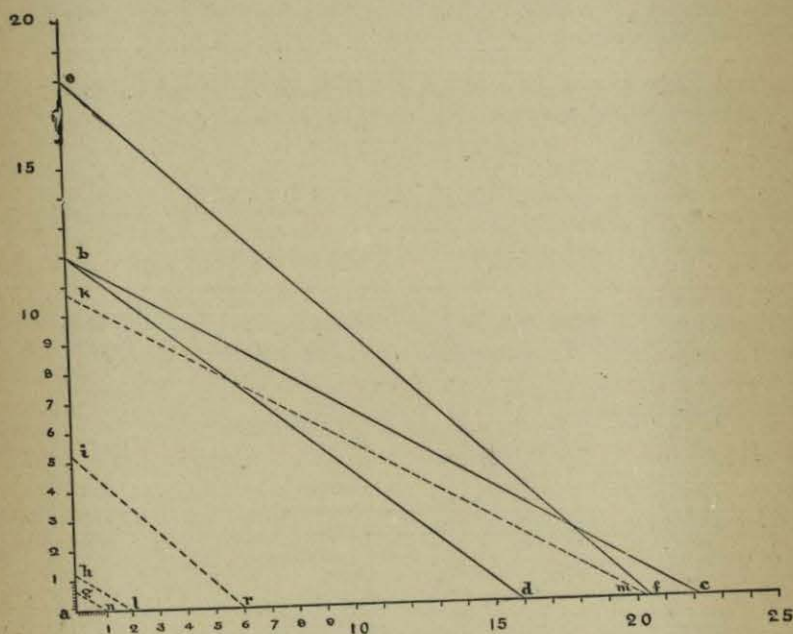
FIG. 146.

the triangles on this scale would be too large, and as only lower figures are used, the triangles may be drawn on a reduced scale, for which the following scheme will be found to answer under all conditions :—

The lime monosilicate requires for base $2CaO = 2 \times 56 = 112$ units of length, and for perpendicular $1SiO_2 = 60$. The magnesia monosilicate requires for base $2MgO = 2 \times 40 = 80$, and for perpendicular $1SiO_2 = 60$. Lastly, the alumina monosilicate requires for base $2Al_2O_3 = 2 \times 102\cdot8 = 205\cdot6$, and for perpendicular $3SiO_2 = 3 \times 60 = 180$. These lengths are reduced in the triangles for monosilicates of lime and magnesia by one-fifth, and in the triangle for the monosilicate of alumina by one-tenth. Thus

the triangle $a\,b\,c$ is that of the lime silicate, $a\,b$ containing $\frac{60}{5} = 12$ units of length for silica, and $a\,c\ \frac{112}{5} = 22\cdot4$ units for lime. Similarly, in the triangle $a\,b\,d$ representing the magnesia silicate, $a\,b$ contains 12 units for silica, and $a\,d\ \frac{80}{5} = 16$ units for magnesia. Lastly, in the triangle $a\,e\,f$, representing the alumina silicate, $a\,e$ contains $\frac{180}{10} = 18$ units for silica, and $a\,f\ \frac{205\cdot6}{10} = 20\cdot56$ units for alumina.

As an illustration of the application of the graphic method, let it be assumed that in a coke blast furnace a charge has to be smelted in which the constituents to be converted into slag average

