

## Slagging Effect of Combustion Gas containing Sulfur on Refractories

Eung-Keuk Lim and Yong-Hi Lee

College of Engineering, Seoul National University

(Received June 12, 1974)

### 내화물에 대한 황 함유 연소가스의 영향

임 응 극 · 이 영 희

서울대학교 공과대학

요 약

본 연구에 있어서는 연료유의 연소에 의한 내화물의 부식을 연구하기 위하여 시멘트소성용 회절가마, 보일러 및 판유리제조용 탱크가마에 쓰이는 여러 내화물을 잘라서 그 가운데에 구멍을 파고 증유재의 주성분인  $V_2O_5$ ,  $Na_2CO_3$ ,  $Fe_2O_3$ , Fe 및 황산철을 미리 그 구멍속에 넣어 응용 확산시킨 다음 이들을 그들의 상용온도인  $1450^\circ C$ 로 황 함유량이 다른 연료유로 소성하여 얻은 결과는 다음과 같다.

일반적으로 5 산화 바나듐—알루미나, 고알루미나질 및 염기성 내화물; 산화나트륨—고알루미나질, 실리카나이트리질 및 염기성 내화물은 2%미만의 황 함유 연료유소성에 의하여 부식이 적고 3.5%이상의 황 함유 연료유소성지는 황에 의하여 대개 침식을 당하였다.

무수 아황산 분위기속에서 규산알루미늄 및 규석계의 내화점토질내화물은 산화철이 환원되어 색이 연해지고 고알루미나질 벽들은 색이 짙어지는 경향이 있고 산화철은 황산철로 변하여 풍화의 원인이 되어 침식을 당하게 되었고, 소성시간이 길면 질 수록 부식은 증가하고 황산소다보다 탄산소다에 의하여 훨씬 더 많이 부식을 당하였다.

#### 1. Introduction

The mechanism of the corrosion of refractories by a fuel oil combustion may be divided into two parts. One of the reasons is caused by sulfur in the fuel oil and another by the fuel oil ash. The latter will take a long time to get practical results as is caused by its deposition on the surface of refractories but  $V_2O_5$  in the fuel oil ash plays a role of a catalyst to oxidize  $SO_2$  to  $SO_3$  as described by Frazer and Kirkpatrick<sup>1)</sup>.

Anderson and Manlik<sup>2)</sup> have shown that nickel,

sodium or vanadium present in fuel oil tends to decrease the corrosion by the reductive effect, the magnitude of the effect increasing in the order given and boiler deposits resulting from the presence of iron in fuel oil tended to increase corrosion due to the formation of catalytically active surfaces, but nickel and vanadium showed a similar effect but to a less degree. Whittingham<sup>3)</sup> worked with gas flames and showed that there was a parabolic relation between the amount of  $SO_3$  formed and the sulfur content of the gas. He also showed that the amount of  $SO_3$  was reduced by various smokes or a number of

inhibitors which combined with atomic oxygen. Taylor and Lewis<sup>4)</sup> investigated the formation of  $\text{SO}_3$  in a small oil-fired furnace, the  $\text{SO}_3$  content of the flue gases being estimated from the dew point.

Many investigations<sup>5)</sup> have been concerned with the action of alkali vapors on alumina-silica refractories principally with the object of elucidating peculiarities that occur in  $\text{SiO}_2$  retorts that carbonize coal at  $1000^\circ\text{C}$ . The combined attack of sodium and vanadium oxides on alumina-silica refractories has received much less attention than the attack by soda alone and investigations appear to be confined to a study by McLaren and Richardson<sup>6)</sup> who conducted cone-deformation tests on alkali-vanadium compositions with three types of brick of varying alumina contents. Reactions between soda and a variety of aluminosilica compositions were investigated at temperatures ranging from  $800$  to  $1700^\circ\text{C}$  by Rigby and Rutton<sup>7)</sup>.

Trojer<sup>8)</sup> found that in the particular case of failure of the magnesite chrome brick linings of a cement rotary kiln, potassium iron sulfide  $\text{KFeS}_2$  was formed in cooler brick zones and deterioration by cracking occurred when the sulfide oxidized to sulfate and reacted with the brick constituents during a shut down.

There are few papers published in the slagging effect of vanadium-containing oil-ash on glass melting tank refractories. A review of the literature has shown that  $\text{V}_2\text{O}_5$  may be one of the most corrosive components of fuel oil ash with its high addition usually as much as 18-25%. Bush<sup>9)</sup> found that the effect on the properties of  $\text{SiO}_2$ , 43%  $\text{Al}_2\text{O}_3$ , and sillimanite bricks containing up to 2% of  $\text{V}_2\text{O}_5$  both with and without addition of up to 5% of  $\text{Na}_2\text{O}$  was almost negligible. Morsanyi<sup>10)</sup> has also proved that the wear of silica refractories is not likely to be increased by the presence of vanadium in the fuel oil.

Schulte<sup>11)</sup> observed that magnesia checker brick of regenerators could be corroded by boric acid and  $\text{SiO}_2$  might be attacked by sulfates at  $700^\circ$  to  $1,000^\circ\text{C}$ , although it is resistant to alkali attack. Mortil<sup>12)</sup> has also observed that basic bricks of regenerators is damaged by  $\text{SO}_3$  gas and  $\text{SO}_2$  gas from fuel oil burning is

catalyzed at about  $800^\circ\text{C}$  by the  $\text{As}_2\text{O}_3$  and  $\text{V}_2\text{O}_5$  vapor to form  $\text{SO}_3$  which reacts with  $\text{MgO}$ . Thus formed  $\text{MgSO}_4$  accompanies the expansion of its volume to collapse. Lehmann<sup>13)</sup> has studied that the basic brick in an open hearth was corroded by  $\text{V}_2\text{O}_5$ . The corrosion of mullite refractory by alkali vapor<sup>14,15)</sup> potassium vapor<sup>16)</sup> has been studied by Yamaguchi et al. He has also studied the corrosion of basic bricks by alkali vapor<sup>17)</sup> and boric oxide vapor<sup>18)</sup>.

There are many literatures on the effect of the reducing atmosphere on the properties of refractories but sulfur dioxide atmosphere. Miyatake and Furumi<sup>19)</sup> has noted that by burning basic bricks at  $1550^\circ\text{C}$  for 3 hours under reducing atmosphere, or oxidizing condition and in cycles of both conditions, expansion and loss in weight of the brick occurred and with cycling of the conditions, the decrease in compressive strength accompanied. Davis and Richardson<sup>20)</sup> noted that the corrosion of clay bricks by potassium salt vapor under  $\text{CO}$ ,  $\text{O}_2$ ,  $\text{H}_2$  and  $\text{N}_2$  atmosphere with the catalyst of Fe compound was observed. A review on the effect of  $\text{CO}$  on clay brick linings of a blast furnace was described by Hayashi<sup>21)</sup>. He stated the mechanism of carbon deposition and its catalytic action.

