2-2 Adhesion Mechanism of Hard Coating

(1) Hard coating has mineral composition of $CaSO_4$ and CaO as main, and of $K_2SO_4 \cdot 2CaSO_4$ is only partially observed. $CaSO_4$, CaO, $Ca_3Fe_2(SiO_4)_3$ are observed as well as $2CaO \cdot Al_2O_3 \cdot SiO_2$ especially on boundary of coating layer with refractory material. The latter is formed by reaction between coating and refractory material.

(2) Formation temperature of hard coating is 1000 ℃ ～ 1200 ℃, which is rather high.

(3) Low melting point compound is hardly observed in boundary layer on refractory material after service life. $CaSO_4$(anhydrous gypsum) is observed in the form of laminated layers to the hot face side.

(4) Judging from (1)～(3), formation and adhesion of hard coating is mainly caused by anhydrous gypsum, and the adhesion mechanism is presumed as below.

① Adhesion startes with adsorbing of alkali components and raw material dust in the atmosphere. Since the atmosphere temperature is high, alkali components are dominated by vapor phase reaction. As the result, rate of reaction is determined and coating development is made quick.

② Adhered raw material dust reacts with SO_3 component in the atmosphere, and forms $CaSO_4$. Crystallinity of this $CaSO_3$ is graded up , sintered and grows rigid coating under the influence of temperature and alkali.

③ Laminated layers of $CaSO_4$ toward hot face that coating is developed by the repetition of processes ①～③.

④ Main component of hard coating is $CaSO_4$. It can be concluded that plugging is caused by mechanical adhesion.

<u>Adhesive Mechanism of Hard Coating</u>

Adhesion of alkali components in the atmosphere and raw material dust

Adhered raw material dust reacts with SO_3 component in the atmosphere, and forms $CaSO_4$

Formed $CaSO_4$ grows to hard coating of high crystallinity under the influence of temperature and alkali

Formed $CaSO_4$ laminates in the direction of hot face, and repetition of above mentioned processes develops coating

3 The characteristics of refractories to prevent plugging

The properties required for raw material adhesion reduction refractories are:

1) Prevention from penetration of alkali and its salt including CaO.
2) Resistance to abrasion
3) Strong resistance to spalling

The research was proceeded from these three view points.

3-1 Proof Test of Anti Alkali Resistance

Prepared test specimens were unburned and burned low cement castables which were mixture of alkali resistant chamotte and silicon carbide, burned silicon carbide brick, and fireclay low cement castable. The quality of the test pieces is shown in Table 1.

table - 1. Quality of Test Sample

Sample NO.	1	2	3	4	5	6	7	8
Name	NEOCAST DC30	NEOCAST DC60	NEOCAST DC80	ETS 15	ULOC BDC30	ULOC BDC60	ULOC BDC80	SCH
Quality	Low cement castable				Burned castable block			brick
	SiC 30%	SiC 60%	SiC 80%	chamotte	SiC 30%	SiC 60%	SiC 80%	SiC 85%
Max. service temperature (℃)	1500	1500	1500	1500	1500	1500	1500	1700
Apparent porosity (%)	9.0	8.5	8.0	8.5	14.0	13.5	12.5	18.6
bulk density	2.30	2.45	2.62	2.20	2.25	2.42	2.60	2.41
Crushing strength(kgf/cm^2)	600	850	900	600	1000	1100	1200	780
Modulus of rupture (kgf/cm^2)	120	170	180	105	180	200	250	160
Thermal expansion(%)1000℃	0.45	0.48	0.48	0.45	0.45	0.48	0.48	0.48
Thermal conductivity(%) (kcal/mh℃) 350 ℃	3.8	7.2	12.5	0.9	4.1	7.8	13.1	2.0
Chemical composition(%)								
SiO_2	33	18	5	46	33	18	5	8
Al_2O_3	29	18	10	48	29	18	10	6
SiC	30	60	80		30	60	80	85

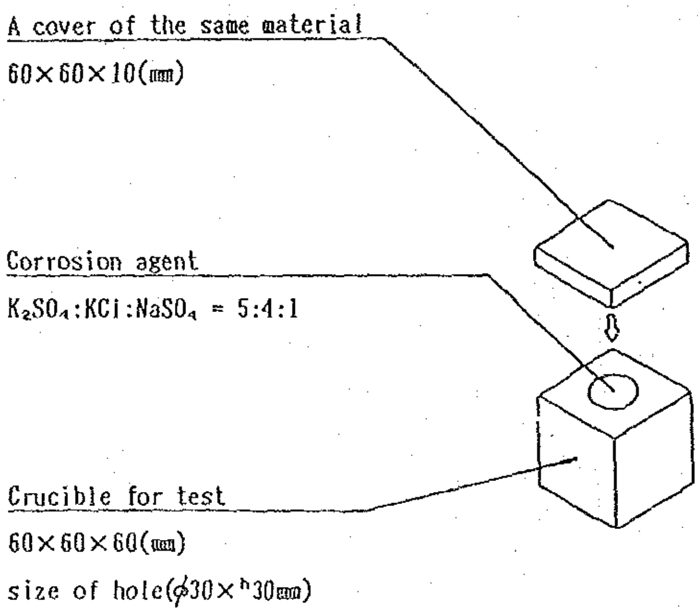
(1)Test Method

① Make crucibles for test ; cut test pieces into 60×60×60 mm and make a hole of φ30×30 mm by core drill.

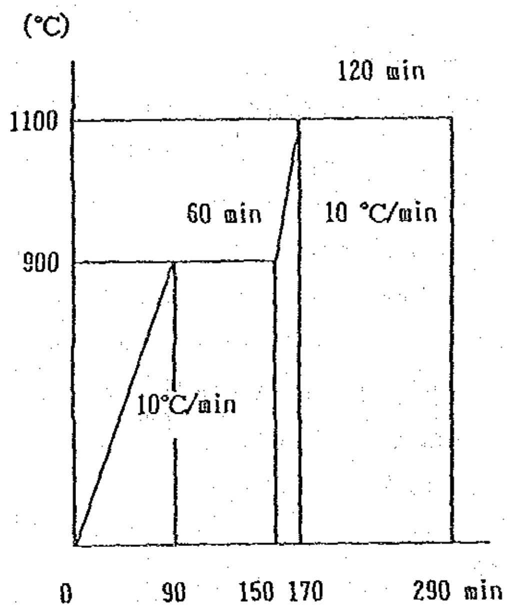
② Fix corrosion agent ; mix potassium sulfate (K_2SO_4), potassium chloride (KCl), sodium sulfate (Na_2SO_4) in the proportion 5:4:1. Fill 25g of the agent in each crucible and close it with a cover of the same material as a crucible.

③ Heat each crucible in an electric furnace up to 900℃ by 10℃/min and keep for one hour, then heat it up to 1100℃ by 10℃ / min, and keep 1100 ℃ for two hours, and then cool down naturally.

Preparation of a crucible



Heating curve



(2) Result of the Test

Figure 1 shows the condition of cross section of the crucibles and the covers after firing. Figure 2 and 3 show EPMA observation of reaction faces of the crucibles.