CaO.	MgO.	SiO₂.	Al₂O₃.
2	1	6	18

The amount of lime to be added is determined in the following manner :—In order to determine the amount of silica converted into slag by the bases already present, from the point l, representing the units of base (in this case 2 parts), a line is drawn parallel to the hypotenuse of $b\,c$ of the lime triangle. This cuts the perpendicular, representing the silica units, at the point h, and the length $a\,h$ represents the units of weight of silica which slag off the lime already present in the charge. Similarly, the line $g\,n$ drawn parallel to $b\,d$ shows the amount of silica required by 1 part of magnesia, and the line $i\,r$, drawn parallel to $e\,f$, that required by 6 parts of alumina. On measuring these lengths with the dividers on a decimal scale they are found to be: $a\,h = 1\cdot07$; $a\,g = 0\cdot75$; $a\,i = 5\cdot23$; giving a total of $7\cdot05$ units as the amount of silica slagged by the bases present in the charge, and there consequently remains $18 - 7\cdot05 = 10\cdot95$ parts of silica to be converted into slag by the addition of lime. If, then, from the point $k = 10\cdot95$ parts of silica, a line is drawn parallel to the hypotenuse of the lime silicate, it cuts the base line at the point m, which represents $20\cdot15$ parts of lime, an amount contained in $20\cdot36 \times 1\cdot785 = 36\cdot34$ parts of calcium carbonate.

This method is extremely rapid, and, with careful graduation, gives results of great accuracy. In order to apply the method to bisilicates, the amount of silica must be doubled, or those of the bases must be halved.

A purely mechanical method possesses certain advantages, and Prof. Balling's table has been simplified by Mr H. C. Jenkins, who devised a special slide rule for the use of the students of the Royal School of Mines, by the aid of which the calculations can be made with great facility (fig. 147). It consists of two equal scales at right angles, one of which (a) is fixed to

a small board, whilst the other (b) is fixed at right angles to a upon a block (c), which is capable of sliding motion in a groove.[1]

The point A, given by the intersection of the zeros of the two scales, is marked upon the board, and from it a line A B parallel to the groove is drawn. With A as centre, lines A C, A D, A E are also drawn, making with A B angles whose tangents are equal to the ratios between the weight of silica to weight of base in the respective silicates which it is desirable to produce in order to
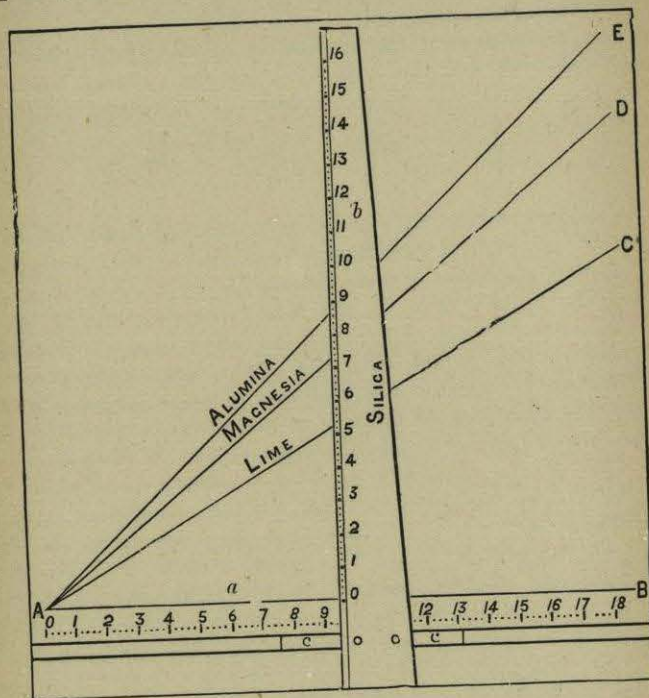
FIG. 147.

form the typical fusible slags ordinarily met with in blast-furnace practice. The lines A C, A D, A E are marked with the names of the bases for which they have been calculated. Thus A C makes an angle of 28° 10′ with A B, this angle having a tangent whose value is 0·5357, which is the ratio of the molecular weight of silica to twice the molecular weight of lime, and corresponds to calcium silicate; this line therefore is marked "Lime."

Similarly the line A D makes an angle of 36° 52′ with A B, the value of whose tangents is 0·75, or the ratio of the molecular weight

[1] *Journ. Iron and Steel Inst.*, pt. i., 1891, p. 151.

of SiO_2 to the molecular weight of $2MgO$; hence it is marked "Magnesia."

Also the line A E is at an angle of 41° 25′, and this, having a tangent corresponding to the ratio of the molecular weight of $3SiO_2$ to that of $2Al_2O_3$, makes the line correspond to the values of the component parts of silica and of alumina in aluminium silicate, and so it is marked "Alumina."

