MTI MANUAL NO. 9

REFRACTORIES FOR THE CHEMICAL PROCESS INDUSTRIES

Materials Technology Institute of the Chemical Process Industries, Inc.

MTI MANUAL NO. 9

REFRACTORIES FOR THE CHEMICAL PROCESS INDUSTRIES

by
Edwin Ruh
Consultant, Refractories and Ceramics
Pittsburgh, Pennsylvania

June, 1984

This document was prepared under the sponsorship of Materials Technology Institute of the Chemical Process Industries, Inc. (MTI) and is approved for release. All data and information contained in this document are believed to be reliable; however, no warranty of any kind, express or implied, with respect to the data, analyses, recommendations or any other information provided is made by MTI or the authors of this document and the use of any part of this document is at the user's sole risk. MTI, the authors, or any person acting on their behalf, assume no liability and expressly disclaim liability, including without limitation liability for negligence, resulting from the use or publication of the information contained in this document or warrant that such use or publication will be free from privately owned rights. Request for republication rights should be addressed to the Executive Director of MTI.

Published by
The Materials Technology Institute of the Chemical Process Industries, Inc.
1570 Fishinger Road • Columbus, Ohio 43221

Information on availability of this document can be obtained from the Executive Director of MTI.

FOREWORD

Refractories are being used in a wide variety of industrial applications principally by the metallurgical, ceramic, glass, and minerals-processing industries and to a lesser extent by the chemical process and petrochemical industries, and the public utilities. Indeed, manuals on refractories exist but as might be expected, none speaks specifically to the needs of the materials engineers of the chemical process and allied industries.

The MTI funded a project with Edwin Ruh, Consultant, Refractories and Ceramics, Pittsburgh, Pennsylvania, for preparation of a manual directed at providing the CPI materials specialist with an improved understanding of these important materials in the context of process industry applications. Professor Ruh is an internationally recognized authority in the field.

The manual covers not only refractories as heat-resistant materials but also as they are used for acid-proof construction. The manual discusses the various ways in which refractories are classified, their manufacture, the methods used to evaluate their physical and chemical properties, their properties, guidelines for designing refractory structures, installation, repair, maintenance and applications. Avoidance of problems and difficulties with refractories is emphasized.

A. M. Hall
Executive Director

Task Group 10 Membership

J. H. Van Sciver, Allied
J. B. Lawlar, Allied
R. A. Mueller, Cities Service
S. Morrow, Dow Chemical
F. W. Thompson, Du Pont
A. B. Misercola, Occidental
M. S. Crowley, Standard Oil (Indiana)
H. G. Clem, Union Carbide

TABLE OF CONTENTS

I INTRODUCTION

Refractories, or heat-resistant materials as they are sometimes called, are used in innumerable industrial processes involving heat or high temperature. Refractories may be defined as materials of construction which are capable of withstanding elevated temperatures and are used to contain heat as well as solid, liquid or gaseous substances in a structure. Frequently, as in the chemical process industries, refractory applications are at comparatively low or moderate temperatures; but the term is still applied universally, as for example in the case of acid-proof construction.

Most refractory products are sold in the form of brick and shapes which are mortared or placed together in the furnace or other vessel. However, advances in refractories technology over the last twenty five years have brought forth many new products known as monolithic refractory materials or specialty products. These include such refractory products as castables, plastics, ramming mixes, gunning mixes, mortars and bulk products. In many instances, these specialty products will give equal or more economical service than the more conventional brick and mortar construction.

In terms of dollar value, of the refractories industry annual sales of over one billion dollars approximately 66% is sold in the form of brick and shapes. The balance is sold as monolithic materials or specialty products—namely, plastics and ramming mixes 11%, castables 6%, gunning mixes 7%, refractory mortars 2.5%, and lump or ground material 7.5%. These monolithic refractory materials are applied directly in the vessel and are subsequently cured or heat treated in situ.

1.1 Brick and Shapes

Within the category of refractory brick and shapes, there are many types, i.e., chemically bonded, phosphate bonded, tar bonded, ceramic bonded or fused-cast. Within the subcategory of ceramic-bonded products, the refractory may be glass bonded, bonded with another mineral or crystal phase, or direct bonded. In the last case, similar or dissimilar materials are sintered or bonded by direct contact and reaction at very high temperatures.