(3) Summary

① Test specimens are categorized into several types as below by observing cross sections of each crucible.

NO. 1~3(unburned): Corrosion agent hardly penetrated. The more SiC was contained the higher reactivity is for the covers.

NO. 5~7(burned) : These were almost same as "unburned", but penetration was still less. Same for the covers.

NO. 4(low cement castable) : Penetration of corrosion agent was almost through. Reaction was little for both the crucible and the cover, but cracking was particially observed.

NO. 8(burned brick) : Corrosion agent almost completed penetration, and both of the crucible and the cover had little reaction with corrosion agent. Quality change by corrosion agent was not observed so much.

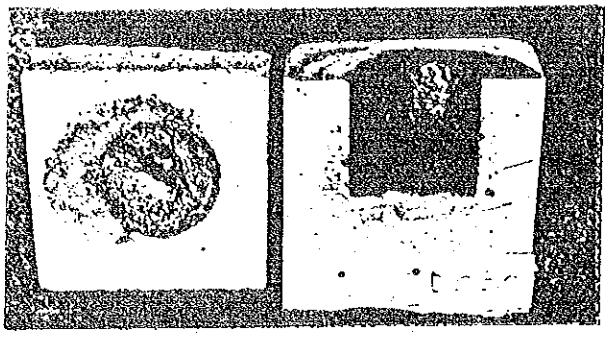
② In the observation by EPMA, the result was same as that of afore mentioned cross section. The more silicon carbide was contained, the higher penetration resistance and reactivity were. This was true for burned pieces rather than unburned ones. However penetration of corrosion agent was remarkably high in burned silicon carbide brick and fireclay low cement castable.

③ Compared with alkali resistant chamotte-silicon carbide low cement castable, porosity of burned silicon carbide brick was high, and the mean radius of pores was 1.65 μm : about 20 times bigger than 0.08 μm of the former shown in Fig. 4. These factors made penetration of corrosion agent easy.

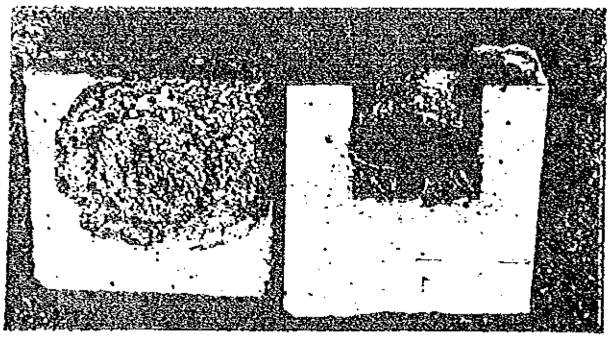
④ Fireclay low cement castable is not greatly different in porosity and mean pore radius, however different kind of aggregate is considered to have served to make penetration of corrosion agent higher.

Results of Anti Alkali Properties Test

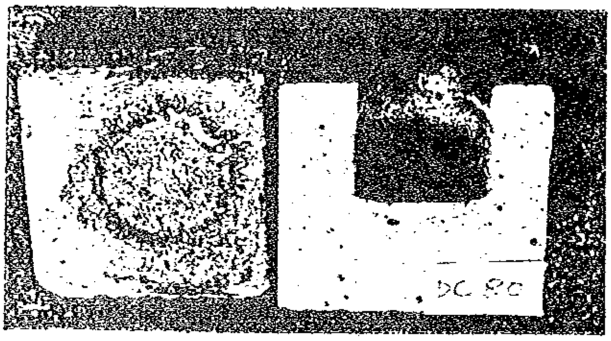
Sample NO.	1	2	3	4	5	6	7	8
Quality	low cement castable				burned castable block			burned brick
SiC content	30 %	60 %	80 %	chamotte	30 %	60 %	80 %	85 %
Anti-penetration property (crucible)	○	◎	◎	X	◎	◎	◎	X
Reactivity (cover)	○	◎	◎	X	○	◎	◎	△