With such a scale it is a very simple matter to at once read off either the excess of silica in any ore, or the amount required to properly flux off the earthy bases present.

As an example, take an ore containing—

					Silica required.
FeO	.	.	.	50	...
MgO	.	.	.	3	2·25
CaO	.	.	.	5	2·68
Al_2O_3	.	.	.	3	2·65
SiO_2	.	.	.	3	...
CO_2	.	.	.	36	...

Then, setting the movable scale b against 3 on the fixed scale a, and looking along b until the line marked "Magnesia" cuts it, the value 2·25 is found as being the amount of silica required to satisfy the magnesia. In like manner, the amount (2·68) of silica required for the lime is found, and the amount (2·65) for the alumina respectively; adding all these together, the total of 7·58 parts of silica required for every hundred of the ore is obtained. But there are already three parts present, so every hundred parts of the ore require 7·58 − 3 = 4·58 parts of silica to flux it. The gangue of the ore is basic to that extent, and the ore itself can be ticketed in the works as—

C. 607.

Fe. 38·8 per cent.

Basic gangue, needing 4·58 per cent. SiO_2.

Another parcel of ore might be found to be deficient in bases, and to require, say, bases to neutralise four parts of silica to every hundred parts of ore. If it contained 35 per cent. iron, its label might be—

E. 1000.

Fe. 35 per cent.

Acid gangue, yielding 4 per cent. SiO_2.

If there is any considerable proportion of ash from the coke, as is often the case, it can be entered as acid or basic, just as in the case of an ore, thus:—

Acid, yielding 2 per cent. silica,

or

Basic, requiring 1 per cent. silica,

and the amount of silica for each part of iron present added (or deducted, as the case may be) to each ore in proportion to the number of parts of iron contained in it.

Any small quantity of sulphur can be considered to be one-half its own amount of silica, or a special vertical scale employed, the length of its divisions being as $28 : 60$.

If, as is usual, several kinds of ores are to be smelted together, they should, for convenience, be subjected to a preliminary mixing, so as to reduce them to three only. Of these, one should have *less* and another *more* iron than is required in the final charge, and one should be acid and another basic after the correction for the ash from the coke has been made. Or one of the three may be a limestone or a siliceous flux; it need not necessarily contain iron.

Then let it be required to have n parts of iron per hundred of the charge, and let a_1, a_2, a_3 be percentages of iron in the ores, and b_1, b_2, b_3 percentages of deficiency (or excess) of silica in the same, and x, y, z the number of parts required of the component ores per hundred of the charge.

Thus—

$$
\begin{array}{cc}
\text{FeO.} & \text{Silica.} \\
x[a_1 & + & b_1] \\
y[a_2 & - & b_2] \\
z[a_3 & \pm & b_3]
\end{array}
$$

Then—

(1) $x + y + z = 100$

(2) $\dfrac{xa_1 + ya_2 + za_3}{100} = n$

(3) $xb_1 - yb_2 \pm zb_3 = 0$

Solving these simple equations, the number of parts of each component required to satisfy the desired conditions of the charge is at once found.

If it is desired to produce a more acid or a more basic slag, it is only necessary that the scale b be replaced by one the length of whose gradations are one-half (for bisilicate slag) or twice (for subsilicate slag) that of the normal scale.

A simpler form of the rule can be made by drawing the lines A B, A C, A D, A E, as before, upon a sheet of card, and then

setting out a scale of equal parts upon the datum line A B, and providing a loose strip of card, one edge of which is graduated to the same scale, taking care, in using the scale, to keep it at right angles to the line A B. This is, in fact, the equivalent of a set of Prof. Balling's diagrams, reduced to one scale, and brought to a common centre.
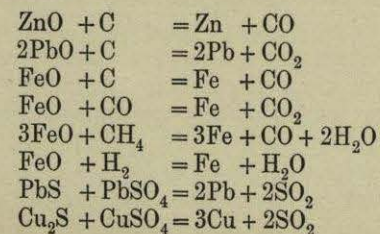
Mr A. Wingham[1] has also devised an excellent slide rule for the same purpose as the foregoing appliance, and by it the additions, as well as the multiplications, are mechanically performed, provision being made for all the ordinary constituents of slags.

