

Studies on Special Basic Seawater Magnesia-Dolomite Refractories for LD Converters

Shimpei HIYAMA* and Shoichiro NAGAI**

(Received September 19, 1968)

This paper contains an account of the increasing use of basic refractory bricks in Japanese practice, particularly in connexion with the trend towards oxygen converter steelmaking. The production of seawater magnesia, which was developed to cope with serious difficulties in obtaining magnesian raw material, is described. The paper deals mainly with a special magnesia-dolomite clinker "Magdolo", which is produced from bittern or brine in the saltmaking plant, and the results are given of initial tests on it, relating particularly to composition and properties.

Introduction

Steel production in Japan has increased considerably since 1951. The production of refractories has also increased in this period although the ratio of refractories consumption to crude steel output has decreased, mainly owing to the use of different refractory materials and different steelmaking processes. The decrease in the use of silica brick and the increasing use of basic brick is most noticeable. This is principally due to the trend away from the open hearth towards oxygen converter steelmaking, and the change from silica brick to magnesia brick in the open hearth.

Refractories for LD Converters

The change in steelmaking processes, particularly in favour of the converter, is clearly shown in Table I.

The problem of refractories for the oxygen steelmaking converter is of great importance to the industry in Japan. Magnesia brick was first introduced in Japan with the LD converter; up to the mid-1930s it was very easy to obtain magnesite or magnesia from Manchuria and Korea, but since then it has become very difficult to obtain magnesian raw material. Consequently magnesite was first imported from India on a small scale before the LD process was introduced, then seawater magnesia clinker was imported from the USA, India, and even the UK, to meet a greatly increased demand from the steel, cement, and other industries.

In Japan, the production of seawater magnesia clinker was gradually increased during these years, as shown in Table II.

An interesting aspect of seawater magnesia production is shown in Table II. This concerns the use of the residue Ca(OH)_2 from carbide acetylene making and various

* Department of Industrial Chemistry

** Faculty of Engineering, Nihon University

Table I Increased converter steelmaking capacity, periods as shown

Company	1958	1959	1960	1961	1962	1963	1964	1965	Total 1000 tons/a
A	50×2	50×2 60×2	50×2 60×3	1700000 tons/a	50×2 60×3 100×2 80×2	50×2 60×3 100×2 80×2	3500000	50×2 60×3 100×2 80×3	4200
B			60×2	60×4	1200000 tons/a	60×6	1800000 tons/a	60×8	2400
C	42×2	42×2 60×2	1020000 tons/a	42×2 60×2	42×2 60×3 40×2	1620000 tons/a 600000 tons/a	42×2 60×3 40×2 60×1	42×2 60×3 40×2 60×1	1620 1200
E				40×2	400000 tons/a	40×2	40×2 60×2	40×2 60×3	1320
F				50×2	500000 tons/a	50×2	50×2 60×2	50×2 60×2	1100
G			30×2	300000 tons/a	30×2	30×2	30×2	30×2	300
H								30×2	300
I						35×2	350000 tons/a	35×2	350
J					15×2	150000 tons/a	15×2	15×2	150
Steel, tons/a	920000		2720000		6795000		10720000		12920
		1370000		4540000		9220000		1220000	
Oxygen (10 ⁶ m ³)	46	68.5	136	227	340	466	536	646	646

Table II Capacity of seawater magnesia clinker production, tons/a

Factory	Process and source	Present capacity	Extension capacity	Total capacity	Process
1	Seawater and slaked lime	100000		100000	By slaking of quick lime
2	Bittern and slaked lime	6000	4000	10000	
3	Seawater and slaked lime	50000		50000	Carbide acetylene residue
4	Seawater and slaked lime	15000		15000	
5	Seawater and slaked lime	2000	18000	20000	By slaking of quick lime
	Total	173000	22000	195000	Factory 5 for domestic use
6	Seawater and slaked lime		50000	50000	Carbide acetylene residue
7	Seawater and slaked lime		60000	60000	
8	Seawater and slaked lime	30000	30000	60000	
9	Seawater and slaked lime		30000	30000	
	Total	30000	180000	210000	
	Grand Total:	203000	202000	405000	

acetylene derivatives, where the carbide acetylene residue is very dirty and has no other commercial value. It is now being used to settle magnesium hydroxide from seawater or bittern.