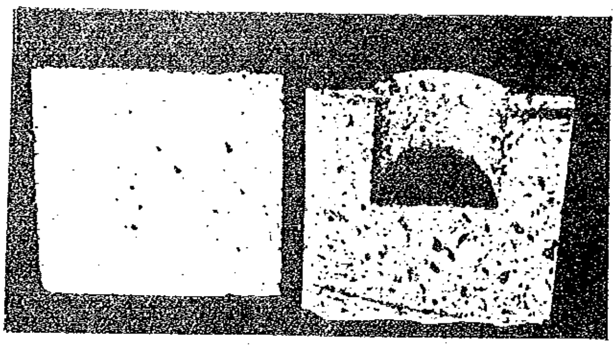
No. 1　SiC 30 % Unburned



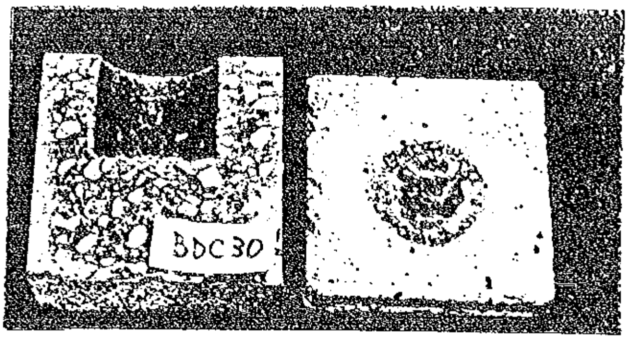
No. 2　SiC 60 % Unburned



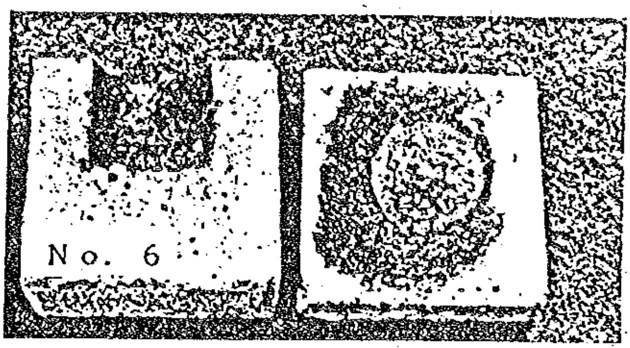
No. 3　SiC 80 % Unburned



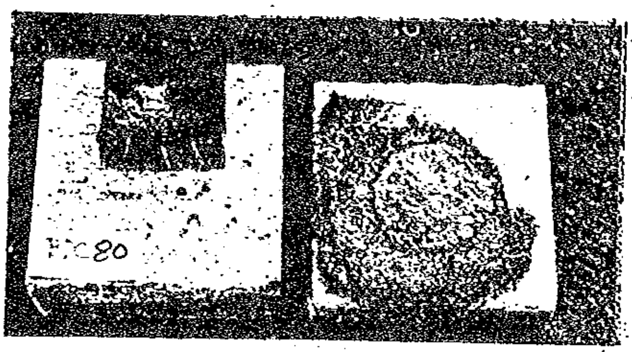
No. 4
Low cement fireclay castable



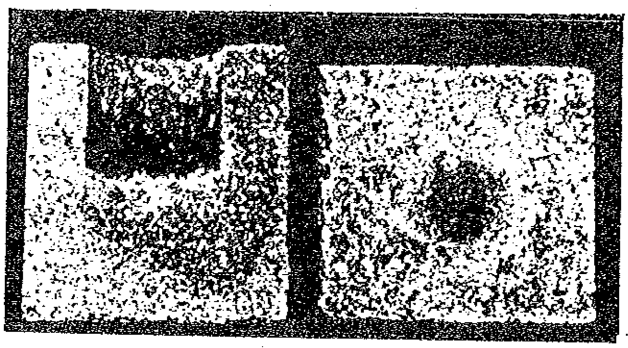
No. 5　SiC 30 % Burned



No. 6　SiC 60 % Burned

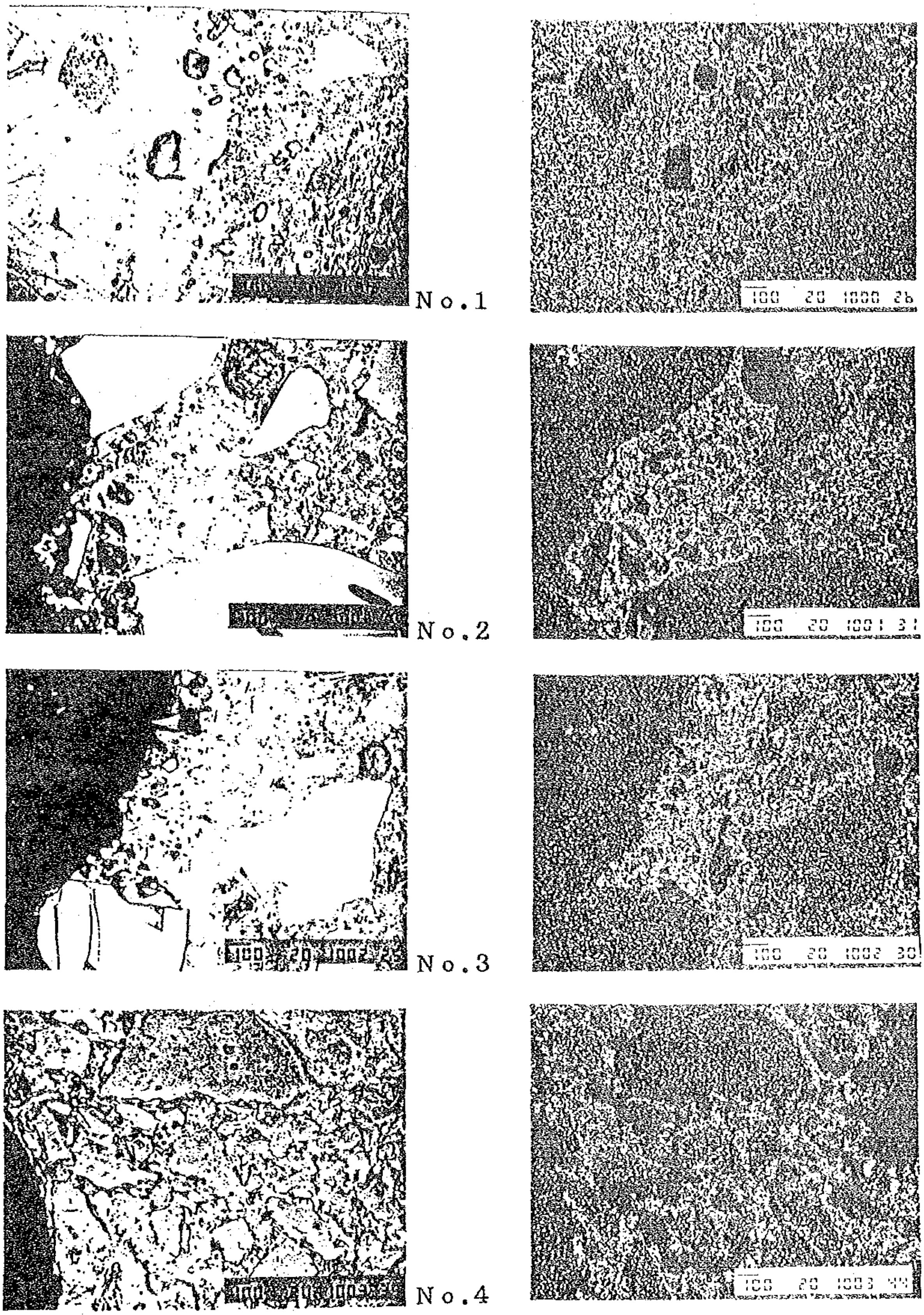


No. 7　SiC 80 % Burned



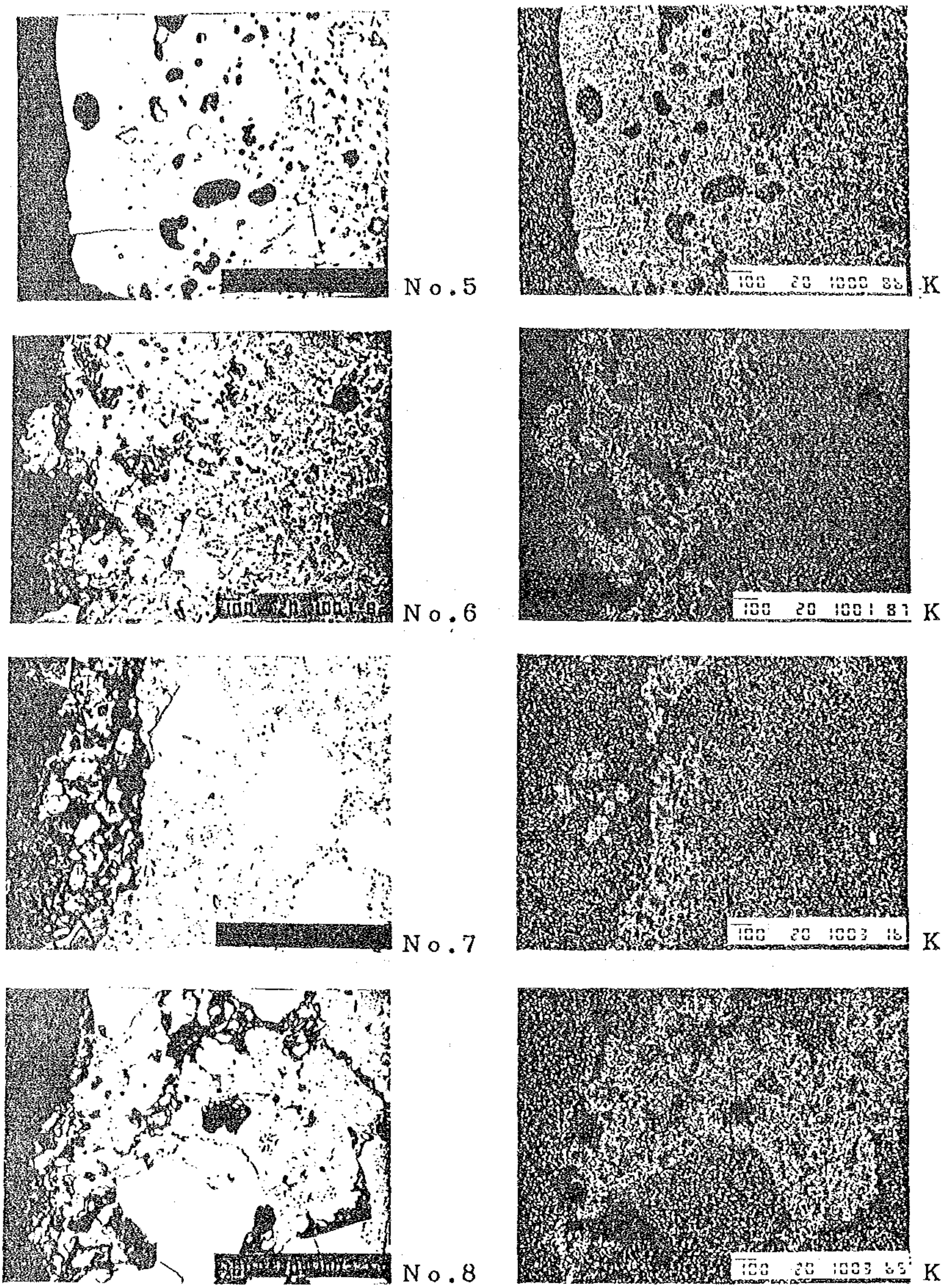
No. 8　SiC 85 % Burned brick

(Fig. 1) Cross section of crucibles and covers after tested



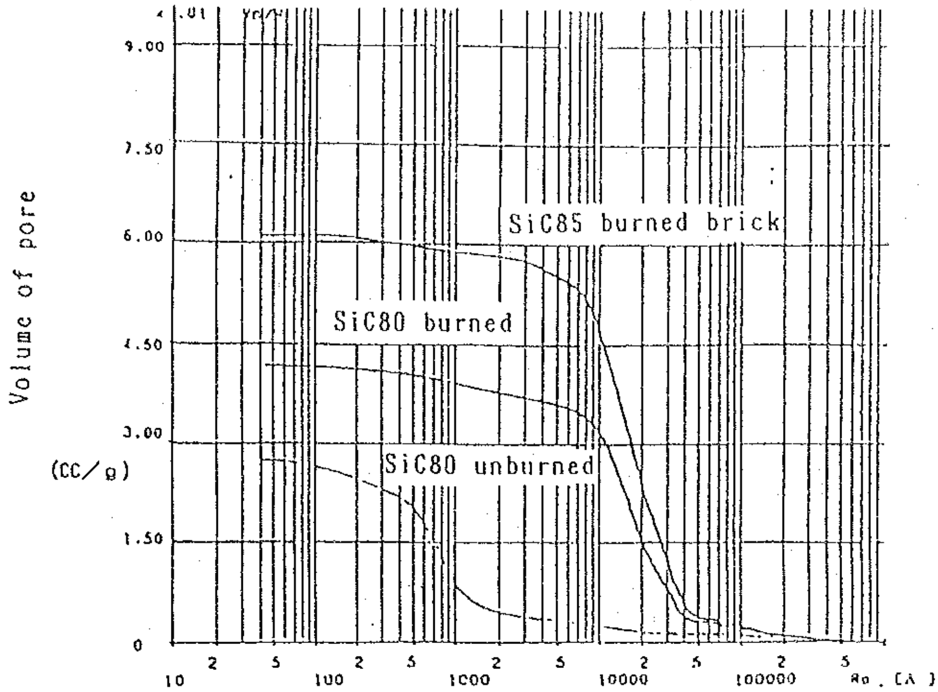
(Fig. 2) Photographs by EPMA at the reacted surface parts of crucibles ×75

(Unburned test pieces)



(Fig. 3) Photographs by EPMA at the reacted surface parts of crucibles ×75

(Burned test pieces)



Mean Radius of Pores (Å)

Distribution of Pore Radius

Vp/W(cc/g) : volume of pore
Rp (Å) : mean radius of pores

Sample name	Pore volume(cc/g)	Mean radius of pores (Å)
SiC85 burned brick	0.061112	16532.7
Sic80 burned	0.038330	14134.5
Sic80 unburned	0.027451	770.3

[Fig. 4] Distribution of pore radius

3-3. Anti alkali properties test