Refractory bricks are sold and stocked in a fair number of common shapes which are usually available in a 2½" and 3" series. In the

3" series, which is more commonly used by the chemical process industries, the standard brick size would be 9" x 4½" x 3" and is called a 9" - 3" straight. Other very common shapes are shown in Figure 1.1. Special shapes are of course available but often bear a premium since the cost of the mold must be amortized over the total number of pieces made. For example, well over 1,000 different special shapes are used in the construction of a by-product coke oven battery, some of which are only required in limited numbers.

1.2 Mortars

Mortars, which are used for joining or laying refractory brick and shapes in the furnace or other vessel, are supplied dry or in a ready-to-use wet condition. Dry mortars are tempered with water or other suitable liquid to the proper working consistency on the site. The two principal classifications for mortars are (1) air setting—which usually contain sodium silicate and develop strong bonds on drying, and (2) heat setting—which develop a strong or ceramic bond only after the refractory structure is heated to an elevated temperature. Phosphate-bonded mortars, while generally considered in the air-set classification, are often thought of as a separate class since they form a cold bond by chemical reaction and a permanent bond when heated over 500° F. Needless to say, it is very important that the physical and chemical properties of the mortar match and be compatible with the brick or shapes that are joined.

1.3 Refractory Castables

A refractory castable, or refractory concrete as it is sometimes called, is a combination of graded or sized refractory aggregate and a suitable bonding agent, which after the addition of a proper liquid, may be poured into place to form the refractory shape and then sets or becomes rigid because of chemical action. The chemical-bonding agent generally is a type of calcium-aluminate cement which when mixed with water produces a hydrate bond in a manner not unlike that of the calcium silicates in Portland cement which hydrate to form concrete. After the castable is placed, time must be allowed for curing or completion of the hydration process. Before use, initially the castable must be heated slowly to remove the unreacted water and chemically-combined water. If the refractory castable suited for the application is installed, cured and heated properly, excellent service life may be expected. Additional attention is given to the installation of castables in Chapter VI.