In this research work, reactions between slagging agents consisted of the components of Bunker C oil ash and 13 kinds of refractories used in power, glass and cement plants under the sulfur dioxide atmosphere have been investigated. The sulfur dioxide atmospheres were controlled by firing light oil which contained 1, 2, 3, 3.5 and 4% of sulfur respectively.

## II. Experimental method

Fuel oils contain various materials which remain as an ash after burning and it was natural to consider whether any of these substances could be causing enhanced attack on refractories. Most crude oils contain a number of substances, which if concentrated, could cause attack on refractories: these include  $\text{Na}_2\text{O}$ ,  $\text{V}_2\text{O}_5$ ,  $\text{Fe}_2\text{O}_3$  and  $\text{CaO}$ . The analytical results of Bunker C oil ash are shown in Table 1. Vanadium was analyzed by means of activation analysis and others by atomic absorption analysis. The ultimate

analysis of Bunker C oil is shown in Table 2.

**Table 1.** Quantitative analysis of Bunker C oil ash(%)

NiO	CuO	Fe <sub>2</sub> O <sub>3</sub>	Na <sub>2</sub> O	Pb <sub>2</sub> O <sub>3</sub>	ZnO	V <sub>2</sub> O <sub>5</sub>
4.20	0.196	7.57	7.07	0.058	0.466	15.55
Al <sub>2</sub> O <sub>3</sub>	SiO <sub>2</sub>	CaO	MgO	SO <sub>3</sub>	Ig. loss	Total
9.40	19.3	4.5	3.10	21.20	6.50	99.11

**Table 2.** Ultimate analysis of Bunker C oil(%)

C	H <sub>2</sub>	N <sub>2</sub>	O <sub>2</sub>	S	Ash
84.57	11.41	0.26	0.65	3.12	0.084

And the constituents of test specimens are shown in Table 3 respectively. The symbols of the table instead of the refractory names will be used hereafter.

**Table 3.** Constituents of refractories

Symbols Names Components	A	B	C	36	SM	S	M	M-M	M-H	F	B&W	Zac	Z
	Hi-Al	SK-34	SK-32	SK-36	Sili- manite	Silica	Chrom- Magnesia	Mono- frax-M	Mono- frax-H	Flux	B&W1 +80	Zac	Zirmul
SiO <sub>2</sub>	24.69	54.28	64.26	44.48	31.41	95.90	5.38	1.09	0.12	63.50	51.90	15.0	10.2
Al <sub>2</sub> O <sub>3</sub>	71.70	42.65	34.47	52.13	61.59	0.55	23.80	94.76	94.34	32.5	45.1	49.0	70.0
Na <sub>2</sub> O	—	—	—	—	—	0.10	—	3.58	5.17	0.88	0.3	1.5	—
CaO	0.20	—	—	1.39	0.06	2.90	—	0.28	0.12	0.20	0.1	tr	—
MgO	0.23	—	—	tr	0.48	tr	26.76	0.15	0.06	0.12	tr	tr	—
Fe <sub>2</sub> O <sub>3</sub>	1.28	2.30	1.50	1.30	1.79	0.50	—	0.06	0.07	0.75	1.4	0.1	—
TiO <sub>2</sub>	—	—	—	0.23	1.59	0.05	—	0.02	0.03	1.47	1.7	0.2	—
ZrO <sub>2</sub>	—	—	—	—	—	—	—	—	—	—	—	34.0	19.5
Cr <sub>2</sub> O <sub>3</sub>	—	—	—	—	—	—	34.49	—	—	—	—	—	—

A hole, a 3/4 inch diameter and a 1/2 inch deep, was made on one face of each refractory cube having a dimension of 2 inches a side to predeposit essential constituents of fuel oil ash before firing. About 3.7 grams of V<sub>2</sub>O<sub>5</sub>, 3.5 grams of Na<sub>2</sub>CO<sub>3</sub>, 5 grams of Na<sub>2</sub>SO<sub>4</sub>, or 3.6 grams of a mixture containing V<sub>2</sub>O<sub>5</sub>, Na<sub>2</sub>CO<sub>3</sub> and Fe<sub>2</sub>O<sub>3</sub> with the ratio of 15.55:12.1:7.07. This ratio found out from the chemical analysis of fuel oil ash was placed respectively in each test specimen. Each specimen was then placed in an electric furnace, the temperature being adjusted at 660°C and maintained for 3 hours for V<sub>2</sub>O<sub>5</sub>-containing test specimen (m.p. of V<sub>2</sub>O<sub>5</sub> is 660°C) and at 880°C for three hours for Na<sub>2</sub>CO<sub>3</sub>-Na<sub>2</sub>SO<sub>4</sub> and the mixture-containing (designated as "F") test specimens. The whole upper pictures of figure 2 to 4 show the resultant diffused area by these fluxes.

This method, one of testing methods for slag action of refractories, gives advantage of getting desired firing effect within a short length of time. By predeposition of essential constituents of fuel oil ash in

the refractories, the present experiment was intended to observe their effects in different sulfur dioxide atmospheres on refractories.

Efforts were made to predeposit cast iron instead of pure iron as its m.p. (1275°C) is lower than the latter (1535°C), but as cast iron was directly oxidized to Fe<sub>2</sub>O<sub>3</sub> without melting at its m.p., such intention was given up. Cast iron-containing test specimens were directly applied to the kiln only in the case of firing using fuel oil of 3.5% sulfur content without predeposition.

Fuel oils containing 1, 2, 3, 3.5 and 4% of sulfur were prepared respectively by adding appropriate amount of CS<sub>2</sub> to light oil with 0.75% sulfur and S. G. of 0.84. A burner has a combustion capacity of 2 gallons per an hour. It took 6 hours of combustion to get to a temperature of 1450°C, which was then maintained for 24 hours. Only one set of specimens was soaked for 36 hours with fuel oil of 3.5% sulfur content in order to observe the effect of different soaking time. The Orsat analysis of flue gas

leaving the combustion chamber showed  $\text{CO}_2$ :9.8%  $\text{O}_2$ :8.0%,  $\text{CO}$ :0.2% and the percentage of excess air was 60. These values were chosen and maintained throughout the firing because a sufficient oxidizing atmosphere is required to favor the oxidation of sulfur.

An oil firing kiln was constructed of high alumina bricks for side walls and basic bricks for the arch with a dimension of 27 inch long by 9 inch high by 9 inch wide.