In order to confirm abrasion resestance of each test piece, Sand blast abrasion test in the room and hot temperature is applied.

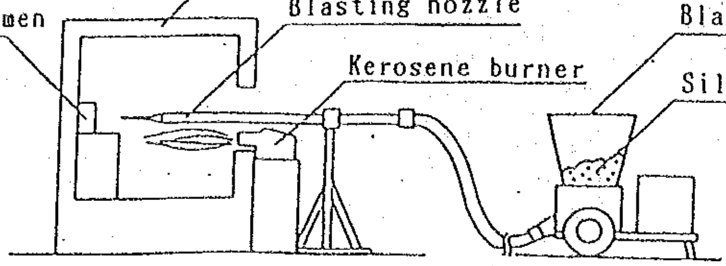
(1) Test Method

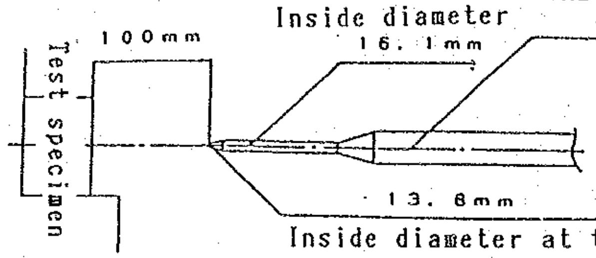
① Outline of test method : blow silica sand as abrading media to a test piece by dry type blast gun, and measure weight and volume loss. Rough drawing of abrasion test apparatus is shown in Fig. 5.

② Grain size of silica sand should be 14/20 mesh, and use 10 kg each time. Blasting air pressure should be 2.0 kg/cm² at the blast machine.

③ Test pieces should be supplied continuously for both tests in the room and hot temperature. Volume loss is calculated from weight loss after testing. The number of test pieces is n = 3 for each.

④ Specimens for hot abrasion test are heated at the rate of 300°C/h and should be kept 2 hours at 800°C. After this, the test should be applied one by one. In case the surface temperature of the specimens become low, the next specimen should be heated up to 800 °C on the surface before testing.





[Fig. 5] Abrasion Test Apparatus

(2) Test Result

The result of the abrasion test is shown in Table - 2.

