REFRACTORY MATERIALS IN THE ROYAL NAVY

BY

COMMANDER C. G. CRILL, R.N. AND E. SCOTT, B.Sc., A.R.C.S.

Although refractories are used in almost every industry, and in a great many other ways are very important, they are largely taken for granted, knowledge of their nature, properties and methods of production being surprisingly limited among their users. The metal industries and most steam raising plants, to mention only the two principal consumers, depend on adequate refractories for their furnace linings. The refractories industry is of long standing, but until comparatively recently there has been little need for technical development, as it has usually been possible to find some natural product capable of supplying the desired properties when made into the appropriate form. As a result, the industry generally has tended to lag behind others, such as textiles, metals or plastics, in its scientific development and it is only in the past ten years or so that firms have realized that much more development was becoming necessary for their products to keep pace with the increasing demands of consumers.

One of the chief difficulties in the development of materials is that of relating practical requirements to the performance of refractories under conditions of test. Whereas, for example, metals can be analysed chemically and examined structurally and mechanically under comparatively simple conditions, positive results being obtained from small but representative samples, the performance of refractories has generally to be assessed on large samples (due to their

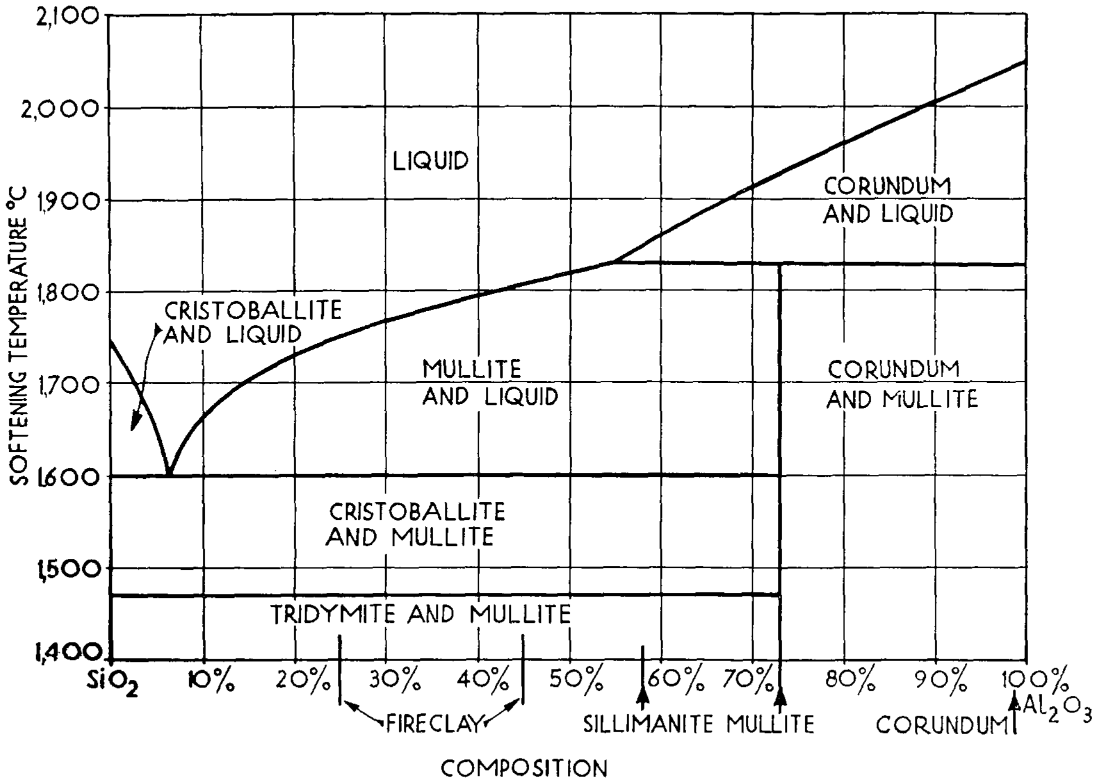

FIG. 1—EQUILIBRIUM DIAGRAM OF THE SYSTEM Al_2O_3—SiO_2
(*Bowen and Greig*)

heterogenous nature) under very high temperatures using large quantities of, say, flue gases, molten metal or slag to produce erosive or corrosive effects over long periods. To demonstrate improved properties convincingly, even large and costly equipment is seldom adequate, necessitating even more costly full scale trials with the possibility of failure and consequent spoiling of a production batch or interruption of a steaming schedule. Naturally, new products tend to be more costly and users are reluctant to pay extra, where for so many years a ' cheap ' product has done the job more or less satisfactorily.