### III. Results

Predepositions of slagging agents in slag holes have been taken place in electric furnace at a temperature of each melting point for a period of 3 hours. As shown in upper parts of Fig. 2, 3 and 4, the diffusibilities of each slag agent are evidently shown. The degree of diffusion can be seen in Fig. 1 by *stund spottos*.

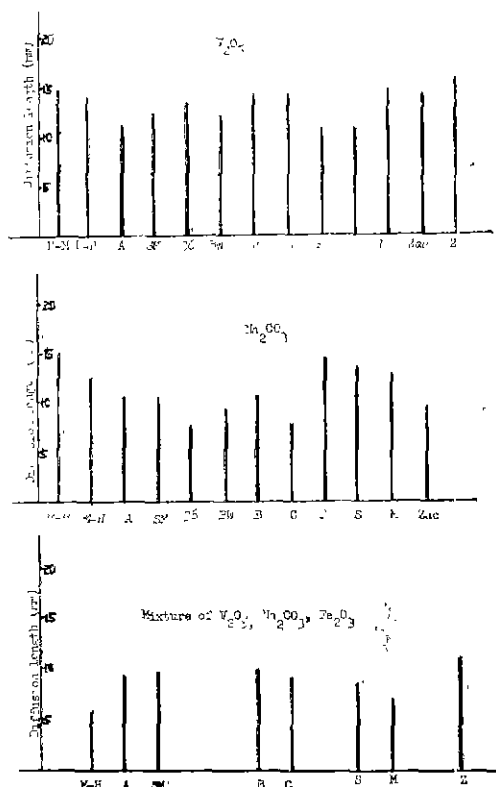


Fig. 1. Degree of diffusion of  $\text{V}_2\text{O}_5$ ,  $\text{Na}_2\text{CO}_3$  and the mixture of  $\text{V}_2\text{O}_5$ ,  $\text{Na}_2\text{CO}_3$  and  $\text{Fe}_2\text{O}_3$  on various refractories at temperatures of their melting points for 3 hours of soaking.

For example, the degree of diffusion of a specimen A was determined by measuring a distance diffused from the circle of the slag hole.

As there are 5 kinds of specimens, A1V, A2V, A3V, A3.5V and A4V, the value was taken as a mean value of five kinds. The values of diffusibilities of  $\text{V}_2\text{O}_5$  group exist between 10 and 15mm which are not so much different each other. 3.7 grams of vanadium pentoxide charged in the slag holes were fired for 3 hours at  $660^\circ\text{C}$  of its melting point. Its slag action with refractories was not found except diffusion. 5 grams of sodium carbonate charged in the slag hole were fired for the same period of time at  $851^\circ\text{C}$  of its melting point. The values of diffusion of sodium carbonate group exist between 5.5 and 15mm which is less than  $\text{V}_2\text{O}_5$  group. This may be due to the decomposition of sodium carbonate. It was found that the degree of diffusion increased with the alumina content decreased and with silica content increased. As shown in the upper part of Fig. 2, 3 and 4, it was found that the slight slag action had taken place.

3.6 grams of the mixture of  $\text{V}_2\text{O}_5$ ,  $\text{Na}_2\text{CO}_3$  and  $\text{Fe}_2\text{O}_3$  charged in the slag hole were fired in the same way at  $880^\circ\text{C}$ . The values of diffusibilities of the mixture group exist between 5.1 and 10.2mm which is less than  $\text{Na}_2\text{CO}_3$  group. Slag actions are also found in the mixture group.

Concerning Fig. 2, 3 and 4 the upper photographs show only the results of predepositions of  $\text{V}_2\text{O}_5$ ,  $\text{Na}_2\text{CO}_3$  and their mixtures at each melting point for 3 hours and the lower photos show the results which fired the predepositions at the temperature of  $1450^\circ\text{C}$  for 24 hours. The mark “·” is put in each lower photos, which means the specimen had gone through with aftertreatment.

The results were reported as to 13 kinds of test specimens shown in Fig. 2, 3, 4, and in Table 4.

In Table 4, V designates  $\text{V}_2\text{O}_5$ ; N,  $\text{Na}_2\text{CO}_3$ ; F, mixture of  $\text{V}_2\text{O}_5$ ,  $\text{Na}_2\text{CO}_3$  and  $\text{Fe}_2\text{O}_3$  as mentioned above; NS,  $\text{Na}_2\text{SO}_4$ ; and Fe, iron. Each specimen was designated and marked using abbreviations, as shown in Fig. 2, 3, and 4. For example, A1V means high-alumina refractory which was fired with fuel oil

Table 4 Corrosion of specimens fired with light oils containing 1, 2, 3, 3.5 and 4% sulfur.

3 \ 2	1	A	SM	B	C	F	S	BW	36	M	M-M	M-H	Zac	Z
V	1.	v-sl	vv-sl	v-sl	v-sl	v-sl	v-sl	sl	—	v-sl	—	—	—	—
	2.	sl	v-sl	v-sl	sl	v-sl	v-sl	—	none	sl	—	—	—	—
	3.	sl	v-sl	v-sl	v-sl	sl	v-sl	sl	v-sl	sl	none	h	m	none
	3.5	sl	v-sl	v-sl	v-sl	—	sl	—	—	sl	none	m	—	—
	4.	sl	v-sl	v-sl	v-sl	m	sl	sl	none	sl	—	—	—	—
N	1.	sl	sl	sl	m	sl	m	—	—	v-sl	—	—	—	—
	2.	m	m	sl	m	sl	m	sl	—	sl	—	—	—	—
	3.	m	m	sl	m	sl	m	—	m	sl	none	—	none	—
	3.5	m	m	sl	m	—	h	—	—	sl	none	—	—	—
	4.	m	m	sl	m	sl	h	sl	v-h	sl	—	—	none	—
F	1.	sl	sl	sl	sl	—	sl	—	—	sl	—	h	—	sl
	2.	sl	sl	sl	sl	—	sl	—	—	sl	—	sl	—	sl
	3.	sl	sl	sl	sl	—	sl	sl	—	sl	—	—	—	—
	3.5	sl	sl	sl	sl	—	sl	—	—	sl	—	—	—	—
	4.	sl	sl	sl	sl	—	sl	—	v-h	sl	—	h	—	sl
NS	3.	v-sl	v-sl	—	—	v-h	—	sl	—	v-sl	—	—	—	—
Fe	3.5	v-h	h	h	v-h	—	v-h	—	—	h	—	—	m	—
%abs.		12.3	8.2	11.0	11.0	5.9	13.9	6.9	7.2	6.2	0.0	—	0.0	4.6

Remarks: 1. Codes of specimens

2. Sulfur content in the fuel oil (%)

3. Constituents of ash; Abbreviation of V means  $V_2O_5$ ; N,  $Na_2CO_3$ ; F, mix. of V, N. and  $Fe_2O_3$ ; NS,  $Na_2SO_4$ ; Fe, iron; v-sl means very slight; m, medium; h, heavy; v-h, very heavy.

of 1% sulfur content and predeposited with  $V_2O_5$ .