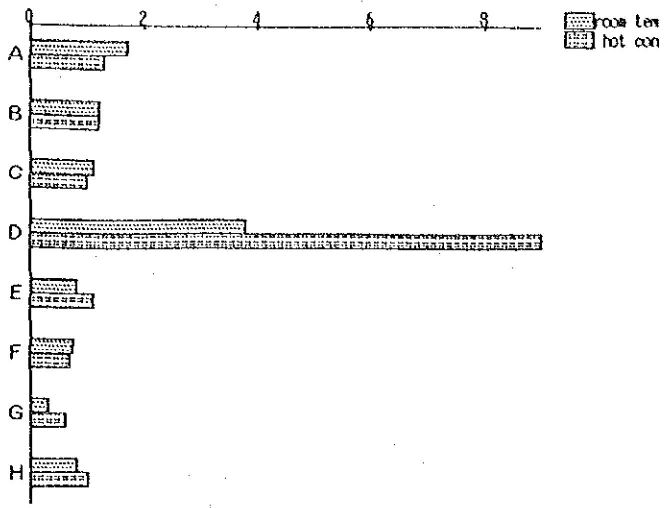
Table - 2. Abrasion Test Results

Sample \ Item		Room temperature		Hot condition	
		Weight loss(g)	Volume loss(cm^3)	Weight loss(g)	Volume loss(cm^3)
1	SiC30 unburned	4.23	1.78	3.43	1.44
2	SiC60 unburned	3.43	1.36	3.45	1.37
3	SiC80 unburned	3.13	1.16	2.94	1.09
4	Low Cement	8.59	3.67	21.04	8.99
5	SiC30 burned	1.99	0.82	2.74	1.13
6	SiC60 burned	1.84	0.73	1.75	0.69
7	SiC80 burned	1.09	0.40	1.72	0.63
8	SiC85 brick	1.90	0.79	2.28	0.95

The Result of Abrasion Test

Volume loss (cm^3)

A : SiC30% Castable
B : SiC60% Castable
C : SiC80% Castable
D : Chamotte Castable
E : SiC30% Burned Block
F : SiC60% Burned Block
G : SiC80% Burned Block
H : SiC85% Burned Brick



(3) Summary

① Abrasion resistance at the room temperature is : SiC80 burned > SiC60 burned > SiC85 brick > SiC30 burned > SiC80 unburned > SiC60 unburned > SiC30 unburned >> Fireclay Low Cement Castable.

② Abrasion resistance in the hot is : SiC80 burned > SiC60 burned > SiC85 brick > SiC80 unburned > SiC30 burned > SiC60 unburned > SiC30 unburned >> Fireclay Low Cement Castable.

③ This sand blast testing method in the hot condition is effective not only for comparison of strength in the hot temperature which is a main factor for abrasion, but also for comparison of spalling resistance (heat shock resistance). Therefore, generally abrasion is higher in hot condition than in the room temperature, as the test result of fireclay low cement castable shows. Abrasion of the specimens containing SiC in the hot and room temperature are almost same. This is because the specimens of SiC type have good spalling resistance as well as strength in hot condition.

4. Application for an Actual Furnace

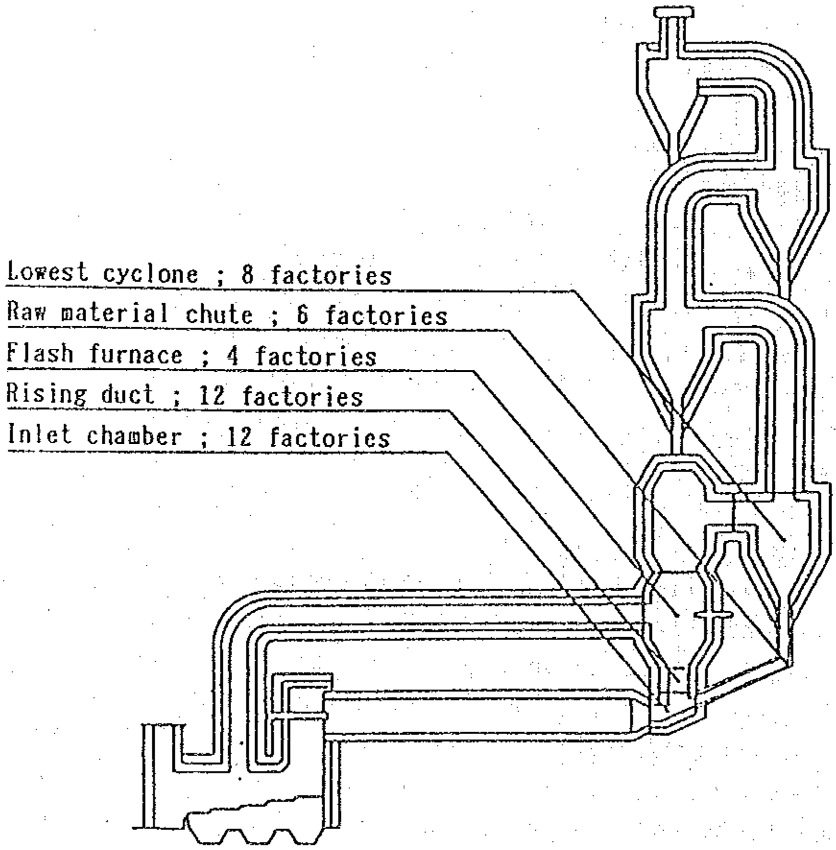
Silicon carbide refractories have already been used as raw material's plugging reduction refractories in 23 factories of 17 cement companies in Japan. Nowadays, to make good use of its characteristics, it is also applied for cooler parts, air extraction ducts and burners not only for preheaters. And effectiveness can be improved by adjusting the content of silicon carbide for each operation condition and position of application. There are many types of lining method : application of a vibrator, application of blocks (unburned, burned), the combined one of the two, and etc.