COMPOSITION AND USES OF REFRACTORIES

Available refractory materials fall into several classes, the various classes each having their special applications. The following summary indicates some of these products and their uses :—

Basic	Magnesite	Melting-steel furnaces.
Acid	Silica and fireclay	Melting-steel furnaces, boilers.
Neutral	Chrome and chrome-magnesite	Neutral courses between above types.
Pure Oxides	Alumina, thoria, zirconia, beryllia.	Jet engines, special application.
Carbides	Silicon carbide	Crucibles of high conductivity and linings of high resistance to thermal shock.
Carbon	Graphite	Metallurgical, blast furnaces, reducing conditions.

The alumina–silica range of materials provides most of the more ordinary types of firebricks and a more detailed summary of these is given below based on the composition–softening temperature diagram (FIG. 1).

	Approximate Composition (Percentage)	*Source*	*App. Soften-ing Temp.*	*Use*
Pure Silica	100 SiO_2	Pure sands	1750°C	Vitreosil. Chemical apparatus. Very low thermal expansion.
Silica brick	84 SiO_2 6 Al_2O_3	Ganister rock Peak District, Wales	1730°C	Steel furnaces, roof particularly, as slight expansion on heating.
Building brick	15—20 Al_2O_3 85—80 SiO_2	Fireclay beds, usually near coal fields	1500°C	Constructional.
Fireclay bricks	25—42 Al_2O_3 75—58 SiO_2	do. Scotland, Tyneside, Yorkshire, Worcestershire	1730°C	Furnaces generally.
Sillimanite	58 Al_2O_3 42 SiO_2	Cyanite mined in N. India, Andalusite mined in America	1790°C	Special high temp. furnaces. Glass industry, etc.
Mullite	75 Al_2O_3 25 SiO_2	Bauxite, diaspore rock, Jamaica	1810°C	do.
Alumina	95 Al_2O_3	do.	2000°C	Laboratory special furnaces.
Recryst. Alumina	99·5 Al_2O_3	do.	2050°C	Pyrometer sheaths, other specialities.

Fireclay bricks, generally, are produced from mechanical mixtures of clay mineral, prefired ‘ grog ’ and sometimes a water-soluble setting agent. The clay mineral is kaolinite in areas having china clay deposits and montmorillonite in areas having fireclay deposits. Kaolinite has slightly higher heat resistant qualities, but tends to shrink more in firing and to have less plasticity than the fireclay types, probably due to the presence in the latter of a variety of impurities. Grog is clay which has been fired, crushed and graded, occasionally being produced in an inferior quality from rejected crushed firebricks. The setting agent is usually sodium silicate or sulphite lye and is added to give products greater ‘ green ’ strength for handling after drying when being set in the kiln for firing. During firing, this dry strength is replaced by the ceramic bond due to the sintering together of particles by formation of a glassy matrix.

SERVICE PROBLEMS

The refractory parts of boiler furnaces for ships of the Royal Navy have for years been regarded as components necessarily requiring frequent replacement. The advent of boilers of higher forcing rate and the greater requirements of

