

Na, Kが関与する耐火材料の腐食

Corrosion Behavior of Refractory Materials Involved with Na and K

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Abstract

The reactivity of various refractory materials with Na and K contained in biomass wastes, which are expected to be recycled for energy, was studied using a Tanmann furnace with the temperature set to 1200°C. An accelerated experiment was also performed at 1300°C using actual incineration fly ash as an example, and a guideline for the selection of refractory materials was obtained.

1. 緒言

現在の焼却炉においては、Na, Kを比較的多く含んだ廃棄物による大きな損傷が問題になっている。たとえば、最近では、リサイクルエネルギーとしてバイオマス廃棄物エネルギーを利用する技術開発が盛んに行われているが、バイオマス廃棄物にはNa, Kを多く含んでいるものがあり (Table 1),

1. Introduction

In existing incinerators, waste materials containing relatively large amounts of Na and K cause significant damage. Various efforts have been made recently to recycle waste materials to produce biomass energy. However, some biomass wastes containing large amounts of Na and K as shown in Table 1 could cause corrosion damage of the walls of high-temperature furnaces. To obtain fundamental technical knowledge and a guideline for the selection of refractory materials used for the walls of such high-temperature furnaces, we studied the reaction of Na and K with various refractory materials and compared the products of Shinagawa Refractories Co., Ltd. for alkali resistance. This report describes the details of the study.

2. Test Method

2. 1 Alkaline reaction test

This alkaline reaction test duplicates the

Table 1 Example of incineration ash generated from biomass waste

	Incineration ash generated only from residue of rape oil	Incineration ash generated only from Japanese wood
Chemical composition	Content (mass%)	Content (mass%)
SiO ₂	0.8	2.6~ 5.2
CaO	2.8	29.9~72.6
MgO	4.2	3.9~24.9
Na ₂ O	41.3	1.0~ 8.3
K ₂ O	3.9	9.8~33.2
P ₂ O ₅	27.3	5.5~11.4
SO ₃	0.9	1.8~ 3.9

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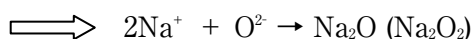
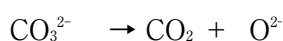
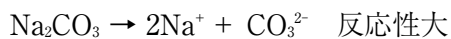
高温炉壁の腐食損傷が危惧される。このような高温炉壁の耐火材料選定の基礎技術とすべく、Na、Kと各種耐火材料との反応研究を実施し、当社製品の耐アルカリ性比較を行ったので、その結果を報告する。

2. 試験方法

2.1 アルカリ反応試験

アルカリ反応試験では、アルカリ成分が多いバイオマス廃棄物等を燃焼したときに生じる焼却灰が高温下において溶融し、内張り耐火材料と接触して反応することを再現している。また、 Na_2O や K_2O は下記のように酸化雰囲気下でも高温でガス化現象があることが知られている¹⁾。一部アルカリ蒸気の影響も加味するため、反応試験方法はタンマン炉方式を採用した (Fig. 1)。

(融点 851°C)



高温 強力な酸化剤



1127°C

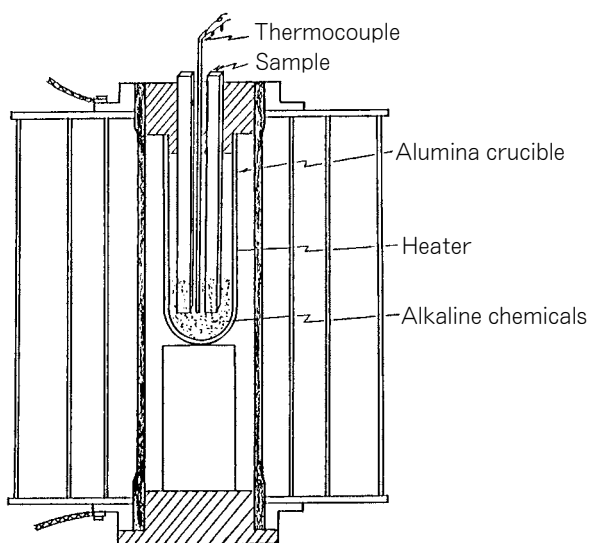
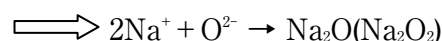
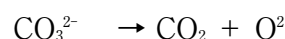