4-1. Application Conditions for an Actual Furnace

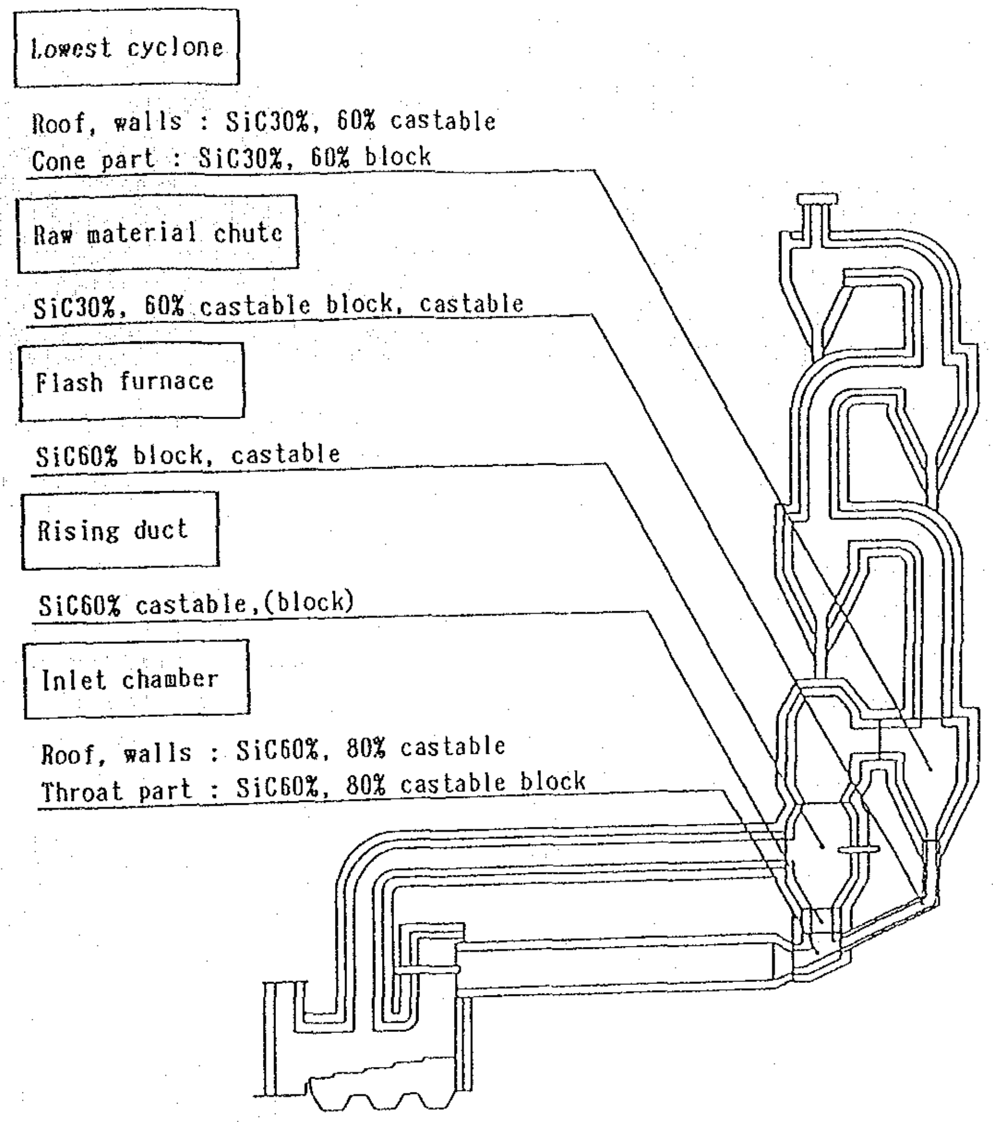
The details of application for an actual furnace is shown below.

Inlet Chamber Part	:	12 factories SiC80 burned and unburned block, castable SiC60 unburned block, castable
Rising Duct Part	:	12 factories SiC60 burned and unburned block, castable SiC30 unburned block, castable
Raw Material Chute	:	6 factories SiC60 unburned block, castable SiC30 unburned block, castable
Lowest Cyclone	:	8 factories SiC60 unburned block, castable SiC30 unburned block, castable
Flash Furnace	:	4 factories SiC60 unburned block, castable SiC30 unburned block, castable

Application Condition for Preheater



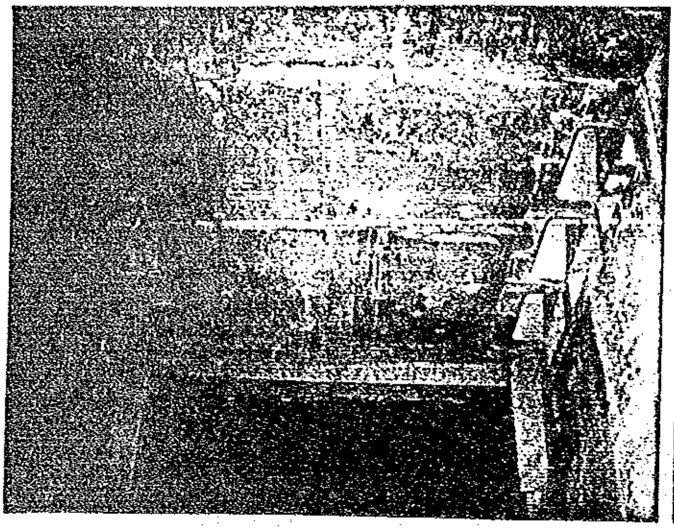
Application of Lining by Quality



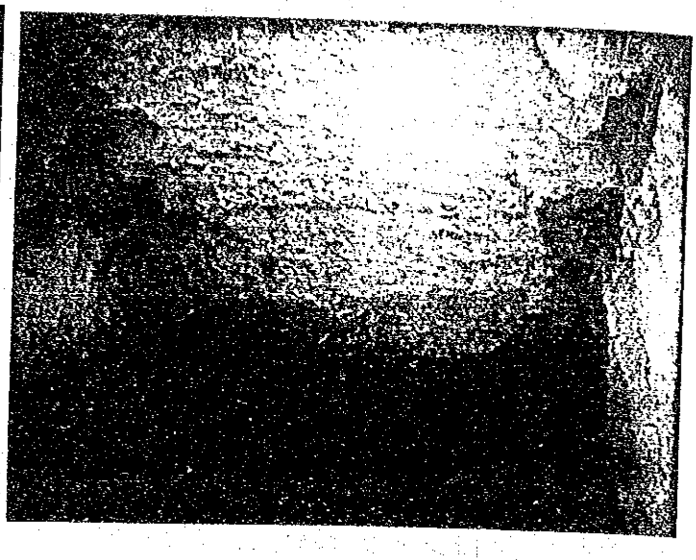
4-2. An Example of Application

Fig. 6 shows the example of the rising duct for NSP kiln of "A" company. This is a typical example of the structure which develops plugging of rigid hard coating, because the atmosphere temperature increases to higher than 1200°C due to various operation conditions and the structure. In the past, treatment was done by low cement castable or gunning materials, and the durability was only one campaign (3 to 4 months). However, after one and a half year service with new material, the duct size is almost same as the original, and the frequency of coating removing work is much less.

The materials used for construction were SiC 60 burned block and castable of the same material. " A" company constructed the inlet chamber with SiC 80 burned and castable, and they are using it in a good condition.