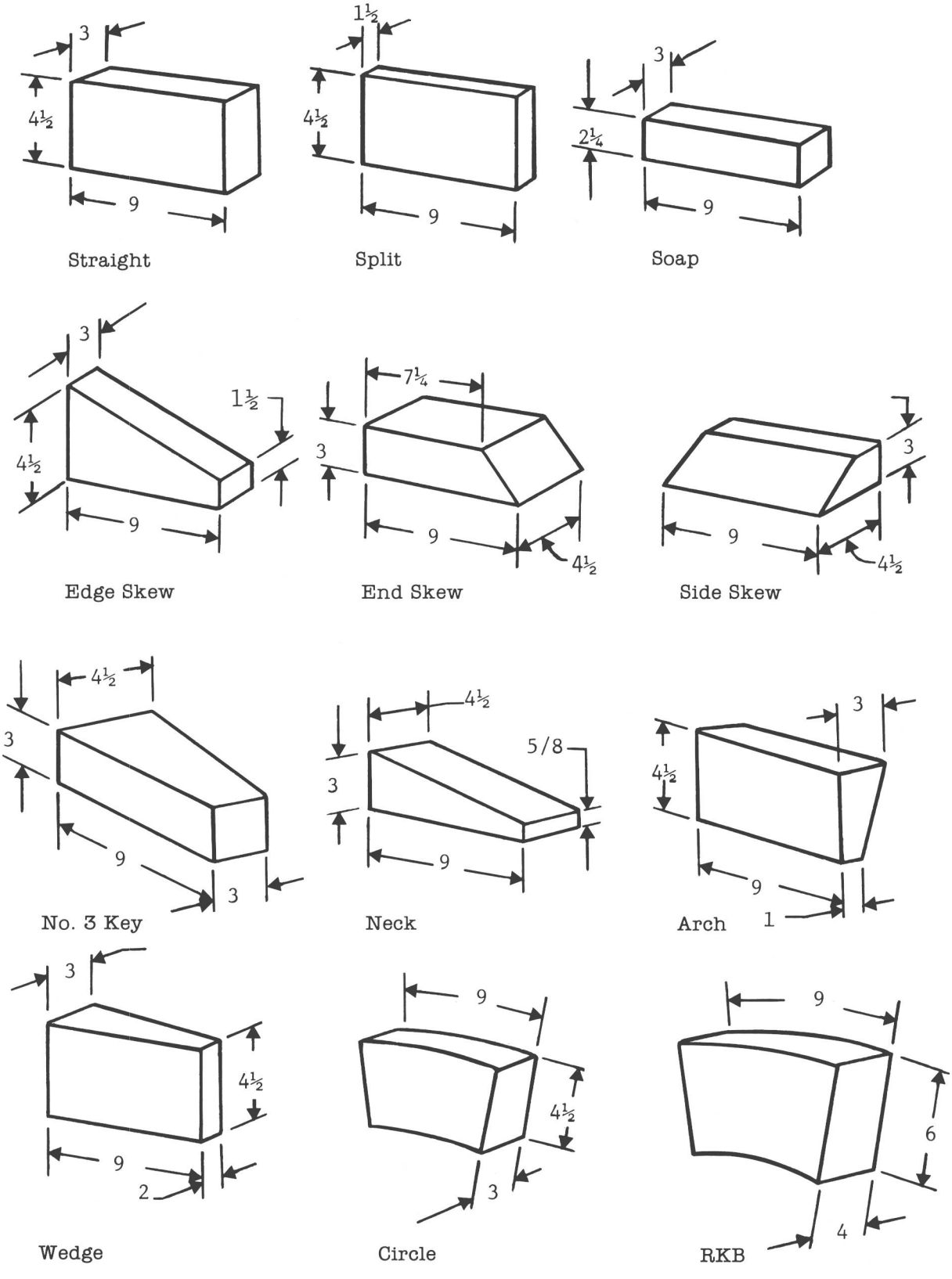

Figure 1.1

Common Refractory Shapes in the 9"-3" Series, excepting the Rotary Kiln Block at the Lower Right. Similar Shapes are also available in a 2½" Series. Above Dimensions are in inches. Standard ASTM Conversion to Metric Units
1½" = 38 mm; 2½" = 64 mm; 3" = 76 mm;
4½" = 114 mm; 6" = 152 mm; 9" = 228 mm.

1.4 Refractory Plastics

The term "plastic" used in the refractory sense differs greatly from the general connotation in the chemical industry. A plastic refractory consists of a graded-refractory aggregate which is tempered with sufficient water, extruded and formed into clots having suitable workability to be rammed into place to form the refractory lining. Thus, a plastic refractory is one that has plasticity or workability before being cured and heated. Plastics are delivered to the job site ready to use in cartons with an inner polyethlyene wrapper to prevent loss of moisture. Again, special drying and heating schedules should be followed to obtain the best service life.

1.5 Gunning Mixes

A gunning mix is a combination of graded-refractory aggregates and bonds which is applied directly to the wall of a furnace or other vessel through a pneumatic gun with water being added at the nozzle. Gunning mixes may be used to install the initial refractory lining in a new vessel, reline or repair a vessel when it is out of production; or in special cases, they may be applied in a repair mode to a hot vessel to keep it in production. Installation or placement of refractory mixes by gunning, or guniting as it is frequently called, requires experience and considerable knowledge and skill on the part of the nozzleman and the pneumatic gun operator. However, it is an installation method which is capable of placing a lot of refractory in a very short period of time. In the U.S., this method of placement is frequently used to line chemical process vessels such as secondary ammonia reformers and catalytic cracking vessels as well as to repair blast-furnace linings.

1.6 Ramming Mixes

A ramming mix is a graded-refractory aggregate usually tempered with water but not capable of being extruded, that has suitable properties to permit ramming into place to form a monolithic structure. As in the case of plastics, a pneumatic rammer is generally used to insure good compaction of the refractory. A ramming mix typically will contain less moisture than a plastic and, in some cases, may be dry rammed or vibrated into place.

1.7 Classification of Refractories by Composition

While refractory products are available in many forms, they are further divided into classes based on chemical composition. The classification includes silica, semi-silica, fireclay, high alumina, magnesia and in combination with chrome ore, zircon and zirconia, silicon carbide and carbon or graphite. Fireclay brick, which accounts for about 13.5% of all refractories sold, may be further subdivided into super-duty, high-duty, low-duty and pouring pit refractories. High alumina brick account for about 11% of all refractories sold and are classified by alumina contents of 50, 60, 70, 80, 85, 90 and 99 per cent alumina or by mineral content as mullite brick. Basic refractories, i.e., magnesia, magnesia-chrome, chrome-magnesia and chrome brick, account for 19%. The remaining segments of the market by class are: silica 2.4%, silicon carbide 2.8%, carbon and graphite stoppers and crucibles 2.1%, and zircon and zirconia 1.2%.