Classification of Metallurgical Processes.—Metals may be extracted from their ores and from metallurgical products by the following methods:—

1. By *liquation*—that is, a separation of the easily fusible metals or metallic compounds from the infusible ones, or the gangue, at a low temperature, by taking advantage of the different melting-points. Bismuth and sulphide of antimony are thus obtained.

2. By *distillation* and *sublimation*—that is, heating the ore until the metal is driven off in the form of vapour, and condensed in a liquid or solid state. Mercury is extracted from its ore by distillation, and arsenic is obtained by sublimation. Mond's unique process for nickel extraction might also be regarded as falling under this heading, the nickel being "distilled" off as the gaseous carbonyl ($Ni(CO)_4$), which is subsequently decomposed and the nickel deposited.

3. By reduction of metallic oxides at a high temperature. In the case of metals possessing a slight affinity for oxygen, the reduction may be effected by merely heating the oxide, whereby it splits up into metal and oxygen. The reduction is usually effected by heating the oxides with carbon or other substances possessing a greater affinity for oxygen than is possessed by the metal. In addition to solid carbon, the substances used are carbonic oxide, marsh-gas, and hydrogen, as well as sulphur in the reverberatory-furnace processes for extracting copper and lead. The reactions are shown by the following equations:—

$$
\begin{array}{lll}
ZnO + C & = Zn + CO \\
2PbO + C & = 2Pb + CO_2 \\
FeO + C & = Fe + CO \\
FeO + CO & = Fe + CO_2 \\
3FeO + CH_4 & = 3Fe + CO + 2H_2O \\
FeO + H_2 & = Fe + H_2O \\
PbS + PbSO_4 & = 2Pb + 2SO_2 \\
Cu_2S + CuSO_4 & = 3Cu + 2SO_2
\end{array}
$$

[1] *Journ. Iron and Steel Inst.*, i., 1892, p. 253.

4. By decomposing metallic sulphides by means of iron at a high temperature. Lead and antimony are extracted from their ores in this way, the equation in the case of lead being—

$$PbS + Fe = Pb + FeS.$$
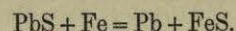
5. By extraction by means of molten lead, as in the treatment of certain argentiferous mattes.

6. By extraction by means of molten zinc, as in the extraction of silver and gold from lead by the Parkes process.

7. By extraction by means of mercury in the cold—*i.e.* by *amalgamation*. It is used for extracting silver and gold from their ores, the mercury being subsequently driven off by heat.

8. By extraction in the wet way and subsequent precipitation, as metal or as oxide or sulphide. In some cases the compound is dissolved in acids, as in the separation of silver from gold, and in the extraction of copper and nickel. In other cases the metal is first converted into a chloride, which is dissolved in a solution of salt or of sodium hyposulphite, as in the extraction of silver by Augustin's process, or the metal is converted into a sulphate, which is dissolved in water, as in Ziervogel's process. The extraction may also be effected by treating oxides with salts, as in the Hunt and Douglas method of extracting copper,

$$3CuO + 2FeCl_2 = Fe_2O_3 + CuCl_2 + Cu_2Cl_2.$$
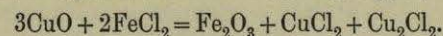
9. By electrolysis, as in the deposition of copper, silver, and gold.

10. By means of the electric furnace.

11. By the action of oxidisers on metallic salts, as in the precipitation of gold from its solution as chloride by ferrous sulphate.

12. By crystallisation, Pattinson's silver extraction method.

13. By the reducing action of some other substance as Al in alumino-thermic processes, Si, Ca, etc., being other examples.

