THE CLASSIFICATION OF REFRACTORY MATERIALS.

Mr. E. P. Page (Sheffield) read a Paper on "The Classification of Refractory Materials."

This Paper is confined in the main to the materials used in the heavy industries, and I have not attempted to deal in detail with the refractory materials used in the lesser known paths of metallurgical practice. To cover the whole field of refractory materials and their application in all branches of industry would be beyond the range of accomplishment in any single Paper.

The collection and tabulation of facts is a laborious task, since much of the information is only to be obtained by association with those who are engaged in industrial practice—further, the science of refractory materials is in its infancy, and much of that which is considered fact requires verification.

The usual method of classifying refractory materials has been to divide them into three classes, viz. acid, basic, and neutral, according to their chemical composition and their behaviour towards each other, and acid or basic compounds brought into contact with them, under such conditions as are favourable for reaction to take place. The classification is somewhat arbitrary, because a clay such as china clay might be expected from its chemical composition to be a neutral material; experience, however, shows that such is not the case, and it is customary to include all refractory clays in the acid class.

The essential property of any material claimed to be refractory is stability at temperatures to which it is exposed, with sufficient reserve of stability to resist chemical and mechanical influences externally applied. The first quality is a question of pure refractoriness, the second is one of refractoriness plus skill in application.

Further, since purely basic or purely acid conditions seldom exist, the successful issue is generally the result of compromise, a certain degree of refractoriness *per se* being sacrificed in favour of increased refractoriness against other influences.

Materials belonging to the "acid" class are always used where it is a case of refractoriness towards heat, because they are widely distributed and comparatively low in first cost, and lend themselves readily to adaptation for particular purposes. Suitable "basic" and "neutral" materials, on the other hand, are not so widely distributed and possess in many instances inherent properties which render them difficult of application.

I propose to follow the usual method of dividing all refractory materials into three classes, viz. acid, basic, and neutral, and to indicate the application of the various materials in each class.

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Acid Materials.

Silicious materials, with a content of SiO_2 ranging from 100 per cent. to 80 per cent. (below 80 per cent. would be included as a clay), embracing quartz, quartzites—sandstones—sand.

The purest forms of silica are used in the manufacture of quartz glass, which is worked up into a variety of articles used mainly in chemical operations.

The less pure forms of silicious rocks (quartzites, ganister, etc.) are used in the manufacture of "silica bricks," and in the preparation of material which is used as a more or less plastic mortar and rammed into position in the raw state.

The best silica rocks for these purposes average from 95 to 98 per cent. SiO_2 , and soften at about 1,800 to 1,850°C. Such rock is widely distributed and exists in many varieties, most of which can be used in the ground state as a prepared mass, and few of which have so far been used successfully in the manufacture of first-class silica bricks and blocks. The quality of a silica brick depends more on the physical and mechanical properties of the stone or rock than on chemical composition. All silicious materials expand on heating, and some expand to an extent which renders them useless in the manufacture of silica bricks. The problem before the silica brick manufacturer is to secure toughness and increasing density in use, and that the problem is not insoluble is proved by the specimen brick shown.

Large quantities of silica are used in the form of sand for forming the hearths of open-hearth furnaces and in iron and steel foundries.

Refractory Clay.

This material is also widely distributed and of great variety. Refractoriness generally varies directly with the content of alumina. The most refractory clay corresponds to the formula $\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot (2\text{H}_2\text{O})$, which softens at about cone 35–36, any increase in the ratio of silica to alumina reducing the refractoriness. Clays corresponding to this composition are scarce, the most abundant being the china clays. The clays obtained from the coal measures contain less alumina, and with one or two exceptions are less refractory. There is another class of refractory clays generally known as "ball" clays, which are generally more silicious than china clay, and vary in refractoriness accordingly.