While insulating brick account for 2%, it is not possible to estimate the total refractory insulation market since many new products such as refractory fiber blankets, fiber board and shapes are not categorized by the Department of Census in the Current Industrial Report, Refractories MQ-32C. Table 1.1 shows a percentage breakdown of the various types and classes of refractories sold, taken from the most recent Census Report. Table 1.2 shows the 10-year shipment history of the various refractory products in the United States.

Table 1.3 contains a percentage breakdown of refractories by type of customer. If the categories of "contractors," "export" and "other" are considered to have the same end-use distribution, then the iron and steel industry would consume 63% of all refractories and the nonferrous metals industry another 9.2%. The ceramic industries would consume 11.8%, glass 6.2%, the minerals industries 6.0%, the chemical and petrochemical industries 2.5%, and utilities 1.1%.

Since all of these classes of refractories, whether by form or by composition, have different physical properties, it is important to know the requirements of the refractories' application. Chapter III discusses the physical properties of the various classes and forms of refractories and how they are measured. The composition, mineralogy and manufacturing process all have an effect on the physical properties.

TABLE 1.1

1979 Refractories Shipments by Kind

Description of Shipment	Percent		Value x $1,000	
Brick and Shapes				
Fireclay	5.2		90,126	
Ladle	2.9		50,454	
High-Alumina Ladle, Slidegates, Sleeves, Nozzles and Runners	2.7		46,077	
Superduty Fireclay	3.0		51,791	
High Alumina, 50 + %	7.9		135,948	
Mullite	1.1		19,599	
Extra High Alumina	2.6		44,168	
Insulating	1.9		33,049	
Pitch-Bonded Magnesia	4.4		76,507	
Pitch-Impregnated Magnesia	1.4		24,410	
Magnesia and Magnesia-Chrome	10.7		184,875	
Chrome-Magnesia and Chrome	2.1		36,603	
Silica	2.4		42,061	
Silicon Carbide	2.8		47,853	
Graphite Crucibles, Stoppers	2.1		36,440	
Clay Kiln Furniture	1.3		22,326	
Hot Tops	0.2		3,020	
Zircon, Zirconia, Dolomite, Fused Cast, Carbon and Other	10.0		172,221	
		64.7		1,117,528
Castables, Hydraulic Setting				
Fireclay	2.0		34,374	
High Alumina	1.4		23,981	
Basic and Other Non-Clay	1.4		24,903	
Insulating	1.1		18,918	
		5.9		102,176
Gunning Mixes				
Fireclay	0.9		15,440	
Basic, High Alumina and Other	6.0		102,513	
		6.9		117,953
Plastics and Ramming Mixes				
Fireclay	2.5		42,830	
High Alumina	2.8		48,314	
Other Non-Clay	3.1		54,520	
Magnesia-Chrome and Dolomite	2.5		42,932	
		10.9		188,596
Mortars				
Fireclay, Wet and Dry	1.4		24,421	
High Alumina and Other	0.8		13,577	
Magnesia and Chrome	0.2		2,852	
		2.4		40,850
Lump and Ground Form				
Fireclay	3.1		54,219	
Non-Clay	4.3		73,974	
		7.4		128,193
Not Specified by Kind				
Not Specified	1.8		31,837	
		1.8		31,837
TOTAL ALL REFRACTORIES		100.0		1,727,133

Source: U. S. Bureau of the Census, Current Industrial Report, Refractories MQ-32C, January 1, 1981.