Dolomite is obtained of which about 80% is being used by the iron and steel industries as dolomite clinker, about 10% by the ceramic industries, and about 10% for dolomite plaster, and dolomite powder fertilizer. Dolomite clinker is produced by rotary kiln and by shaft kiln on a small scale, and is mainly used for OH steelmaking. It is now mixed with magnesia clinker to produce baked magnesia-dolomite brick for the LD converter.

Special Seawater Magnesia-Dolomite Clinker

The common magnesia-dolomite refractories are obtained, as described, by mixing magnesia clinker and dolomite clinker produced separately, kneading with plastic binding materials of organic or inorganic origin, and baking or burning. The magnesia content of this magnesia-dolomite refractory for the LD converter is usually about 55-65%.

The authors are continuing the studies on seawater magnesia clinker products in factory 5 (referred to Table II). This magnesia clinker is of a special kind produced from bittern or brine in the saltmaking plant by separating magnesium hydroxide $\text{Mg}(\text{OH})_2$ with slaked lime milk water. In this precipitation of magnesium hydroxide, almost all boric acid in the seawater is accumulated in the bittern, and is settled with magnesium hydroxide. This magnesium hydroxide is very easily burnt to periclase, by the mineralizing effect of $\text{Mg}_3\text{B}_2\text{O}_6$, in which the content of B_2O_3 is about 0.03-0.05%. When the bittern is mixed with dilute sodium borate or borax solution of suitable boric oxide content, better periclase clinker can be very easily obtained, e.g. B_2O_3 content of 0.1, 0.3, and 0.5%.

The samples of seawater magnesia clinker produced in factory 5 were tested continuously, and proved to have the properties shown in Table III.

This seawater magnesia clinker is the only one in Japan and contains a small amount of B_2O_3 , which was precipitated with magnesium hydroxide from bittern containing almost all the B_2O_3 in the seawater. In these samples of magnesia clinker and magnesium hydroxide, there is a slightly higher content of calcium oxide CaO (2.5-3.5%), which is not high enough to affect adversely the present study, because the other mixing component (dolomite) contains a larger amount of lime (about 35-36%), as shown in Table IV. The samples of magnesium hydroxide and dolomite were analysed, and the results are given in Table IV.

The dolomite sample was ground to fine powder, mixed, kneaded with magnesium hydroxide to granule (about 10-15 mm dia.), and dried. This seawater magnesium hydroxide obtained from the saltmaking plant contains about 45-50% of water, which it is convenient to make into granules by granulator or pelletizer. In some cases, dolomite was burned to "light burned dolomite" (about 1000-1100°C) and ground to fine light burned dolomite powder, then mixed with seawater magnesium hydroxide and made into granules, as described above. The mixing ratios are shown in Table V, as dry matters, and the mineralizing matter Fe_2O_3 , B_2O_3 , or both, was added.

Table III Special magnesia clinker from bittern and slaked lime in the saltmaking plant

SiO ₂ , %	Fe ₂ O ₃ , %	Al ₂ O ₃ , %	CaO, %	MgO, %	CaO×Mg-(OH) ₂ /MgO	Grain size mm	Water Absorption, %
3.40	3.61	0.79	2.91	88.77	1.9	4-7	1.3
3.84	3.17	1.02	2.60	88.76	1.9		2.3
						3-4	1.8
3.40	3.61	0.79	2.91	88.79	2.2	4-7	1.7
						3-4	1.4
3.35	2.82	1.03	2.44	89.84	2.3	4-7	0.8
						3-4	0.6
3.45	3.07	1.03	2.87	89.12	2.3	4-7	1.1
						3-4	0.9
3.56	3.15	1.17	1.79	89.92	2.1	4-7	1.7
3.52	2.84	0.99	1.86	90.45	1.9		1.5
3.47	2.99	1.26	1.80	90.08	2.0		1.2
3.63	2.83	1.09	1.87	90.30	2.1		1.3
3.53	2.84	1.05	2.47	89.88	2.1		1.4
3.71	2.94	1.09	2.24	89.83	2.1		1.3
3.70	2.96	1.03	2.93	88.86	2.2		1.1
3.29	2.60	0.91	2.51	90.28	2.1		2.1
3.47	2.88	0.98	2.72	89.43	2.3		1.4
3.25	2.85	0.96	2.81	89.53	2.47		1.6
3.23	2.81	0.93	2.37	89.25	2.8		1.2