after lining



after 1 year and 6 months use

Fig. - 6. Using Condition of Rising Duct of "A" Company

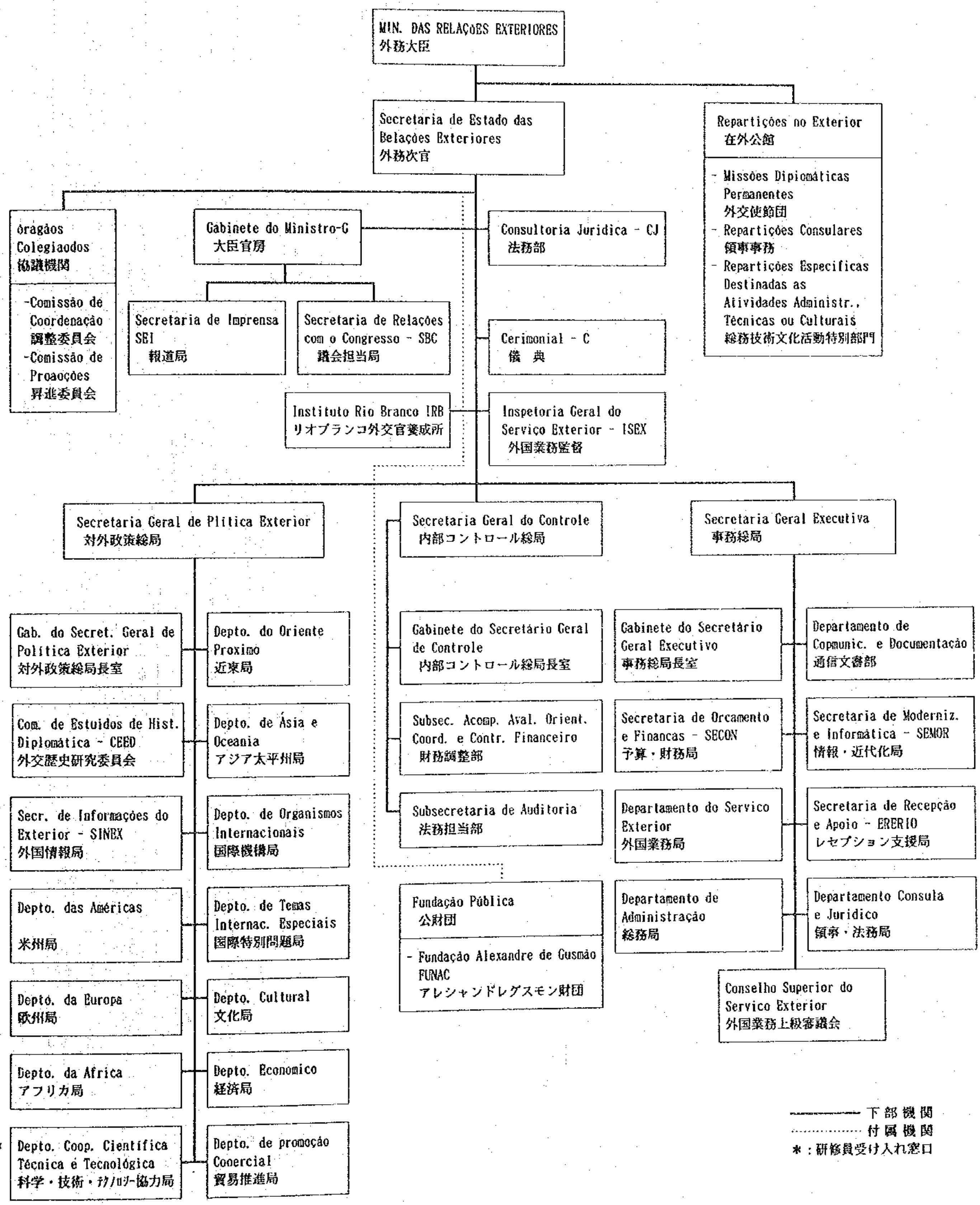
5. Conclusion

There are many factors for raw material plugging at preheater, and the causes can not be specified, as mentioned before. However, in the aspect of refractories, a great deal of improvement was carried out and obtained good results by use of silicon carbide refractories. From now on, more effective refractories from the overall point of view including lining methods and usage will be developed.