Intensive tests have been made for such refractories. For instance, M-M and Zac refractories were examined only in cases of  $V_2O_5$  and  $Na_2CO_3$  deposition as they usually are used in contact with molten glass. Refractories are manufactured so as to meet their practical applications and their qualities have been all the time being improved.

Refractories used in the present experiment can be divided into several groups according to their main components: alumina brick group, M-M and M-H; basic brick, M;  $ZrO_2$ -containing high alumina brick group, Zac and Z; alumina-silica brick group of the others. Alumina content of high alumina refractories are decreasing in the order of A, SM, 36 and B&W. The content of  $SiO_2$  is increasing in the order of B, C, F and S as shown in Table 3. Results of the experiment was arranged in such orders.

To begin with, the effect of  $V_2O_5$  on refractories was examined. The M-M, which is the highest in alumina content, showed no sign of corrosion on refractories after firing, but only changing their colors to black, turned out to be stable in most of the atmospheres.

Test specimens designated as A, which is the secondly higher in alumina content, changed its original color (light brown) to a slight deeper one after firing, but as they were still light brown, they clearly showed the ring in which  $V_2O_5$  was diffused. In the specimen, A3.5V such ring appeared greenish grey and in specimen, A4V the ring color became thinner. This shows the evident influence by sulfur when the content of sulfur in the fuel oil exceeds 3.5%. As shown in Fig 2-1, the diffused ring in the specimen after firing was widened compared with those before firing but no sign of reaction was obse-

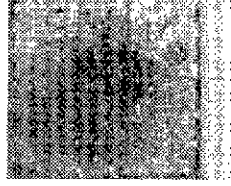
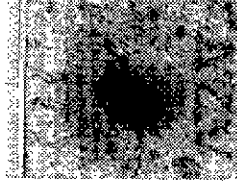
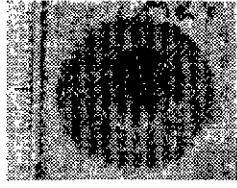


Fig. 2-1  
High alumina series

Fig. 2-2  
Sillimanite series

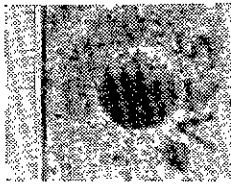
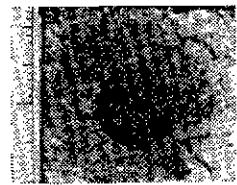
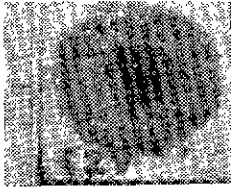
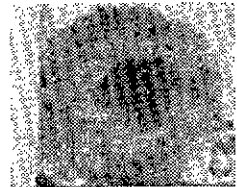


Fig. 2-4  
SK-32 series

Fig. 2-5  
Silica series

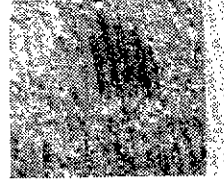
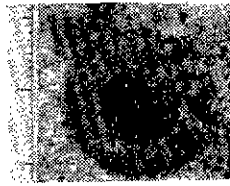
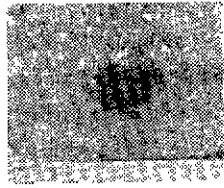
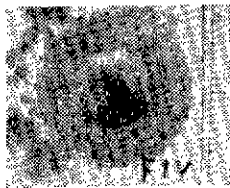


Fig. 2-6  
Flux series

Fig. 2-10  
Chrom-magnesia series

Fig. 2. Upper photos show the degree of diffusion of  $V_2O_5$  at its melting point for 3hrs of soaking, lower photos showing its slagging effect on each series of refractories after fired at 1,450°C for 24hrs.

rved. In the specimen, A2V and thereafter, the color of the diffused ring became thinner on firing, showing some cracks and slight corrosion.

The SM test specimens, which are 10% lower than the specimen A in alumina content, changed their colors of surfaces to deeper and darker ones, showing no sign of corrosion due to  $V_2O_5$ , and no cracking. Although the traces of  $V_2O_5$ -diffused ring still remained after firing at the elevated temperature as shown in Fig. 2-2, the greenish-grey colors in the specimens were very hard to find as the colors of specimens changed darker upon firing.

In the specimen B&W containing 45% of  $Al_2O_3$ , which is lower than the specimen SM, their colors became lighter with increasing sulfur content in fuel oil and a certain ring of them already showed slight corrosion where  $V_2O_5$  was predeposited before firing. Brown color of  $V_2O_5$  still remained in the specimen, B&W1V and specimen B&W2V showed brownish-grey, the colors of which became thinner with increasing sulfur content in fuel oil. But they showed severe diffusion even to the sides of the test specimens possibly due to their porosity. The specimen, 36 having similar composition as in the specimen B&W was more stable against  $V_2O_5$ , showing no sign of reaction but only slight traces.

With a decrease in the content of alumina, which corresponds to an increase in the content of silica, test specimens B and C showed a tendency to become whiter upon firing and the ferric oxide-spots in them appeared more clearly. These bleaching actions seem to be due to  $SO_2$  gases. Ferric oxides are believed to react with  $SO_2$  to form a certain type of ferric sulfate accompanying expansion and if these were maintained at high temperatures for a long time, they would be decomposed. The colors of traces of  $V_2O_5$  diffusion becoming thinner upon firing appeared pale black as a whole. Though the specimen F is similar to the specimen C in composition, they showed different phenomena each other. This may be caused by the different manufacturing processes. The former was fused cast in vacuo, whereas the latter was formed in an ordinary way.

Test specimens diffused with  $V_2O_5$ , showed their traces more clearly upon firing at the high temperature. For instance, the specimen, F1V showed a dark orange ring around the slag hole beside which the color became black. The specimen F2V showed no orange color but black ring around the slag hole and this portion was a little bloated. The specimen, F3V showed no bloating but only the black ring; whereas in the specimen F4V about one third of the orange color was still remained. On firing with fuel oils containing more than 2% of sulfur, test specimens showed a little cracking, the specimen, F4V being rather severe. No corrosion due to the combustion was found out in each case, as shown in Fig. 2-6.

The color change from light yellow to pale cream in test specimens S which is the highest in silica content seems to be due to bleaching effect of  $SO_2$ .

As shown in Fig 2-5, the trace of  $V_2O_5$  diffusion of the specimen S1V was almost disappeared. Each test specimen except S1V showed cracking, becoming heavier as was in the specimens S3.5V and S4V. There seems no reaction between  $V_2O_5$  and  $SiO_2$  in these cases. The influence of  $SO_2$  on test specimens was hardly appreciable.