Fig. 2

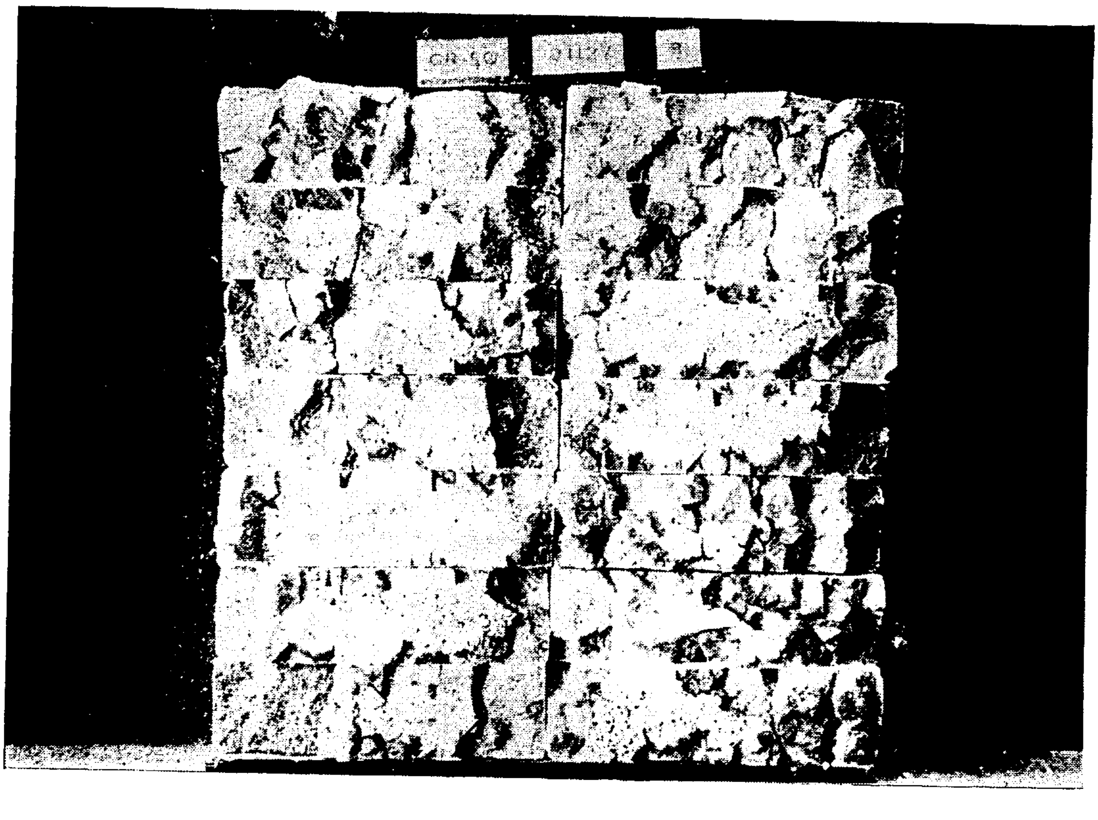

Fig. 3

aircraft carriers and their accompanying destroyers for manœuvring, have considerably aggravated the damage rate.

In order to achieve some improvement in furnace life, two lines of action were taken. The first was an alteration in the method of assembly of the structure to a type similar to that of the U.S. Navy, a requirement of the A.B.C. grouping of allies. This brought certain benefits automatically, as the number of brick shapes required could be reduced from upwards of a hundred to three, and storing problems were much simplified. Further, the new shapes, which are standard in industry, are rectangular blocks with special bolt slots, and are simpler to produce by machine pressing which results in a better product at a lower cost. The bricks thus being virtually ' tailor made ' can be given reduced dimensional tolerance whereby the joints (a primary source of trouble) can be improved. The system of attachment to the boiler casing, previously requiring bolt holes, now makes use of eyelets welded on the inside of the plates, at intervals, into which bolts are hooked, thus avoiding leakage of extraneous cold air into the furnace.

The second approach to improved performance was a long term investigation aiming at the use of higher quality material in the bricks themselves and at amended production methods, producing enhanced properties of the current material. Selected manufacturers were given development contracts towards this end and their productions were tried out at the Admiralty Fuel Experimental Station and in portions of the boiler furnaces of an aircraft carrier.

To decide in what direction alterations might be profitable, it is necessary to look at the principal causes of trouble leading to disintegration in a furnace structure. These are two in number, namely Spalling and Slagging.

Spalling

This is the name given to damage to refractories caused by shock—either mechanical or thermal. It is the latter that is particularly important as most Naval vessels, during manœuvring, have their oil burners, often 9 in a furnace, shut off and relit in rapid succession, as frequently as one every few seconds. During the shut down period the forced draught system continues to send relatively cold air over the brickwork, chilling and cracking the surface. Aircraft carriers and destroyers, being most concerned with rapid speed changes for flying operations, are most prone to this kind of damage. After a series of repetitions the cracks develop and cause the front layers of the bricks to fall away in a characteristic fashion (FIGS. 2 and 3).