TABLE 1.2

Value of Refractory Shipments by Kind x $1,000

	1980	1979	1978	1977	1976	1975	1974	1973	1972	1971
Brick and Shapes										
Fireclay	78,456	90,126	84,941	79,135	77,772	74,049	69,707	55,483	49,475	47,420
Ladle	47,191	50,454	49,882	48,936	43,720	38,406	43,232	35,618	32,213	26,519
High-Alumina Ladle, 50+%	*	46,077	7,914							
Sleeves, Nozzles, Runners and Slidegates	29,959		30,299	25,038	21,858	19,858	23,738	21,393	18,605	14,762
Superduty Fireclay	47,731	51,791	42,355	38,876	36,130	39,940	35,019	26,730	24,930	21,980
High Alumina, 50+%	135,421	135,948	114,357	90,791	78,943	82,051	81,552	64,135	51,845	39,780
Mullite	17,106	19,599	15,150	13,653	13,087	12,892	14,253	10,160	8,917	9,750
Extra High Alumina	40,096	44,168	33,539	28,650	24,215	20,345	16,475	11,433	8,629	9,188
Insulating	35,636	33,049	31,924	26,207	27,225	27,223	22,825	18,332	14,824	13,270
Pitch-Bonded Magnesia	58,374	76,507	69,600	46,599	40,731	37,275	39,185	39,492	30,475	20,704
Pitch-Impregnated Magnesia	19,098	24,410	23,228	19,095	20,529	20,240	19,535	17,450	12,518	12,170
Magnesia and Magnesia-Chrome	158,943	184,875	175,827	147,492	125,939	106,231	120,120	88,741	64,627	61,875
Chrome-Magnesia and Chrome	34,507	36,603	37,547	30,319	29,410	26,820	30,536	24,420	20,044	16,881
Silica	*	42,061	36,707	31,029	36,313	31,744	20,004	15,306	12,877	12,126
Silicon Carbide	56,489	47,853	35,245	30,337	27,155	25,131	25,644	20,296	13,347	13,313
Graphite Crucibles, Stoppers	34,509	36,440	31,072	26,825	25,030	21,762	23,863	18,391	15,759	13,774
Clay Kiln Furniture	23,845	22,326	19,423	17,790	15,632	13,438	13,140	13,568	11,883	9,724
Hot Tops	1,855	3,020	4,061	6,485	2,645	2,167	2,918	2,571	2,782	1,912
Zircon and Zirconia	*	172,221	148,244	15,999	13,299	17,436	11,380	8,785	6,571	6,944
Dolomite, Fused Cast, Carbon + Other				109,066	91,193	88,054	97,085	72,644	64,019	55,852
Castables, Hydraulic Setting										
Fireclay	33,025	34,374	33,750	32,912	28,505	35,633	24,956	28,273	24,528	21,029
High Alumina	21,932	23,981	19,909	17,729	15,673	15,266	28,384	15,665	12,813	10,308
Basic and Other Non-Clay	25,321	24,903	21,416	17,969	20,376	16,359				
Insulating	18,860	18,918	17,428	14,999	14,282	12,967	11,000	7,985	7,647	6,548
Gunning Mixes										
Fireclay	14,236	15,440	10,382	86,727	74,554	68,907	58,609	41,665	35,817	34,451
Basic, High Alumina + Other	101,512	102,513	91,458							
Plastics and Ramming Mixes										
Fireclay	35,210	42,830	26,791	28,123	23,931	19,494	17,007	21,858	18,162	15,577
High Alumina	47,458	48,314	38,414	28,866	23,289	16,145	14,678	24,149	19,394	16,281
Other Non-Clay	51,269	54,520	44,129	31,205	29,621	23,870	23,713			
Magnesia-Chrome and Dolomite	42,461	42,932	36,306	25,798	22,501	21,338	25,024	21,926	18,371	17,038
Mortars										
Fireclay, Wet and Dry	19,836	24,421	19,308	17,739	17,250	19,432	19,079	18,320	12,525	11,038
High Alumina and Other	12,748	13,577	10,742	9,103	7,541	6,778	9,649	7,047	5,995	5,922
Magnesia and Chrome	2,290	2,852	2,829	2,517	2,086	2,571	2,596	1,639	1,355	1,626
Lump and Ground Form										
Fireclay	62,179	54,219	38,438	26,957	26,155	16,282	14,589	12,999	10,046	9,224
Non-Clay	56,058	73,974	68,193	24,710	27,800	25,172	18,277	13,835	11,620	8,152
Not Specified by Kind	8,499	31,837	27,746							
TOTAL ALL REFRACTORIES	1604,567	1727,133	1498,554	1197,676	1084,390	1005,281	977,772	780,299	646,616	565,138

* Data withheld to avoid disclosing figures for individual companies.

Source: U. S. Bureau of the Census, Current Industrial Reports, Refractories MQ-32C, January 1, 1981.