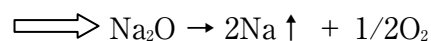
Fig. 1 Schematic diagram of Tammann furnace.

process of melting incineration ash generated from the combustion of biomass which contains large amounts of alkaline components under high temperature, and the resulting reaction when melted ash contacts the inner refractory materials. It is known that Na_2O and K_2O show gasification at high temperature even under an oxidizing atmosphere, as given by the equations below¹⁾. To evaluate the effect of alkaline steam under certain test conditions, the Tanmann furnace method was used for the reaction test:

(At melting point of 851°C)



Elevated Strong oxidizing agent
temperature



1127°C

Fig. 1 shows a schematic diagram of the inside of the Tanmann furnace used for the alkaline reaction test. The temperature of the alkaline reaction test was determined as below by assuming the actual operating conditions of incineration furnaces. The amount of corrosion agent to be used for the test was set to be sufficient to immerse test specimens to the predetermined height.

Conditions of alkaline reaction test

Test temperature :

1200°C (at the tip of test specimens)

Holding time at test temperature :

30 minutes

Rate of temperature increase :

$10^\circ\text{C}/\text{min}$

Corrosion agent :

Special grade reagents of Na_2CO_3 , K_2CO_3 ,
 NaCl

Amount of corrosion agent :

55, 50 and 60g, respectively for reagents

Table 2 Classification of refractory products

Classification	Type	Main chemical composition
Acid refractory	Silica Fireclay(Roseki, Chamotte) Zircon	SiO ₂ SiO ₂ , Al ₂ O ₃ ZrO ₂ , SiO ₂
Neutral refractory	Alumina, High-alumina Spinel Chrome Alumina-carbon	Al ₂ O ₃ (SiO ₂) Al ₂ O ₃ , MgO Cr ₂ O ₃ , Al ₂ O ₃ , MgO Al ₂ O ₃ , C
Basic refractory	Magnesia Magnesia-chrome Dolomite Magnesia-carbon	MgO MgO, Cr ₂ O ₃ MgO, CaO MgO, C
Non-oxide refractory	Silicon carbide Carbon	SiC C

Fig. 1にアルカリ試験に用いたタンマン炉内の概略図を示す。アルカリ反応試験の試験温度は、焼却炉の操業条件を想定して下記のように定め、侵食剤の使用量については、試験片が所定の高さまで浸漬されるように決定した。

(アルカリ反応試験条件)

試験温度	1200℃ (試料先端部温度)
温度保持時間	30分
昇温速度	10℃/分
侵食剤	Na ₂ CO ₃ , K ₂ CO ₃ , NaCl 特級試薬
侵食剤使用量	55, 50, 60g
試料形状	17 × 17 × 180mm (平面研磨機仕上げ後)

2. 2 アルカリ反応試験後の試験

アルカリ反応試験後の外観および切断面を調査したが、外観では熔融後の侵食剤が付着して腐食状況がわかりにくいので、切断面で腐食状況を判定した。先端まで健全なものは、試験後の線変化率も測定した。また、腐食先端部のアルカリとの反応生成物を粉末X線回折法によって調べた。

2. 3 供試耐火材料

Table 2に示す各種耐火物が現在窯炉で使用さ

Dimensions of test specimen :

17 × 17 × 180mm

(After finishing by surface grinding)

2. 2 Observation after alkaline reaction test

The appearance and cutting surface were observed after the alkaline reaction test. However, the state of corrosion was not visible from the external appearance because of the adhesion of corrosion agent after melting. Therefore, the state of corrosion was observed on the cutting surface. The permanent linear change after the test was also measured for specimens that were in good condition to the tip. In addition, mineral products by reaction with alkali at the tip of the corrosion portion were observed by powder X-ray diffraction.

2. 3 Refractory materials used for the test

Various refractory products as shown in Table 2 are currently used for kilns and furnaces. The alkaline reaction test was conducted by selecting typical refractory brick products and monolithic refractory products which can be used in an oxidizing atmosphere from these wide ranges of products. Tables 3 and 4 show refractory products used for the alkaline reaction test. Monolithic refractory products used in the test had already been heated at 1000℃.

3. Reaction Test Results with Na₂O and Discussion

Figs. 2 and 3 show the results of the reaction test with Na₂O including state of corrosion, l permanent linear change and mineral products by reaction at the tip of test specimens.