Test specimens Z containing  $ZrO_2$  showed no reaction with  $V_2O_5$ , but the specimen Zac reacted with  $V_2O_5$  resulting in corrosion, vitrifying their surfaces, changing their color to yellow.

As shown in Table 4 and in Fig 2-10, test specimens M changed their color from light grey to black upon firing and the surfaces of which except the specimen M1V were vitrified showing a slight sign of reaction together with cracking, which became heavier with increasing sulfur content in fuel oil. Especially the vitrification of specimen M2V seems to be due to sodium vapors circulating above these test specimens during the combustion which are then deposited upon its surface while colling. Because the specimens M were placed on both sides of damper in the kiln located at the end of the combustion chamber, sodium vapor could easily deposit on their surfaces. The fact that the specimen M1V remained unreacted upon firing while M2V was vitrified, as shown in Fig. 2-10 seems to be related with sulfur

content in the fuel.

Results were obtained by the application of sodium carbonate as a slag of fuel oil ash to refractories as are shown in Fig 3 as follows.

Test specimen A showed corrosion to the inside; specimens SM, B and C showed corrosion accompanying bloating by the reaction with alkali; specimen S showed the moderate to severe slagging effect on the surface, changing its original cream color to light blue with a slagging coarse surface. Specimens F1N and F2N showed melted glass of  $Na_2CO_3$  in the hole without slagging, while F3N and F4N showed neither bloating nor glass but changing its grey color to vitrified dark brown together with slight corrosion. In contrast, E&W showed coarse surface with slight corrosion. These test specimens had experienced corrosion during preliminary treatment with  $Na_2CO_3$  and traces of its diffusion were observed though they were not clearly appeared in the figure.

Corrosion seems to be most severe with the specimen, 36 among these specimens. The fact that specimens M-M and Zac showed no corrosion by firing with light oils containing 3 and 3.5 or 4% of sulfur respectively, indicated their stability against alkalis. This is the reason why they are used for constructing bottoms and walls of glass tank furnaces in contact with alkalis.

Basic refractory M used either as checker bricks in contact with alkali vapor or as refractories for rotary kiln in contact with limestone, showed a ring in the portion where alkali vapor had contacted, but showed no corrosion during the preliminary treatment. During the aftertreatment, the combustions with fuel oil of different contents of sulfur, specimen M1N showed no corrosion while specimen M2 N and others showed slight corrosion being vitrified by alkali vapor, changing their color from brownish grey to black without exception, accompanying severe cracking.

$Na_2SO_4$  was also predi-posed in the slag holes of the test specimens in the same way as that of  $Na_2CO_3$ , only in case of firing with fuel oil containing 3% of sulfur. After firing, the specimen A3NS showed

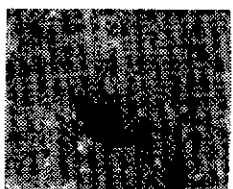
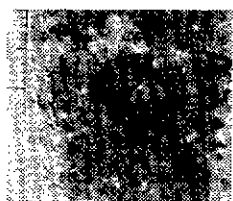


Fig. 3-1  
High alumina series

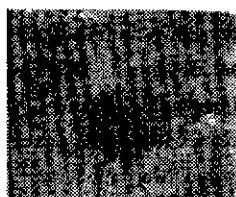


Fig. 3-2  
Sillimanite series

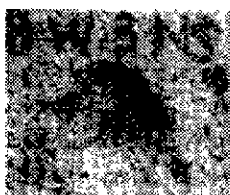
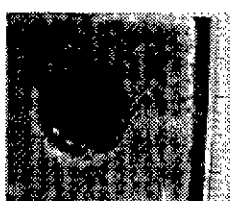
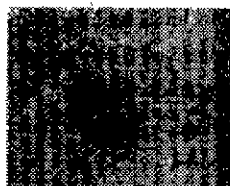


Fig. 3-6  
Flux series

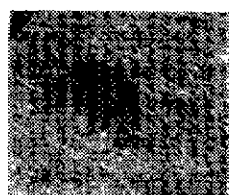
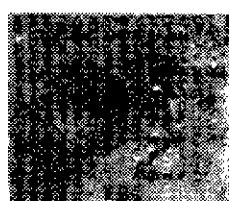


Fig. 3-10  
Chrom-magnesia series

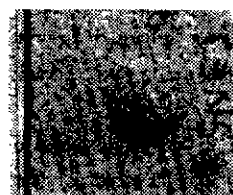
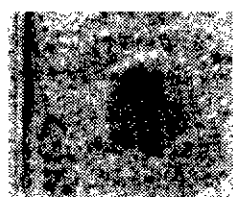


Fig. 3-4  
SK-32 series

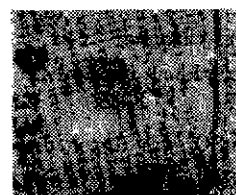
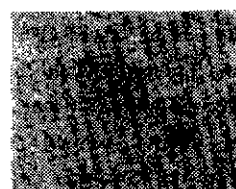
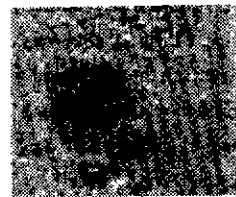


Fig. 3-5  
Silica series

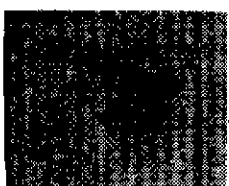
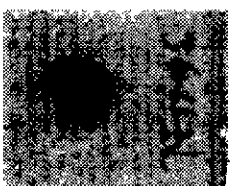


Fig. 3-11  
SK-36 series

Fig. 3. Upper photos show the degree of diffusion of  $\text{Na}_2\text{CO}_3$  at  $880^\circ\text{C}$  for 3hrs., middle photos, showing its slugging effect; the lower the slugging effect of  $\text{Na}_2\text{SO}_4$  on each series of refractories after fired at  $1450^\circ\text{C}$  for 24 hrs.

complete diffusion without any trace and without corrosion. The specimen SM3NS showed vitrified surface changing its brown color to dark brown. The surface of the specimen B&W3NS was completely bleached to white without corrosion. Only the specimen F3NS showed appreciable corrosion while the specimen M3-NS showed no corrosion, but their cross-section ap-