5. 外務省組織図

(1) ブラジル

ブラジル外務省組織図
MINISTERIO DAS RELAÇOES EXTERIORES

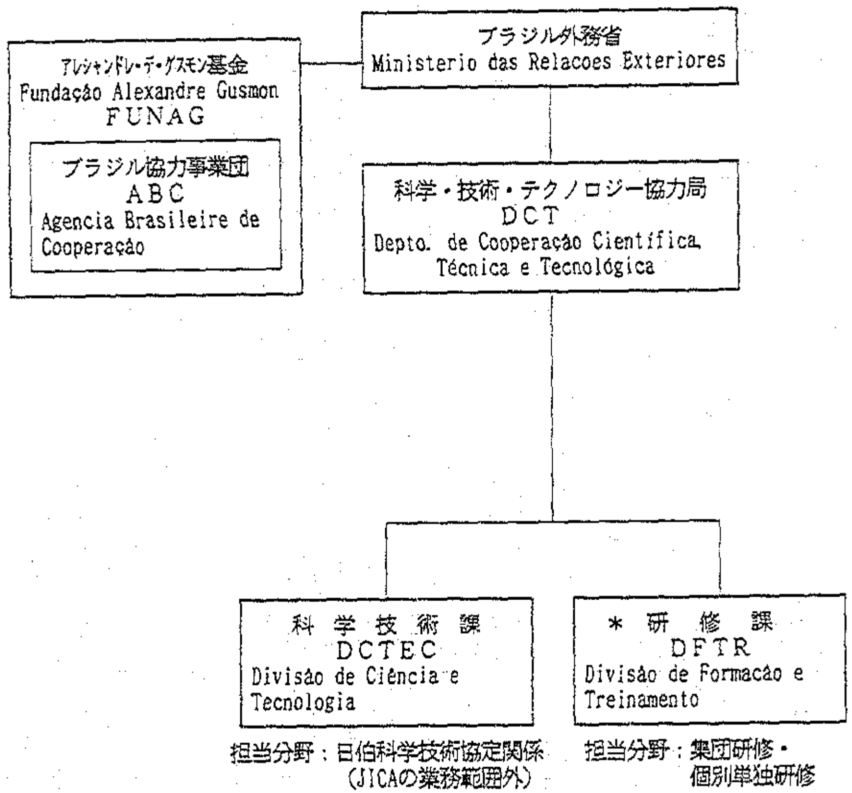


ブラジルの技術協力実施体制

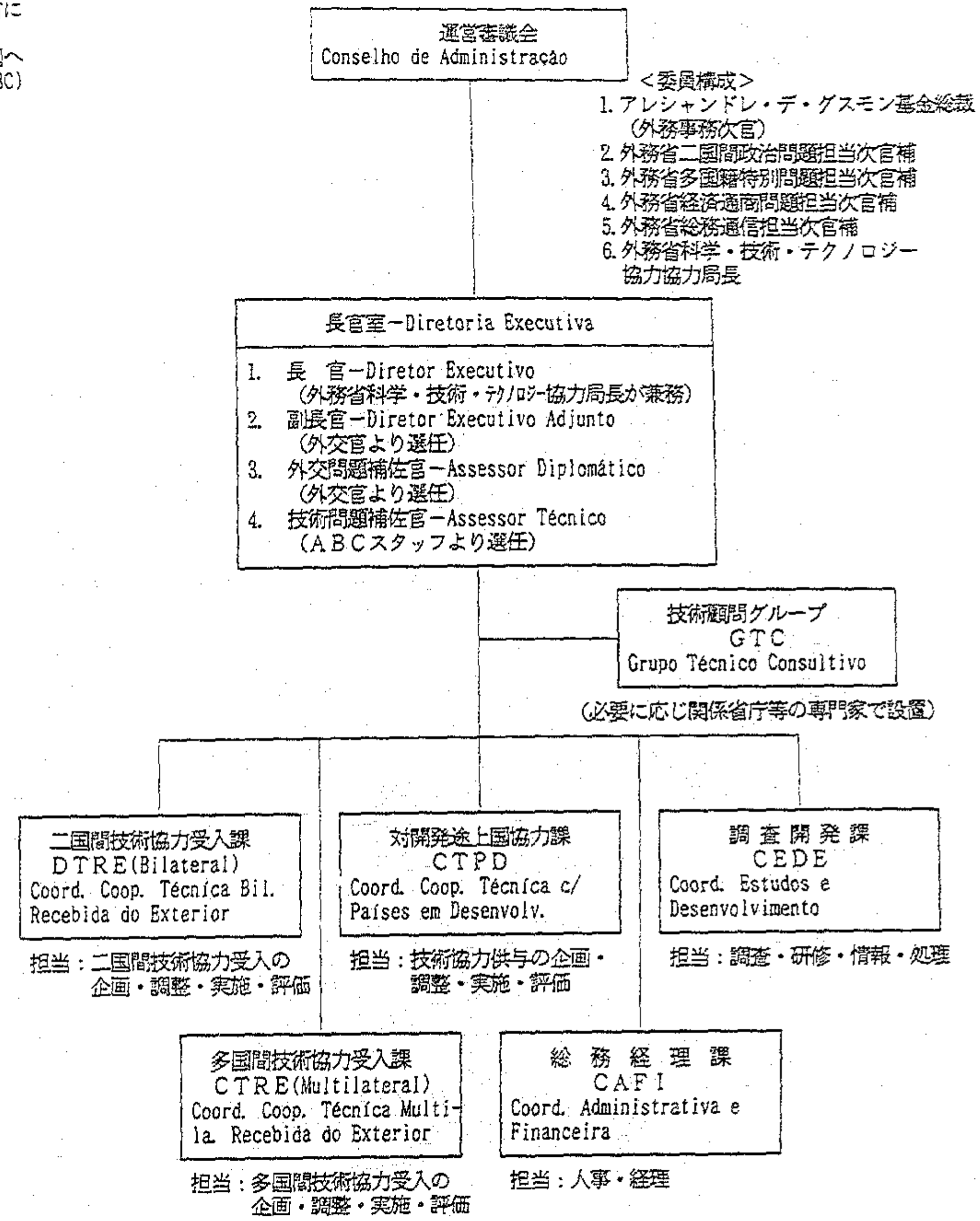
１９８７年４月の大統領令により企画省の権限が縮小され、技術協力に係る権限は全て外務省にに移り一元化された。

さらに、同年９月２５日付政令９４．９７３号をもって、技術協力の受け入れ及び発展途上国への技術協力の供与を総合的に行う「ブラジル協力事業団(Agência Brasileira de Cooperação-ABC)が伯外務省の下部機関として創設された。

これにともないブラジルの技術協力体制は下図の組織図の通り整備された。



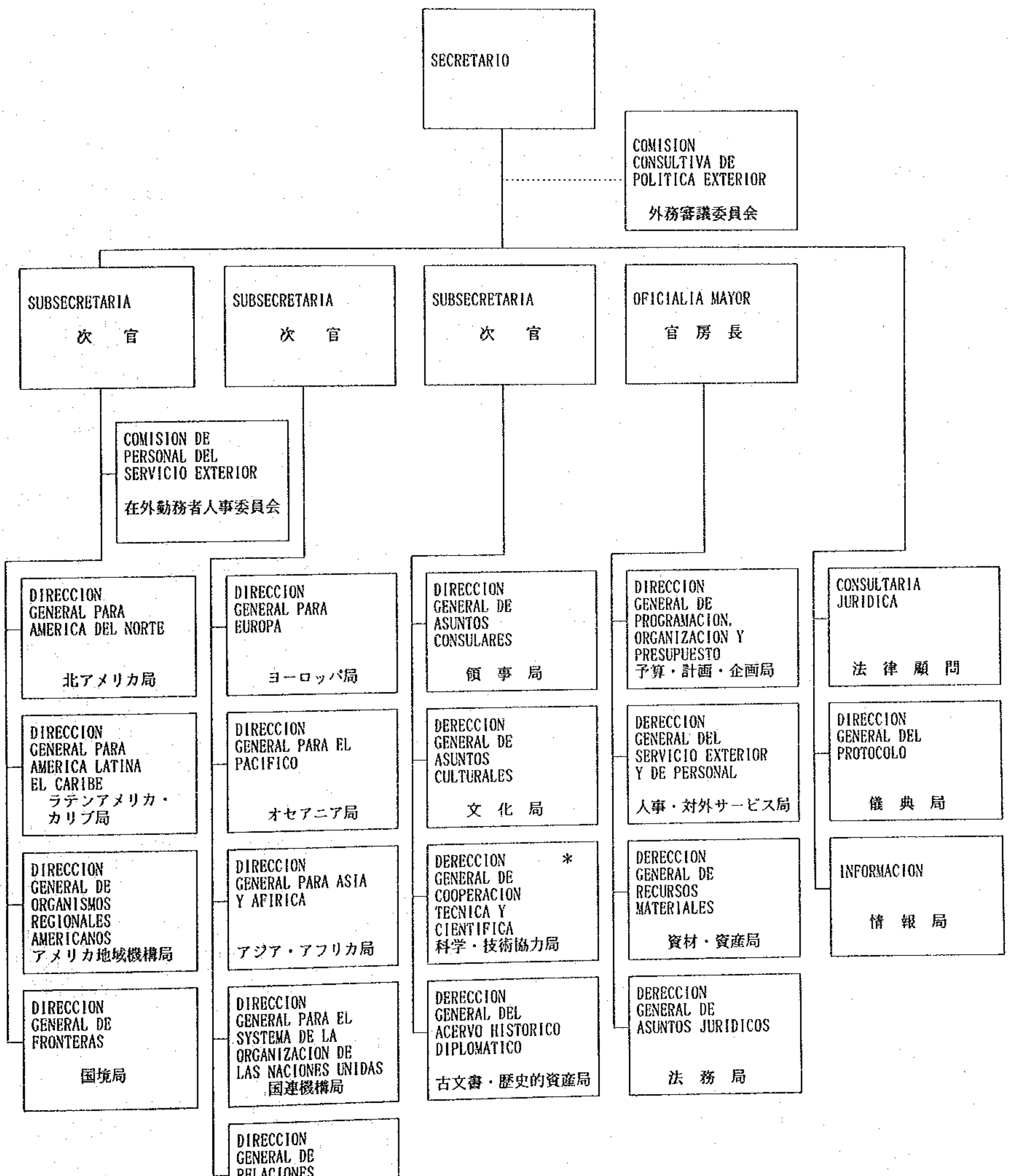
ＡＢＣの組織図



(2) メキシコ

メキシコ外務省組織図

SECRETARÍA DE RELACIONES EXTERIORES



＊：研修員受け入れ窓口