Note: B₂O₃ content is about 0.03-0.05%

Table IV Chemical composition of magnesium hydroxide and dolomite, %

	MgO	CaO	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	Loss on ignition
Magnesium hydroxide						
1	64.46	1.45	0.59	0.58	0.10	32.38
2	65.12	1.38	0.23	0.35		34.25
3	63.09	0.98	0.62		0.19	35.73
4	62.20	1.48	0.76	0.41	0.91	34.35
5	64.00	1.28	0.44	0.45	0.65	34.44
6	62.23	1.55	0.60	0.61	0.77	33.39
7	63.38	1.92	0.42	0.29	0.39	35.58
8	64.59	1.85	1.06	0.66	0.49	35.32
Dolomite						
a	18.52	33.49	1.42	0.04	0.64	45.09
b	18.92	34.63	0.34	0.04	0.34	46.42
c	18.83	33.70	1.15	0.55		45.16
d	18.28	35.18	0.16		0.34	45.78
e	18.29	33.25	0.72	0.63	0.17	46.64
f	18.79	34.75	0.35	0.51	0.74	45.17
g	18.63	34.81	0.43	0.13	0.45	45.44
h	18.89	34.82	0.35	0.14	0.53	45.21
i	18.68	34.59	0.51	0.12	0.37	45.67
j	18.11	34.15	0.40	0.46	0.31	46.74
k	20.91	33.23	1.46	0.19	0.44	44.23
l	20.50	32.45	1.46	0.15	0.65	45.08

Table V Mixing proportions of magnesium hydroxide, dolomite, and mineralizers, parts

		Dolomite (CaCO ₃ -MgCO ₃)	Magnesium hydroxide (Mg(OH) ₂)	Mineralizer Fe ₂ O ₃ B ₂ O ₃	
1	M ₅₅ F ₈	120	50	3	—
2	M ₅₅ F ₄			4	—
3	M ₅₅ F ₅			5	—
4	M ₆₀ F ₈	100	65	3	—
5	M ₆₀ F ₄			4	—
6	M ₆₀ F ₅			5	—
7	M ₆₅ F ₈	85	70	3	—
8	M ₆₅ F ₄			4	—
9	M ₆₅ F ₅			5	—
10	M ₅₅ F ₅ B	120	50	5	0.3
11	M ₆₀ F ₅ B	100	65	5	0.3
12	M ₆₅ F ₅ B	85	70	5	0.3
13	LDM ₆₀ F ₅	55	65	5	—
14	LDM ₆₀ F ₅ B			5	0.3

Note: "Light burned dolomite" used instead of dolomite.

Table VI Chemical composition of special magdolo clinker, %

	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO
M ₅₅ F ₈	2.35	1.21	3.20	35.55	55.88
M ₅₅ F ₄	2.20	0.99	4.23	35.31	55.00
M ₅₅ F ₅	2.23	1.06	5.80	35.19	54.55
M ₆₀ F ₈	1.99	1.38	3.07	32.89	59.13
M ₆₀ F ₄	2.00	1.38	4.09	32.62	58.83
M ₆₀ F ₅	1.96	1.36	5.10	32.51	58.43
M ₆₅ F ₈	0.94	0.95	3.16	30.75	62.96
M ₆₅ F ₄	0.94	0.93	4.11	30.68	62.37
M ₆₅ F ₅	0.91	0.90	5.25	30.13	62.55

Results of Testing of Special Basic "Magdolo" Clinker

The dried granule samples were "heavy burned" over 1710-1730°C (SK 27-28) to magnesia-dolomite ("Magdolo") clinker and analysed; the results shown in Table VI were obtained. The magnesia content is about 55-62%, which is a little less than the expected amount (65%), calcium oxide is about 30-35%, silica 1-2 %, alumina about 1 %, and ferric oxide varied from 3 to 5%, as expected by the mixing proportion.