The materials found to resist this kind of damage best are those possessing a relatively open texture, indicating that very little glassy matrix has been formed during production. It is also an essential, of course, that the material has been so blended that it possesses only slight reversible thermal expansion. Inclusion of an amount of sillimanite or other high grade material, greatly improves the quality of spalling resistance, but this is an imported material and would, in time of war, be difficult to obtain. Hence the development contracts, referred to above, stressed the use of indigenous materials, permitting only limited additions of foreign products. Considerable improvements were achieved by means of selected ingredients and special particle grading, but it became obvious that the best U.S. types could not be matched without using more than about 25 per cent boosting material.

These special products are necessarily much more costly then current types, though probably the prices would fall with increased production, but the particular point to be noted here is the reduced number of periods a ship may have to spend in harbour for refractory repairs, and to a lesser degree the reduced labour bill of fitting. At the moment, a material cost increase of some

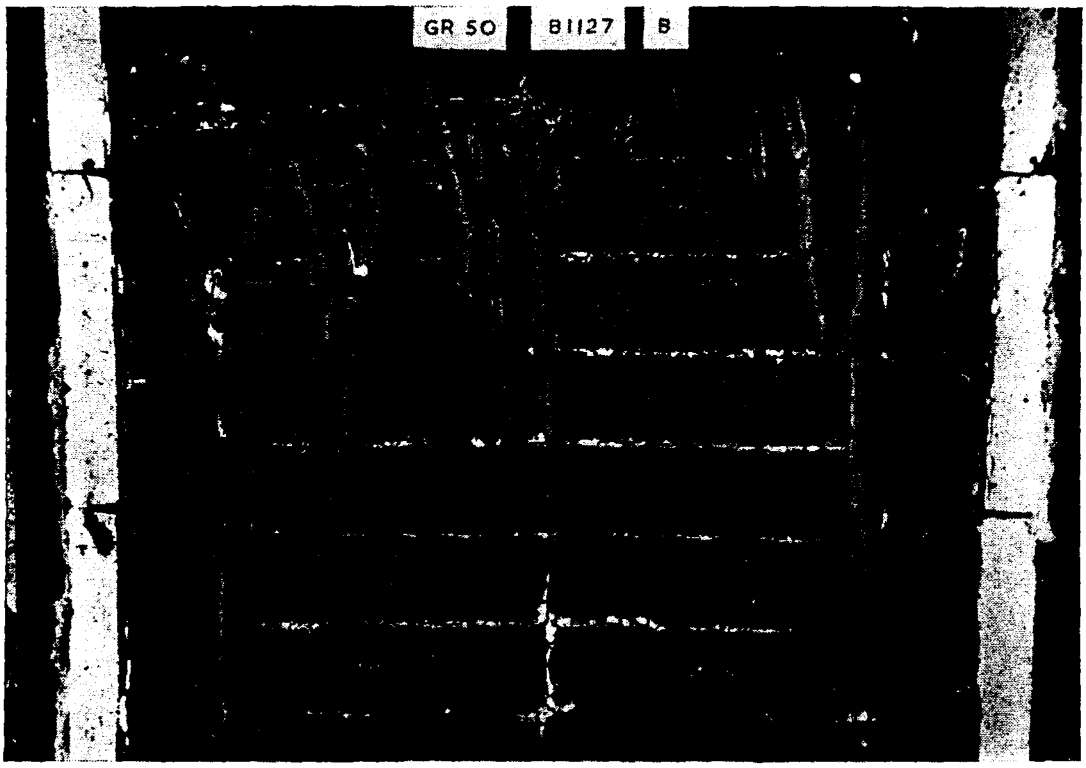

FIG. 4

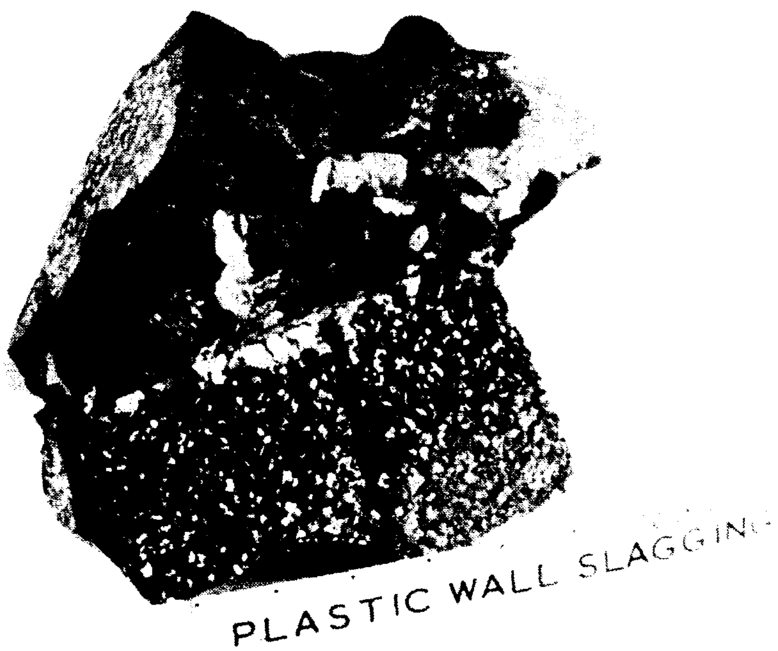

FIG. 5

FIG. 6

four times is being offset by a ' life ' increase of 3–6 months, up to 12–24 months, using the new materials. It is difficult to assess these with any certainty as so few ships are continuously in service.

Slagging

The softening temperature of a firebrick is about 1730°C/3146°F. but the presence of certain impurities can cause a serious reduction in this figure. The worst offenders, called fluxes, are alkali oxides, iron oxide and titanium, calcium and magnesium oxides, all found in small proportion in natural clays to a total maximum of about 5 per cent, the clay quality depending on that total to a very large extent.