Roasting and Calcination.—These terms are frequently used indiscriminately to indicate the operations of expelling water, carbonic anhydride, or sulphur from the ore by heating it to a temperature below its melting-point. The term "calcination" should be confined to the application of heat in the expulsion of carbonic anhydride or volatile matters, whilst the term "roasting" should be used in all cases where a chemical change is involved, resulting in the addition of an element.

Roasting is one of the most important of metallurgical processes. In the treatment of almost all ores it is required as a preliminary process to render them more porous and more suitable for the subsequent smelting, the success of which depends on how the roasting is effected.

The various methods of roasting are dealt with in the other volumes of this series,[1] and more exhaustively by Peters.[2] They

[1] Rose, *Metallurgy of Gold*; Collins, *Metallurgy of Silver and Lead*.
[2] Peters, *Copper Smelting*.

may be roughly divided into those which treat the materials (1) in lumps or (2) in powder. For the furnaces employed see next chapter.

There are several kinds of roasting. An *oxidising* roasting is one in which the metalliferous substance is oxidised by heating it in contact with air. A *reducing* roasting consists in heating the substance in a reducing atmosphere. When it is required to obtain chlorides instead of oxides, the material is roasted with salt. This operation is termed a *chloridising* roasting. It is especially important in the treatment of silver ores. Under the action of a high temperature the salt acts on the sulphates present and forms chlorides. Its action may also be due to the formation of chlorine by the action of silica and sulphuric anhydride on the salt, or to the evolution of hydrochloric acid, due to the presence of moisture in the atmosphere in which the material is being roasted. *Sulphating* roasting, or roasting in such a manner that sulphates are formed. It necessitates a low temperature and a limited supply of air.

Several processes which may be considered under the general term *lime roasting* have recently come into prominence, owing to the success they have met with in rapidly desulphurising galena and leaving it in a very suitable physical condition for subsequent blast-furnace treatment. Of these processes the Huntington-Heberlein comprises two operations : (1) heating slowly in a reverberatory furnace a mixture of galena and lime, 6 to 15 per cent. being used according to the amount of sulphur in the ore ; (2) transferring the partially desulphurised hot mixture into a pear-shaped vessel made of sheet iron, and blowing air through, with the result that nearly all the sulphur is oxidised, and the temperature is raised sufficiently to agglomerate the mass. The Carmichael-Bradford process consists of feeding a mixture of galena with 10 to 35 per cent. of dehydrated gypsum into a converter on the top of a small bed of glowing coal kept incandescent by a gentle blast. The Savelsberg process resembles the latter process, but limestone is used instead of gypsum. A modification of these processes, known as pot-roasting, has been introduced into some American works, and is worked on charges low in lead and nearly free from limestone. The apparatus consists of a cast-iron kettle, 8 feet 6 inches in diameter, with a detachable hood. The kettle has a cast-iron plate near the bottom, drilled with $\frac{3}{8}$-inch holes. A barrowload of ashes is first charged, then follow 1 to 2 tons of hot roasted ore, used to ignite the remaining 8 to 9 tons of charge. The ore mixture is made up to contain Pb 7–10, SiO_2 30, S 20–25. The remaining 8 to 9 tons are slightly moistened and added to the previously ignited charge, and the blast kept on until the process is finished.

Oxidising Agents.—Atmospheric air is the simplest source of oxygen ; it is employed at the ordinary pressure or at a pressure

of several atmospheres, for the temperature of combustion increases with the pressure.

Water is an active oxidising agent in the case of certain metals which have a strong affinity for oxygen, but in other cases its oxidising action is sensible only at a high temperature. The decomposition of water absorbs much heat, and aqueous vapour can therefore be employed only as an oxidising agent when its cooling effect is desirable. Aqueous vapour is also used for separating zinc from lead. In passing steam over sulphides of oxidisable metals at a red heat the sulphur is eliminated as sulphuretted hydrogen, while the metal is oxidised. This reaction is employed in the roasting of sulphides of iron, and in the treatment of sulphides, arseno-sulphides, and antimonio-sulphides of copper and silver.