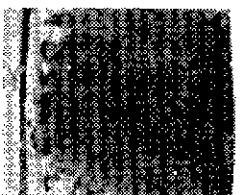
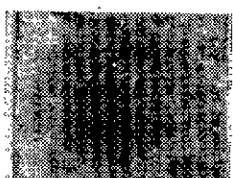
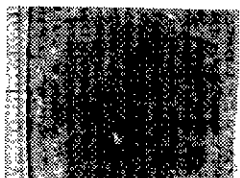
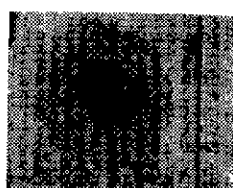
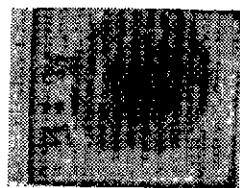


Fig. 4-1  
High alumina series

Fig. 4-2  
Sillimanite series

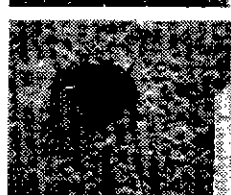
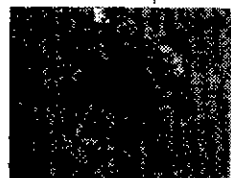
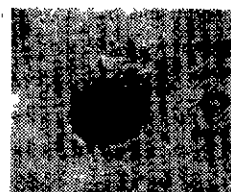


Fig. 4-10  
Chrom-magnesia series

Fig. 4. Upper photos show the degree of diffusion of the mixture of  $V_2O_5$ ,  $Na_2CO_3$ , and  $Fe_2O_3$  at  $880^\circ C$  for 3 hrs., the middle, showing its slagging effect; the lower, the slagging effect of iron on each series of refractories after fired at  $1450^\circ C$  for 24hrs.

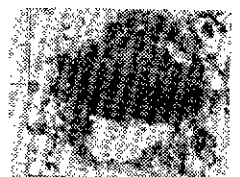
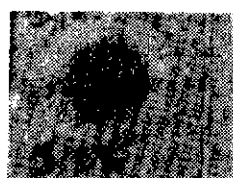
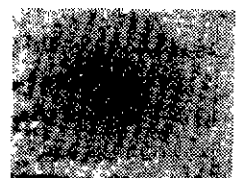


Fig. 4-4  
SK-32 series

Fig. 4-6  
Silica series

peared to be black. This seems ferric oxide was reduced to magnetite or wucstite compound inside the bricks during firing. They had almost same degrees of corrosion, as a whole.

Test specimens B and C showed slight corrosion with their brown surfaces and their black cross-sections were similar to test specimens SM. their degrees of corrosion were almost equal to the specimens SM. Judging from the fact that these degrees of corrosion are inversely proportional to alumina content, in other words, degrees of corrosion decreases in the order of A, SM, B and C, it is evident that silica is resistant to both irons and alkalis. This fact was also found in the preliminary treatment that test

specimens S showed little corrosion compared with other silicates. And their diffused portions were light brown.

Specimens S2F and S3F revealed a trace of yellowish ring traces around the slag holes by the aftertreatment, whereas specimens S3.5F and S4F revealed brown around the slag holes by the preliminary treatment. These colors might be due to  $Fe_2O_3$ . This means that both  $V_2O_5$  and  $Na_2CO_3$  were vaporized away remaining only  $Fe_2O_3$ .

Specimens M-H were also subject to the moderate corrosion, remaining iron slag in the bottom of the holes which hardly reacted with bricks and reduced to magnetite or wustite compound. This fact may be evident that the specimen M3.5Fe revealed pure iron in the bottom of the slag hole by aftertreatment even if corrosion was slight. The degree of corrosion of silica-alumina bricks on the soda increases with increasing silica content.

As shown in Fig 4-6, test specimens corroded by slag mixture designated as F appeared black at the inner side of the ring, light brown in the middle and dark blue in the outer shell. Traces of preliminary treatments are hardly appreciable in the specimen Z2F but clearly appeared in the specimen Z4F. The color of the specimen Z1F became thinner compared with others. The phenomena of color change in the innermost ring of black and middle of brown can be explained in the same way as above-mentioned and the dark-blue of outer shell will be the color of  $V_2O_4$ .

The specimen Zac was corroded by  $V_2O_5$  but resistant to alkalis. The specimen Zac 3.5Fe showed a yellowish surface vitrified and a certain molten metal which is believed to be iron, was observed at the bottom of the holes of the test specimens. Slight corrosion was also observed.

As is shown percent absorption and other data in Table 4 corrosion of refractories was increased with the increase in porosity of each refractory.

#### W. General Consideration

The results obtained in this work are confusing at

first glance, but on careful study of the fundamentals of the problem, some order is brought into them. Appropriate evidences were obtained for the effects of firing temperature and firing atmosphere on the corrosion tendency.

Relating sulfur content in the fuel oil, the sulfur is oxidized to give a mixture of  $SO_2$  and  $SO_3$ , during normal combustion in the presence of excess air. A small fraction of gas converts to  $SO_3$ , which in turn combines with the water vapor always present in combustion gases to form sulfuric acid. Its amount in the flue gas is generally small (20-50ppm.)

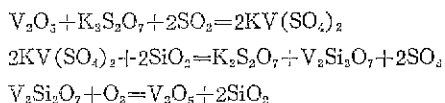
In many respects the conditions existing in the boiler are similar to those employed in the manufacture of sulfuric acid. In this process  $SO_2$  gas is passed over a catalyst usually an oxide of iron, vanadium and platinum, at a temperature of 800-1150°F. The contact time varies between 2 and 4 seconds and 90 to 98% of  $SO_2$  is converted to  $SO_3$ .

Less than 5% of sulfur in fuel oil is converted to  $SO_3$ , which represents a concentration of  $SO_3$  in the flue gas of not more than 0.005% by volume or 50 ppm. The amount of  $SO_3$  formed varies from unit and is influenced mainly by the fuel fired and the ash characteristics. The reaction of the trioxide with certain constituents of the residual fueloil ash (notably sodium) is an important contributory factor in the formation of the ash deposits, which are problems common to all types of power plant which burn these residual fuel oils. Catalytic surfaces consisting of iron oxide of the tubes, vanadium and iron-bearing ash deposits are present to accelerate the reaction. Because of selective deposition of ash constituents and longer residence time on the part of the slag deposits, marked differences in physical characteristics and chemical properties exist between slag and fly ash. Since the oxides of S contact fly ash and deposits throughout the combustion chamber it is natural to expect that these materials may affect the reactions leading to corrossions

##### a) Effect of $V_2O_5$

Bushy<sup>9)</sup> found that the use of fuel oils containing quantities of  $V_2O_5$  of the order of 0.04% was unlikely to cause any serious slagging of the superstruct-

ure fire clay brick. McLaren<sup>6)</sup> found also that  $V_2O_5$  did not form any crystalline compounds with  $SiO_2$  or  $Al_2O_3$ . It may however act as a mineralizer. The mechanism of the action of the catalyst was explained by Frazer<sup>1)</sup> as follows:



These phenomena were found all over the aluminosilicate refractories. The diffusion of  $V_2O_5$  into the bricks caused at its melting point a vanadium ring without slagging.