If firebricks are heated in any way with a flux, a reaction occurs resulting in formation of a low melting glass (1150°C/2102°F) to the great detriment of a furnace wall (FIGS. 4 and 5). A common cause of such trouble is the use of fuel oil containing sea water in an emulsified state, which renders separation almost impossible by ordinary mechanical means. The sources of this adulteration are :—

(*a*) Oil displacement and ballasting by sea water.

(*b*) General tank and pipe leaks may occur either on the user ship or on the supply tankers.

The fuel oil contains asphaltic bodies which act as emulsifying agents and, due to ship motion, the oil and water become extensively mixed, a typical water content being up to 10 per cent. In the laboratory it has been shown that as much as 75 per cent of water can be emulsified into oil fuel, but the maximum burnable figure is about 45 per cent. This amount burns with some difficulty, but the amounts usually experienced, of less than 10 per cent, give little or no evidence of their presence during combustion.

That slag attack is a very real problem is shown by the fact that ships have found layers of slag on the furnace floors up to six inches in thickness obviously produced by reaction products (FIG. 6) flowing from the sides. The slag layer, when steaming, can be seen to flow to and fro with the ship's motion. This

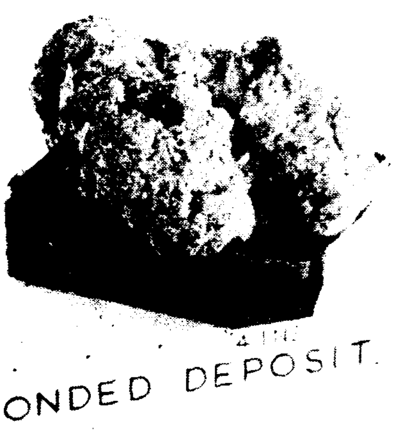

FIG. 7

problem became accentuated during the war when the sea water ballasting process became general and more ships received wet oil. Before the war it had been found that a thin skin of slag on the brick face was desirable, forming a slightly plastic seal which tended to control spalling trouble, and such a skin was often produced by putting a few glass bottles into the furnace while steaming.