The chemical composition gives no clue on which to base any conception as to its physical properties—

	1			China Clay.	2	Grunstadt Clay.
Silica ...	...	...	...	54'65		47'69
Alumina ...	...	...	...	44'51		38'15
Oxide of iron ...	...	...	...	'22		'077
Lime ...	...	...	...	'13		'21
Magnesia ...	...	...	...	'09		'12
Potash ...	...	...	...	'34		'26

Formulae.

No. 1. $\text{Al}_2\text{O}_3 \cdot 2'09 \text{SiO}_2 \cdot 0'027 \text{RO}$; refractory cone, 36.

No. 2. $\text{Al}_2\text{O}_3 \cdot 2'125 \text{SiO}_2 \cdot 0'0775 \text{RO}$; refractory cone, 35.

In composition these two clays are very similar, but the result of heating to approximately 1,300°C. is to reduce No. 2 to a dense vitreous structure, whilst No. 1 will be found to be strongly absorbent and porous. In the raw

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state No. 1 is not plastic and has no bonding power, whilst No. 2 is plastic and has great bonding power.

This comparison of two clays of similar composition and unlike physical properties will give an idea of the problems which the manufacturer has to solve. It is sometimes necessary to construct a vessel which will keep its shape at high temperatures, and at the same time withstand the solvent action of molten slag or glass. Now, however perfectly refractory the clay may be as regards heat, it is useless if it absorbs the slag or glass, because this immediately reduces the refractoriness towards heat. Hence, as already mentioned, it is necessary to compromise between the two qualities.

Large quantities of "acid" materials are used in the raw state. Silica is ground, sometimes with clay and sometimes without, to a semi-plastic mass, and used for lining steel converters, ironfounders' cupolas, steel ladles, etc.; for this purpose inferior kinds of quartzites are used, according to the resources of the district. In Sheffield the crucible pot furnaces are formed by ramming ground ganister round a plug or core.

Converters are lined with silica brick, and all wear is made up with ganister, which is "daubed" on.

The iron and steel founder uses acid materials for making moulds. Sands suitable for iron castings are plentiful and the ironfounder has little difficulty in getting supplies. The demands made on moulding materials in the steel foundry are very much more exacting than is the case with iron, and much ingenuity is used by the steelfounder to adapt his moulding materials to meet his needs. The size and shape of the casting, the class of steel, and many other factors have to be considered.

Sand is used very largely for small and medium-sized steel castings. "Composition" is also used; this consists of a mixture of old crucible pots, ganister, calcined and raw, fire-clay, blacklead, and sand. Every foundry has its own mixings and recipes. The essential property of a moulding material is sufficient "bond" to enable it to keep its shape, which is often very intricate, and when dry it must be firm enough to stand the flow of the metal, and finally, especially in the case of "cores," it must break up and leave the casting clear.

The problems which arise in connection with moulding materials are quite distinct from those arising in brick-making, and provide sufficient matter for research on their own account.

Basic Materials—Magnesite : Dolomite : Alumina.

Magnesite is one of the most useful of the basic materials. It can be used in the form of bricks and special shapes, and also as a rammed mass for furnace bottoms, etc.

It is highly refractory, but possesses the disadvantage of being a good conductor of heat. It is obtained in a form suitable for use in metallurgical operations by burning the naturally occurring magnesium carbonate rock at very high temperatures; not only must all traces of CO_2 be driven off, but the oxide resulting from the first stage of calcination must be heated until it has attained its maximum density. In the discussion on a paper read before this Society by E. Kilburn Scott in 1905 it was stated that as the result of heat the density of magnesium oxide varied as follows:—

Heated to 350° C.	...	...	3'193
„ dull red	...	...	3'248
„ white heat	...	...	3'670
Fused in electric arc	...	...	3'684

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and Dr. Hutton goes on to say that "fused magnesia, as also fused alumina, behaves like fused quartz in being able to withstand somewhat sudden changes of temperature without fracture, although, of course, the behaviour varies in degree."

Bricks made of magnesia, shrunk at the highest temperature short of the electric arc, are in many respects unsatisfactory, being unstable at moderately high temperatures; they are unsuitable for the construction of arches, and even if used in plain furnace walling they disintegrate. They are used in large numbers in the bottoms of Siemens basic furnaces underneath the dolomite hearth, and are for this particular purpose quite satisfactory.