Metallic oxides are frequently used as oxidising agents. Oxides of manganese, iron, and lead are those most generally employed. Oxide of copper is used more rarely. Manganese peroxide is occasionally useful in the oxidation of impurities in metals. Ferrous oxide, or ferrous silicate, acts as a carrier of atmospheric oxygen. When ferrous silicate, containing less than 30 per cent. of silica, is exposed in a molten state to the action of air, the iron in excess gradually becomes oxidised, and crystals of magnetic oxide are formed. These render the silicate less fusible, and fall by their superior density to the bottom of the mass. Sometimes, as when such a slag covers a bath of impure metal, the magnetic oxide thus formed gives up its excess of oxygen to the elements in the metal to be refined, and again becomes ferrous oxide, and thus acts as a carrier of atmospheric oxygen to the carbon which has to be oxidised. An illustration of this is afforded by a stage of the puddling of iron, a process which is conducted in the presence of a layer of ferruginous cinder.

Lead oxide is an energetic oxidising agent on account of its being readily reducible to the metallic state. It is, however, expensive, and yields but 7 per cent. of oxygen. Lead oxide and lead sulphide, when heated together, give metallic lead—

$$2PbO + PbS = 3Pb + SO_2.$$
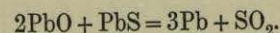
Oxides of copper and antimony serve as oxidisers in the treatment of these metals. In heating together the sulphide and oxide of copper, copper is obtained. Potassium and sodium nitrates are employed in refining silver and antimony, and in the "Heaton" process sodium nitrate was employed to convert phosphorus in certain varieties of pig-iron into sodium phosphate.

Metallic sulphates are often used as oxidising agents, the sulphate oxidising the sulphide and reducing the metal. In the case of iron in the blast furnace, carbonic anhydride also acts as an oxidiser.

Reducing Agents.—When a metal is separated from a state of chemical combination, it is said to be reduced, and the process of separation is termed *reduction*. The agents employed for this purpose are mainly carbon and hydrogen, or their compounds. Occasionally, however, the metallurgist makes use of iron, manganese, lead, aluminium, calcium, or of sulphides and arsenides. The efficacy of a reducing agent depends on the absence of oxidised or inert elements. Thus, on account of the water and oxidised compounds they contain, wood, peat, and lignite are less energetic as reducing agents than coal. Similarly, coals rich in carbon are more valuable as reducing agents than coals rich in oxygen.

Carbon can take up $1\frac{1}{3}$ or $2\frac{2}{3}$ of its weight of oxygen according to the oxide in whose presence it is used, to the temperature at which the reduction is effected, and to the relative proportion between the oxygen to be removed and the carbon employed. In the first case carbonic oxide is formed, and in the second carbonic anhydride. The reduction of metals, of which the oxides are easily reduced, such as lead and copper, is complete even if carbonic anhydride alone is formed. In the case of iron, however, total reduction is not possible unless carbonic oxide is present in excess, on account of the oxidising action of carbonic anhydride. Indeed, a mixture of equal volumes of carbonic oxide and carbonic anhydride will not reduce iron oxides below ferrous oxide. This is also true of manganese oxides.

Reduction by solid carbon is slow, and is effected merely by cementation, that is, by a gradual transmitting action, if carbonic oxide is not formed. This gas is the most important reducing agent. It penetrates to the centre of the oxidised substance, absorbs its oxygen, and is converted into carbonic anhydride. In this way 1 part by weight of carbonic oxide gives 1·57 parts of carbonic anhydride. Besides this, Gruner[1] and Sir Lowthian Bell[2] have shown that, even at low temperatures, carbon, in the presence of iron, separates out from carbonic oxide,

$$2CO = CO_2 + C,$$
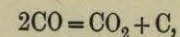
and has a powerful reducing action. Hydrogen is a powerful reducing agent, but is only used incidentally, or as water-gas.