The mechanism of the slag attack seems to rely on the conversion of volatile sodium chloride to non volatile sodium sulphate, by the sulphur trioxide and dioxide present in the flame gases produced by the sulphur content of the fuel oil. At high temperatures silica becomes a very active acid and reacts with the deposited molten sodium sulphate.

$$2\ NaCl + H_2O + SO_3 \longrightarrow Na_2SO_4 + 2\ HCl$$

$$Na_2SO_4 + Si\ O_2 \longrightarrow Na_2Si_3 + SO_3$$

Firebricks usually contain an amount of free silica which reacts as shown, but those of high alumina content, having free alumina, also react (not unexpectedly) and there is evidence to indicate that the brick least likely to show slag attack is one of a ' satisfied ' composition of about 44 per cent alumina. This figure is the maximum alumina content of clays natural to this country and it seems possible that indigenous bricks may be produced having the maximum all round resistance to slagging and spalling.

The texture of a firebrick has a good deal to do with its resistance to slag attack and it is found that a dense (low porosity) brick is best, presumably due to its reduced tendency to soak up the molten alkali and resultant slag. Penetration of the slag into the pores would increase the spalling tendency by destroying the open texture.

From the foregoing it is evident that the two forms of attack require opposing properties, i.e. a porous structure designed to resist spalling would be more prone to slag attack and vice versa. A compromise is necessary, but the real answer rather lies in the direction of dry oil supplies. It is not considered that other adventitious flux agents (e.g. vanadium oxide from fuel oil ash) occur in sufficient quantity to cause trouble to brickwork.

Another possible method of slag resistance is to coat the bricks with a refractory composition of a non-slagging nature such as chrome or zircon base but, in spite of many proprietary products, little success has been achieved so far. One interesting product was supposed to protect due to the surface tension properties of a vanadium oxide composition giving a slag repellant or non-wetting surface.

A secondary result of burning contaminated fuel oil, damaging to furnace refractories, are the 'bonded deposits' found in the various uptake passages of a boiler, particularly in superheater and economizer tube banks (FIG. 7). These deposits become quite massive and it is necessary, at intervals, for them to be removed before they block the passages. Formerly this was done by the troublesome and unpleasant method of scraping and brushing. When it was shown that the deposits were 75 per cent sodium sulphate, it was evident that they would be disintegrated by hot water hosing and this method of external boiler cleaning was adopted. Unfortunately, the products were washed down into the furnace and the refractories were thus saturated with the dissolved alkali. To guard against this the brickwork was coated with bitumastic paint, a very unpleasant operation and one using a material with a flash point in a confined space. Many alternative materials have been examined, the one showing most promise being a water emulsion of geon. This produces a tough, waterproof skin, has no flash point, is not toxic, burns away leaving no ash residue to attack the bricks and is easy to apply.

APPLICATIONS IN CURRENT NAVAL USE

Following the amendments to structure and material, the refractories at present being used in Naval boilers comprise the following types :—

Firebricks

Three classes are in use or are contemplated for the future :—

(*a*) A low grade product with an alumina content of about 35 per cent for use in ships not subject to arduous duty.

(*b*) A first quality British firebrick with an alumina content of about 42 per cent for all general service.

(*c*) A heavily 'boosted' type or sillimanite product in the 'super' class to match the top grade U.S. material.

Plastic Refractory

This is a mouldable firebrick composition to be rammed into shape and fired *in situ*. It has a composition similar to that used for firebricks of the first quality, as shown at (*b*). This material is becoming prominent in the revised furnace arrangements which drastically reduce the number of brick shapes. The old style arrangements of bricks to form a burner hole, using many patterns, is being replaced by plastic material rammed round a former. In fact, entire fronts are now being built up in this way, giving a monolithic structure, preliminary trials having indicated much increased durability of such an arrangement. Another asset, here, is the facility with which damage can be repaired, simply by ramming more plastic into any cavity that may develop. Its disadvantage is the unfired nature of the material in the layers remote from the flame.

Heat Insulating Material

(*a*) High temperature insulation forms a layer immediately behind the firebrick. This material is basically firebrick material rendered very porous by a frothing process or by introducing finely divided organic material during manufacture so that, on firing, the brick is left full of air spaces.