The specimens of aftertreatments were not corroded by  $V_2O_5$  or  $SO_2$  atmosphere, but the decoloration of the ring was shown. These are listed in Table 4 in the form of very slight, specimens A-V cracked except AIV were shown as slight. This cracking might be caused by mullite formation, sudden  $V_2O_5$  vaporisation or the direct contact of the flame. When the reaction between silica and alumina occurred substantially in the solid state, mullite formation was accompanied by a slight volume expansion.

When  $V_2O_5$  is present in a fairly high proportion, it may be a cause of refractory corrosion. Another property of  $V_2O_5$  which has focused attention on this constituent of the fuel ash is its ability to cause color changes both in glasses and refractories. Quite small quantities of  $V_2O_5$  has diffused into refractories and show a distinct grey-green coloration as appeared on the surface of specimen A3.5V both under pretreatment and aftertreatment. As the sulfur content increases the coloration became weaker as in the case of A4V. This discoloration may be caused by the bleaching effect of  $SO_2$ . This kind of effect may also be found in all over the aluminosilicate bricks such as specimens B and C. On the contrary the coloration of specimens A and SM became darker. This may be dependent on the iron content, specially on its fineness.

The colors of vanadium oxides are listed in the Handbook of Chemistry. Color changes shown on the aluminosilicate refractories are also dependent on the kiln atmosphere and specially on the position set in the kiln. The color of vanadium pentoxide shows

red-yellow; tetra oxide, black; and dioxide, grey depending on the degree of the reduction. Silica brick did not react with  $V_2O_5$  to show its deep or light red-yellow color depending on the kiln atmosphere.

The brownish grey specimen, chrom-magnesia brick (M) turned black and vitrified by the aftertreatment. This shows that specimen M reacted with  $V_2O_5$  slightly. Specimen Z<sub>ac</sub> reacted with  $V_2O_5$  alone moderately, turning the color of the surface yellow with some vitrification. But the Zinnul (Z) is not affected by  $V_2O_5$ . This may be caused by the content of  $ZrO_2$ .

#### b) The effect of alkali

Many investigations have been concerned with the action of alkali vapor on aluminosilicate refractories<sup>11-17</sup> principally with the object of elucidating peculiarities that occur in silica retorts that carbonize coal.

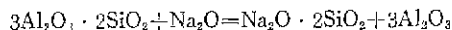
The  $Na_2O-Al_2O_3-SiO_2$  ternary diagram gives three sodium silicates,  $2Na_2O \cdot SiO_2$ ,  $Na_2O \cdot SiO$  and  $Na_2O \cdot 2SiO_2$ ; two sodium aluminates,  $Na_2O \cdot Al_2O_3$  and  $Na_2O \cdot 11Al_2O_3$ ; and three ternary compounds, albite ( $Na_2O \cdot Al_2O_3 \cdot 6SiO_2$ ), nepheline and its high temperature modification corneigeite ( $Na_2O \cdot Al_2O_3 \cdot 2SiO_2$ ).

Specimens A and SM consist largely of mullite. The soda first attacked the excess alumina grains in the specimen, forming sodium aluminate before decomposing the mullite to form nepheline and more sodium aluminate, accompanying volume expansion.

Whereas, when the soda diffused into them at 880°C, they did show very little volume expansion accompanying slight surface attack. When they were fired at a temperature of 1,450°C, the largest expansion occurred with mixtures that resulted in the formation of sodium aluminate. Rigby and Hutton<sup>1)</sup> reported that the mixture with a silica/alumina ratio of 60:40 showed a volume expansion of 19% after heating to 900°C and successive heatings between 1,000 and 1,300°C showed further slight expansive effects until appreciable melting occurred at 1,400°C. These phenomena were shown by specimens SM, B, and C. in Fig. 3-2, 3-4

The 95% silica brick showed that the soda was combined with the silica to form sodium silicates that melted near 800°C. Specimens C and F with a alumina/silica ratio of 30:60, corresponding roughly to the composition of a superduty fire clay brick,

showed medium shrinkage at 800°C. The soda might first be combined with cristobalite to form sodium silicate and then began to decompose the mullite to form nepheline and liberate corundum according to the reaction,



They concluded that when aluminosilicate refractories were attacked by soda, if the silica/alumina ratio is 1.5 or higher, the brick would generally show shrinkage at the hot face. The higher this ratio becomes, the higher the shrinkage will be and the lower the temperature of melt formation will be.

It was found that specimens 3G-3N and -4N were attacked by the soda most severely as these were exposed directly to the flame.

Specimens F-N were slightly reacted with the soda among aluminosilicate refractories as they were fused cast to have the lowest % absorption. Specimens M-M and Zac which are vitrified were not also reacted with the soda. It is clear that these two are most resistive to alkali attack.

It may also be expected that the  $\text{SO}_2$  reacts with clay minerals to form aluminum, calcium sodium and magnesium sulfates ( $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$ ,  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ,  $\text{Na}_2\text{SO}_4 \cdot \text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ ), and  $(\text{Na}, \text{K}) \text{Al}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$  may be present which are effloresced in varying degrees on the specimens fired in sulfur dioxide atmospheres.

As Morsanyi<sup>10)</sup> noted that whilst  $\text{V}_2\text{O}_5$  promoted the transformation of quartz and fused silica into cristobalite at 1,450°C, sodium carbonate and sodium sulfate showed far greater activity in promoting the transformation of fused silica, quartz and even cristobalite into tridymite, but all the specimens were cracked more or less even in the process of pretreatment.

Specimen M-M is a pure fused cast corundum brick without any clay bond. The soda formed sodium aluminate after heating to 800°C and this reaction was accompanied by a slight expansion which became very larger after heating to 900°C. A further appreciable expansion occurred after heating to 1200°C even after heating to 1600°C, but the specimen had not shrunk

to the original size. At 1300°C only beta-alumina was present along with sodium aluminate. But as specimen M-M was fused cast molded, it was not attacked by the soda at all.

c) Effect of the mixture of  $\text{V}_2\text{O}_5$ ,  $\text{Na}_2\text{O}$  and  $\text{Fe}_2\text{O}_3$

The  $\text{Na}_2\text{O}-\text{V}_2\text{O}_5$  binary diagram shows that three sodium vanadates exist and the compound  $\text{Na}_2\text{O} \cdot \text{V}_3\text{O}_5$  formed a melt at 650°C. Mullite appeared to be resistant to the action of  $\text{V}_2\text{O}_5$  up to 1700°C. Vanadium compounds act as a mineralizer so that sodium aluminosilicates are formed after heating to 800°C in the presence of vanadium oxide whereas they do not appear below 900°C when soda alone was the slagging agent.