J. Horhager* gives some particulars of magnesite deposits in Austria and Greece, and states that the crystalline varieties of stone found in Austria, containing 2 to 8 per cent. of Fe_2O_3 , are the most suitable for use in making dead burnt magnesite; though he states that very satisfactory material is made in England from the purer amorphous form of magnesite obtained from Eubœa. He mentions the following figures as representing the ideal composition:—

Minimum,	83	per cent.	MgO .
"	3	"	Fe_2O_3 .
Maximum,	5	"	CaO .
"	2	"	Al_2O_3 .
"	5	"	SiO_2 .

In America and on the continent of Europe magnesite is used for ramming up the furnace bottoms of both basic open-hearth and electric furnaces, on account of its refractoriness towards basic slags and metallic oxides; in Great Britain, however, dolomite is found to be satisfactory.

Dolomite.—This material, as used, is the product obtained after burning magnesian limestone at a very high temperature until it has not only lost all the CO_2 , but has attained great density; its refractoriness is affected by the content of silica and iron and the ratio of the two latter to each other.

Shrunk dolomite hydrates at a rate dependent on atmospheric conditions, and is always used as "fresh" as possible. It is very refractory towards heat, basic slags, and metallic oxides, though at the temperature of the open-hearth furnace it is "friable."

For furnace bottoms it is crushed, mixed with dehydrated tar, put on in thin layers and rammed with hot rammers to the required shape. For lining basic Bessemer converters the material is crushed, and after mixing with tar is pressed in hydraulic presses into the form of blocks.

Dolomite has also been made into bricks of a density equal to magnesite bricks; the temperature at which the bricks are burnt must, however, be sufficiently high to sinter the particles together.

The combination of dolomite and tar under the influence of heat gives much better results than magnesite and tar. The tar oils and acids react with the lime, and after the volatile constituents of the tar have been driven off a compact homogeneous mass of dolomite and carbon is left.

Alumina.—This is a valuable refractory material, but the price at which it is obtainable is against any very extensive use. For very special purposes, and where first cost is not a consideration, it can be mixed with plastic clays in any proportion, and will raise the refractoriness of the clay to a degree depending on the amount of the alumina added.

* *Stahl und Eisen*, 24, 1911.

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Neutral Materials—Chrome : Carbon : Zirconia : Bauxite.

Chrome is a very useful refractory, under certain conditions. It can be made into bricks and special shapes or used in the lump and ground condition. In the early days of the basic steel process chrome bricks were always used as an insulating material between the magnesite bricks in the bottom and the silica bricks of the side walls. This practice is not now generally followed, because it has been found that magnesite and silica bricks can be laid in contact with each other.

Chrome bricks are difficult to manufacture, inasmuch as the material has a low softening-point, and the bricks if subjected to any weight in the kiln collapse. Ground chrome is an exceedingly useful material. It can be used as a mortar in contact with dolomite, to repair a dolomite hearth. Electric furnace operators use it extensively for all sorts of purposes.

Bauxite.—This is a naturally occurring hydrate of alumina always mixed with some clay matter or hydrated oxide of iron. The content of water in the raw material varies from 5 or 6 per cent. to 30 per cent. Before it can be used it requires shrinking at very high temperatures, and some varieties require repeated burning before all the shrinkage is taken out. The best material is that which has been fused in the electric furnace. A fused bauxite known as alundum has been tried for the roofs of electric furnaces; it was found, however, that the vapours of lime and magnesia attacked the bricks and caused them to fail.

Carbon.—This is a useful refractory material, but it cannot of course be used under oxidizing conditions. Carbon blocks were, I believe, imported to line the hearth of a blast furnace in the north-eastern district. The result of the experiment will be of much interest.

Zirconia.—This material has been the subject of investigation, and experiments to determine its value in metallurgical operations are in progress.