In addition to the above-mentioned reducing agents, metals and metalloids are sometimes used to remove oxygen. Thus, iron deoxidises the salts and oxides of copper, of lead, and of mercury, sodium liberates the metals magnesium and aluminium from their haloid salts, and aluminium liberates the metals chromium, manganese, etc. from their oxides. Sulphides and arsenides are also employed. Thus, sulphides of iron and zinc separate copper

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[1] *Ann. de Chim. et de Phys.*, 4th Series, vol. xxvi. (1872), p. 5 ; *Traité de Métallurgie*, vol. i. (1875), p. 172.
[2] *Chemical Phenomena of Iron Smelting.*

from certain slags. Silicates of iron and zinc are formed, while sulphur retains the copper in the regulus.

Chemical Agents.—Certain sulphurising agents are employed in metallurgical processes. These are specially useful in the treatment of silver and copper. The agents are iron or copper pyrites, barium or calcium sulphates, and, less frequently, alkaline sulphides. Nickel and cobalt behave with regard to arsenic as silver and copper do in the case of sulphur. These metals may be protected, by means of their affinity for arsenic, from the scorifying action of silicates.

Chlorine is largely used in the treatment of gold and silver ores. It is employed in the gaseous state as an aqueous solution, or in the form of alkaline hypochlorites. The perchlorides of iron, copper, and mercury act as chloridising agents by being converted into lower chlorides. They are obtained usually by the direct action of hydrochloric acid on peroxides. Iodine in the form of iodide is used in the metallurgy of silver, and bromine in that of gold.

The agents employed for effecting the solution of metallic substances are very varied. The most important solvent is water, which is used for dissolving sulphates of iron, copper, zinc, and silver, and chloride of gold. Other salts are dissolved by salt solutions; thus, chloride of silver is dissolved by an aqueous solution of sodium chloride, or hyposulphites of sodium or calcium. The use of very dilute solutions of potassium cyanide in the extraction of gold[1] has assumed great importance, and numerous patents for its production have been secured;[2] sodium cyanide, also, is now largely used in the treatment of gold and silver ores. Metallic oxides are dissolved by acids; gold and platinum are dissolved by aqua regia; and in the amalgamation of gold and silver, mercury is the solvent employed.

In metallurgical processes there are scarcely any limits to the use of ordinary chemical reagents beyond those imposed by the price of the material.

[1] Rose, *Metallurgy of Gold*.
[2] *Mineral Industry*, 1894, p. 79.

CHAPTER IX.

FURNACES.

Materials used in the Construction of Furnaces.—In addition to the ordinary building materials used for the exterior portions of furnaces, refractory bricks and materials are required for the interior where a high temperature and the scouring action of metallic oxides have to be resisted.

There are three classes of refractory materials:—

1. *Acid*—Dinas rock, ganister, and most fire-clays.
2. *Basic*—Dolomite and magnesite.
3. *Neutral*—Bauxite, chrome-iron ore, graphite, and a few fire-clays.

Acid Refractories.—Siliceous materials are most generally employed, as in the great majority of cases all that is required is a material capable of resisting high temperatures, and also mechanically strong under great variations of temperature. It is only when the chemical reactions involved are such that a siliceous lining would interfere or be fluxed away that neutral or basic linings are used. For roofs, side walls, and all those parts of the furnace which do not form part of the hearth or "laboratory," siliceous bricks are almost universally employed in all metallurgical works. Thus all copper-smelting furnaces, all reheating and annealing furnaces, whether for copper, steel, or other metals, ore-roasting furnaces, many steel-smelting furnaces, and practically all blast furnaces, are built with some kind of siliceous fire-bricks, sometimes nearly pure silica, when very high temperatures have to be resisted, at other times of different kinds of fire-clay.

The question of contraction and expansion is an important consideration in selecting a fire-resisting material, as some expand much more than others, and for certain parts of a furnace this may be a serious disadvantage, while for others it is of no consequence, and may even be an advantage.

These materials may be used either in the natural state or as bricks. Of the natural materials, sandstones are most largely employed, the best varieties being those in which the quartz