3. 1 Refractory brick products

Magnesia-chrome bricks after the test showed little change of structure compared to those of original bricks. Alumina, zirconia and spinel refractories tended to swell at the tip of test specimens. Dense chamotte bricks showed slight wear and tended to swell slight at the

Table 3 Refractory brick products used for alkaline reaction test

	Alumina	Alumina-mullite	Chamotte	Zircon	Zirconia
Brand name	DRL-100F	ALT-85	BFD	ZBK-L	ZCN
Main chemical composition (mass%)					
Al ₂ O ₃	99	84	41		
SiO ₂		10	56	33	
ZrO ₂				65	95
Apparent porosity(%)	15.5	23.0	14.0	17.5	15.0

	Spinel	Magnesia-chrome	Silicon carbide	Silicon carbide-chamotte
Brand name	SP-10P	DIRCO-7C	SCX-S90	SCX-S40
Main chemical composition (mass%)				
Al ₂ O ₃	70			
SiO ₂			5	34
MgO	29	70		
Cr ₂ O ₃		15		
SiC			87	42
Apparent porosity(%)	13.0	15.5	11.0	11.0

Table 4 Monolithic refractory products used for alkaline reaction test

	Low cement castable			Ordinary castable		Dense gunning mix	
Brand name	CST-A81	CST-A62	CST-N51	CN-150	CS-145	SNG-A601	SNG-S851
Main chemical composition (mass%)							
Al ₂ O ₃	98	58	40	39	4	58	3
SiO ₂		39	53	47	5.0	39	8
CaO	1.3	1.5	1.5	8.5	85		
SiC							85
Apparent porosity(%)	13.3	13.8	16.2	20.8	21.6	17.0	16.2

れている。これらの広い範囲から酸化雰囲気で使用できる代表的な耐火れんがおよび不定形耐火物を選んでアルカリ試験を実施した。Table 3, 4に試験に供した耐火材料を示す。ただし、不定形耐火材料は1000℃加熱処理品を使用した。

3. Na₂Oとの反応試験結果および考察

Na₂Oとの反応試験結果（腐食状況，線変化率，先端部の反応生成鉱物）をFig. 2, 3に示す。

3.1 耐火れんが

マグクロ質れんがはほとんど原れんが組織に比べ組織変化が少ない。アルミナ質，ジルコニア質，スピネル質は試料の先端部が膨張する傾向が見ら

れている。tip of the specimen which was immersed in corrosion agent. Alkali penetrated into the back side of the worn portion with 2 to 3 mm in thickness, and dense structures were formed. Zirconia bricks showed large wear when the temperature was 1150℃ or higher. Silicone carbide bricks and silicone carbide chamotte bricks showed some wear at 1150℃ or higher, and especially severe wear was observed for the silicone carbide bricks.

3.2 Monolithic refractory products

Alumina low cement castables showed swelling starting from a temperature of around 1000℃, and the swelling gradually increased when they were exposed to higher

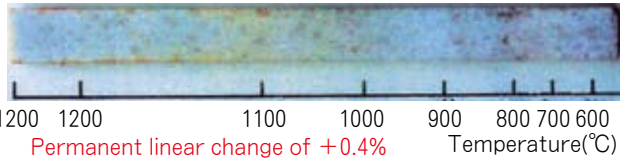
	Cross section and permanent linear change after test	Chemical formula
Alumina (Brand name: DRL-100F)	 1200 1200 1100 1000 900 800 700 600 Temperature(°C) Permanent linear change of +0.4%	β -Al ₂ O ₃ NaAlO ₂ (MP 1700°C<)
Chamotte (BFD)	 Permanent linear change of +0.6%	NaAlSiO ₄ (MP 1526°C) Na ₂ O•2SiO ₂ (MP 870°C) NaAlO ₂
Zircon (ZBK-L)	 Permanent linear change of +0.6%	Na ₂ O•ZrO ₂ •SiO ₂ ZrO ₂ 2Na ₂ O•2ZrO ₂ •3SiO ₂ Na ₂ O•ZrO ₂
Zirconia (ZCN)	 Permanent linear change of +1.1%	Na ₂ O•ZrO ₂
Spinel (SP-10P)	 Permanent linear change of +1.2%	NaAlO ₂ MgO
Magnesia- chrome (DIRCO-7C)	 Permanent linear change of +0.4%	(MgO) (Cr-Spinel)
Silicon carbide (SCX-S90)	 Permanent linear change of +0.4%	SiO ₂ Na ₂ O•2SiO ₂ (MP 870°C)
Silicon carbide- chamotte (SCX-S40)	 Permanent linear change of +0.4%	NaAlSiO ₄ (MP 1526°C) Na ₂ O•2SiO ₂ (MP 870°C)

Fig. 2 Bricks after chemical reaction test with Na₂O agents.