Refractoriness was tested by the method defined in the Japan Industrial Standards (JIS R 2204) and the results of four samples M₅₅F₅, M₅₅F₅B, M₆₀F₅B, and M₆₅F₅B have refractoriness higher than SK 38 (1850°C).

The softening temperature under load 2kg/cm² was tested also by the method defined in the Japan Industrial Standards (JIS R 2209); the result shown in Table VII was obtained.

Table VII Softening temperature ($^{\circ}\text{C}$) under load $2\text{kg}/\text{cm}^2$ (load test)

	T_1	T_2	T_3
M_{55}F_5	1629	1748	1790
M_{60}F_5	1641	1752	1820
$\text{M}_{55}\text{F}_5\text{B}$	1647	1741	1840
$\text{LDM}_{60}\text{F}_5\text{B}$	1607	1695	1820

The slaking test and the autoclave test defined in the Japan Industrial Standards (JIS R 2211) were applied to the powdered sample and compared by the amount of residue on various sieves. This showed that generally the slaking tendency is comparable to the amount of lime content ($\text{M}_{55}, \text{M}_{60}, \text{M}_{65}$) and the addition of Fe_2O_3 , B_2O_3 , or both, as a mineralizer is effective to reduce the slaking tendency.

This special basic magdolo clinker was tested by microscopic and X-ray diffraction analyses, and its mineralogical components of M_{60}F_5 are roughly as follows: periclase MgO , about 60%; CaO , about 23%; $2\text{CaO}\cdot\text{Fe}_2\text{O}_3(\text{C}_2\text{F})$, about 8%; $3\text{CaO}\cdot\text{SiO}_2$, 3-6%; $4\text{CaO}\cdot\text{Al}_2\text{O}_3(\text{C}_4\text{AF})$, 2-3%; and $\text{Mg}_3(\text{BO}_3)_2$ or $\text{Mg}_3\text{B}_2\text{O}_6$, about 0.2%. The solid solution state of reddish brown $\text{C}_2\text{F}-\text{C}_4\text{AF}$ was clearly seen under the microscope.

The actual magdolo refractory brick is now being produced and will be tested in the LD steelmaking plant.

Summary

In Japan, seawater magnesium hydroxide and magnesita clinker are now obtained in increasing amounts, mostly by reaction between seawater and lime water from carbide acetylene making plants as calcium hydroxide "mud". In only one case, brine or bittern in the seawater salting plant reacts with lime water from quicklime slaking process to give magnesium hydroxide, which contains nearly all of B_2O_3 in the seawater. This magnesium hydroxide is mixed with dolomite powder or light burned dolomite powder, mineralizing agents Fe_2O_3 , B_2O_3 , or both in proper proportions, kneaded, granulated, and burned to special magnesita-dolomite or magdolo clinker at about $1710-1730^{\circ}\text{C}$ (SK 27-28). The various properties of this sample of special "Magdolo" (high magnesita-dolomite) clinker were examined to assess its suitability for use as raw material for refractory bricks for LD converters.

This special basic magdolo clinker has the main components: MgO , 55-63%; and CaO , 30-35%. The mineralizing effect by Fe_2O_3 (3-5%), is due to the solid solution between $2\text{CaO}\cdot\text{Fe}_2\text{O}_3$ (or 2CF or C_2F), and $4\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot\text{Fe}_2\text{O}_3$ (or 4CAF or C_4AF) as $2\text{CF}-4\text{CAF}$ (or $\text{C}_2\text{F}-\text{C}_4\text{AF}$) of low melting temperature. The small amount of B_2O_3 from seawater magnesita makes the special compound magnesium borate $3\text{MgO}\cdot\text{B}_2\text{O}_3$ or $\text{Mg}_2\text{B}_2\text{O}_6$, which has a remarkable effect as mineralizer for periclase formation.

The content of Fe_2O_3 (3-5%) and B_2O_3 (about 0.5%) gives the magdolo clinker superior resistance to slaking. The magdolo clinker (55-62% MgO) was clearly of superior quality, having high softening temperature under load $2\text{kg}/\text{cm}^2$.

This special magdolo clinker is now being tested as refractory brick for the LD-oxygen steelmaking converter, but final results have not yet been obtained.