(*b*) Low temperature insulation is built as the final layer of a furnace wall, bedding on the steel boiler plates. The nature of the material is a soft, woolly asbestos made up in slab form.

Jointing Material

With the old types of brickwork the mortar was a mixture of equal parts of fireclay and crushed firebrick, wetted to a suitable consistency on the job. This was usually adequate as the brick shapes had a poor dimensional accuracy.

The introduction of the new-style brickwork with its tailor-made bricks makes possible the use of much closer joints, a very desirable feature, for with wider joints the material soon slips out and leaves a large crevice into which the flame easily penetrates to set up disintegration. For these closer joints, proprietary brands of bonding mortar are being supplied which are premixed and graded to give fineness and high strength and ensure uniformity of the cement.

Chrome Plastic Refractory

This product is a recent introduction with the appearance of water-wall boilers having studded boiler tubes. The space between the tubes is filled with the chrome plastic, the tube studs serving to retain the material in position to form a ' water wall'. It is material having a good rate of heat transfer which quickly sets hard in position and is composed of chrome (oxide) ore compounded with fireclay and setting agent.

Refractory Concrete

For the moment this is a material of the future, but it clearly has considerable prospective uses. It is a castable material which can be poured into suitable moulds, either *in situ* or separately, giving any required shape with a high unfired strength. When fired in a boiler wall for instance, the front layers become fully fired and develop the necessary strong ceramic bond, and the less fired back layers retain their green unfired cement bond. Until recently such materials were of a low grade type due to the presence of a large amount of hydraulic setting cement (fluxing agents), but products are appearing using cements of a non-fluxing character so that the finished concrete then has quite a high resistance to heat. There are difficulties in erecting shuttering for casting boiler fronts but these are mechanical and will probably be easily overcome.

LABORATORY EQUIPMENT AND TESTING

The same apparatus is normally employed for both routine production control and the assessment of new materials. Various forms of high temperature furnaces are required and the tests carried out cover a selection of the following properties :—

(1) Refractoriness.
(2) Refractoriness under load.
(3) Reheat–permanent linear change.
(4) Spalling loss.

(5) Slagging resistance.
(6) Workability.
(7) Thermal conductivity.
(8) Modulus of rupture.
(9) Apparent porosity and bulk density.

The first test uses a Hirsch type electric resistance furnace for assessing the temperature at which a small sample cone bends over ; the second uses a similar furnace to estimate the temperature at which a block shows 5 per cent compression under load.

The reheat test determines the inherent contraction or expansion remaining after the manufacturer's firing that might appear with unfortunate results during a subsequent firing in service.

The spalling test is interesting and new to this country, being based on a U.S. Navy test. It is designed to simulate rapidly alternating heating and cooling conditions, so often found in service, and to assess the loss suffered by a test panel subjected to those conditions.

To determine the resistance to slagging, a small brick-lined furnace uses a low consumption air-atomized oil burner in which fuel oil emulsions of sea water can be burnt so that bricks are slagged at temperatures and conditions similar to those of a Naval boiler furnace.

The workability of a plastic is a measure of the deformation produced in a small rammed cylindrical block when compressed by successive 2 in. drops of a 14 lb weight, and is a very good guide to the ' rammable ' qualities for erecting boiler fronts.

The thermal conductivity of insulating materials is determined by a flowing-water calorimeter method, multiple thermocouples being used to magnify the temperature rise due to heat transfer, and others to indicate conditions of parallel heat flow. The furnace uses ' Globars ' (silicon carbide resistance rods) to produce uniformly distributed hot face temperatures up to 1450°C.

A standard Denison testing machine is in service to determine the modulus of rupture of bricks, a guide to handling strength and resistance to damage in transit and storage. The jointing strength of bonding mortars and the dried and fired strengths of plastic refractory bars are also useful properties determined on this machine.

The foregoing summarizes laboratory or pilot scale apparatus giving a practical approach to service properties, but even these are inadequate to assess fully the possibilities of a material. This type of apparatus can compare and differentiate different makers' products, however, but full scale trials usually have to be carried out for the ultimate quality of materials.