The effect of the presence of vanadium oxide was twofold: First, it combined with the soda to form sodium vanadate, which resulted in less soda being available to form nepheline or sodium aluminate with the silica-alumina specimens, on the other hand, sodium vanadate acted as a flux and increased the total amount of melt at any given temperature.

## V. Conclusion

Reactions between slagging agents which consist of components of Bunker C oil ash and a variety of refractories under the sulfur dioxide atmospheres have been investigated. Slagging agents such as vanadium pentoxide, sodium carbonate, sodium sulfate,  $\text{Fe}_2\text{O}_3$ , Fe and some of their mixture were predeposited in the slag hole in order to get the results earlier. After they were fired in a kiln at a temperature of 1450°C with 24 and 36 hours of soaking time and with light oil containing 1 to 4% sulfur, the results presented in this paper brought out the following facts.

- 1) From the data of test pieces, A-V, M-V, SM-N, M-N and F-V series, fuel oils containing less than 2% of sulfur caused very little corrosion on refractories as a whole.
- 2) Silica-alumina series and silica refractories were subject to alkali attack.
- 3) Most of the refractories were subject to severe corrosion by iron when fired with fuel oil containing more than 3.5% of sulfur.
- 4) SK-34, SK-32, B&W, Zirmul, (36) and silica

bricks revealed a tendency to become lighter in color whereas high alumina and sillimanite bricks were deepened their colors.

- 5) Iron existing on the surfaces of each refractory has already been oxidized to  $Fe_2O_3$ , but was liable to be changed to the sulfate under the sulfur dioxide atmosphere to be effloresced.
- 6) Sodium sulfate attacked most of the refractories far less than sodium carbonate in spite of the same soda salts.
- 7) Corrosion of refractories was increased with the increased firing time.
- 8) Corrosion of refractories was increased with the increase in porosity of each refractory.
- 9) The degree of corrosion by  $V_2O_5$  to each refractory exists between 10 to 15mm at the melting point of  $V_2O_5$ .
- 10) The degree of corrosion by sodium carbonate to each refractory exists between 5.5 and 15mm at the melting point of sodium carbonate. The degree of diffusion increases as the alumina content decrease and silica content increase.
- 11) The degree of corrosion of the mixture of  $Na_2CO_3$ ,  $V_2O_5$  and  $Fe_2O_3$  in each refractory exists between 5.1 and 10.2mm at 880°C.

#### BIBLIOGRAPHY

- (1) J.H. Frazer and W.J. Kirkpatrick, "A New Mechanism for the Action of the Vanadium Pentoxide Silica-Alkali Pyrosulfate Catalyst for the Oxidation of Sulfur Dioxide". *J. Am. Chem. Soc.* 62, 1659-60(1940).
- (2) Donald R. Anderson and Frank? Manlik, "Sulfuric Acid Corrosion in Oil-Fired Boilers-Studies on Sulfur Trioxide Formation"., *Trans. ASME*. 80(8), 1231-37(1958).
- (3) G. Whettingham, "Third Symposium on Combustion, Flame and Explosion Phenomena"., pp.453(1949).
- (4) R.F. Taylor and A. Lewis, " $SO_3$  Formation Oil Firing"., *A Paper 151 to 4th Int. Congr. Industr. Heating*, (1952).
- (5) F.H. Clews. A. Green. and A.T. Green, "Action of Alkalies on Refractory Materials at 1000°C". *Trans. Ceram. Soc.* 36(4), 217-24 (1937). "Experiments in Alterations in Strength when Refractory Materials Are Exposed to KCl Vapor at 1,000°C"., *ibid.* 426-29(1929).
- (6) J.R. McLaren and H.M. Richardson, "Action of Vanadia on Alumino-Silicate Refractories". *Trans. Brit. Ceram. Soc.* 58(3), 188-97 (1959).
- (7) G.R. Righy and R. Hutton, "Action of Alkali and Alkali-Vanadium Oxide Slags on Alumina-Silica Refractories"., *J. Am. Ceram. Soc.* 45 (2), 68-73(1962).
- (8) Felix Trojer, "Deterioration of Cement Rotary Kiln by Alkali Sulfides and Sulfates"., *Am. Ceram. Soc. Bull.* 47(7), 630-34(1958).
- (9) T.S. Bushby, "A Study of the Effect of Fuel Oil Ash in Glass Tank Refractories". *Glass Techn.* 4(1), 18-22(1963).
- (10) Anna V. Morsanyi, "The Effect of Vanadium Compounds on Silica Refractories". *Glass Techn.* 4 (1), 23-28(1963).
- (11) Klaus Schulte, "Über die Korrosion von Magnesitgittersteinen durch Alkalisulfate und  $SO_3$ "., *Glastech. Ber.* 38(11), 457-61(1965).
- (12) G. Mortl, Radentheim, *Radex-Rundschau*(4-5), 315-20(1968).
- (13) H. Lehmann, S. Kienow and P. Artelt, "Korrosionfeste Magnesitsteine durch  $V_2O_5(I-II)$ ". *Tonind. Ztg.* 88(7/8), 153-59(1964).
- (14) S. Okawara and A. Yanguchi, "Corrosion of Mullite Refractory by Alkaline Vapor". *J. Ceram. Assoc. Japan* 77(6), 208-16(1969).
- (15) A. Yamaguchi, S. Okawara and A. Yamanka, "Corrosion by Vapors of Potassium Salts." *ibid.* 77 (11), 357-66 (1969)
- (16) Akira Yamaguchi, "The Effect of Acid Radical Components of Alkali Salt on Corrosion of Mullite and Zircon by Alkaline vapors"., *ibid.* 79 (4), 124-31 (1971).
- (17) Akira Yamaguchi, "Corrosion of Basic Bricks by Alkaline Vapors"., *ibid.* 237-49 (1970).
- (18) S. Okawara and A. Yamaguchi, "The Corrosion Process of Magnesia Brick by the Vapors of Boric Oxide"., *ibid.* 76 (2), 29-36 (1968).
- (19) K. Miyatake and K. Fujiwara, "Effect of Atmo-

- sphere on properties of Magnesium-Chrome Brick", *Taikabutsu Kogyo* 13(65), 337-48 (1962).
- (20) W.R. Davis and H.M. Richardson, "Effect of Alkali Salt on CO Corrosion", *Trans. Brit. Ceram. Soc.* 59(3), 75-86(1960).
- (21) Takeshi Hayashi, "Effect of CO on Refractories I, II", *J. Ceram. Assoc. Japan* 71(1) C7-15, (3), C97-109(1963).