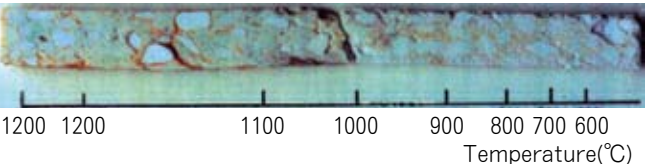
	Cross section and permanent linear change after test	Chemical formula
Alumina low cement castable (Brand Name: CST-A81)	 Permanent linear change of +3.9%	β -Al ₂ O ₃ NaAlO ₂ (MP 1700°C <) NaAlSiO ₄ (MP 1526°C)
Chamotte low cement castable (CST-N51)	 Permanent linear change of -0.6%	Na ₂ O•Al ₂ O ₃ •6SiO ₂ (MP 1100°C)
Chamotte castable (CN-150)	 Permanent linear change of -0.5%	NaAlSiO ₄ (MP 1526°C) Na ₂ O•2SiO ₂ (MP 870°C)
Silicon carbide castable (CS-145)	 Permanent linear change of -0.5%	NaAlSiO ₄ Na ₂ O•2SiO ₂ (MP 870°C)
High alumina Dense gunning mix (SNG-A601)	 Permanent linear change of -0.5%	NaAlSiO ₄ NaAlO ₂ β -Al ₂ O ₃
Silicon carbide dense gunning mix (SNG-S851)	 Permanent linear change of -0.5%	Na ₂ O•SiO ₂ (MP 1080°C)

Fig. 3 Monolithic refractories after chemical reaction test with Na₂O agents.

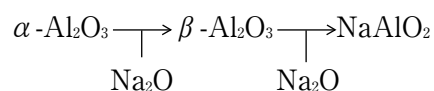
れた。緻密質シャモットレンがは侵食剤に浸漬された先端部が若干溶損し、膨張傾向も見られた。溶損部の背部にアルカリが2～3mmの厚さ侵入し、緻密な組織を形成していた。ジルコン質レンがは1150℃以上が大きく溶損した。炭化珪素質レンがや炭化珪素－シャモット質レンがは1150℃以上で溶損が見られ、特に炭化珪素質の溶損が大きい。

3. 2 不定形耐火物

アルミナ質ローセメントキャストブルは、1000℃付近から高温側に向かって漸次膨大しており、アルミナ質レンがに比べ膨大傾向が大きい。組織内部に横亀裂が発生しているが、比較的組織はしっかりしている。シャモット質ローセメントキャストブルは1150℃以上で若干溶損が見られ、シャモット質の一般キャストブルは溶損が大きい。高アルミナ質緻密吹付材は1200℃付近で若干溶損が見られるが、シャモット質のローセメントキャストブルや一般キャストブルより溶損が少ない。炭化珪素質キャストブルや炭化珪素質緻密吹付材は1150℃以上で溶損しており、特に炭化珪素質緻密吹付材は大きく溶損した。

3. 3 各耐火材料の反応性

(1) アルミナ質レンがはコランダム (α - Al_2O_3), アルミナ質ローセメントキャストブルはコランダム (α - Al_2O_3) が主体で少量の $\text{CaO} \cdot \text{Al}_2\text{O}_3$ からなり、これらの鉱物はアルカリ Na_2O が侵入すると次式に示すような反応を生じる²⁾。

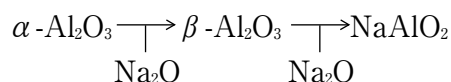


α - Al_2O_3 が結晶構造の大きい β - Al_2O_3 に変化すると、耐火材料の組織は膨大し亀裂が入りやすくなるものと考えられる。

temperatures. This swelling tendency was larger than that of alumina bricks. Although transverse cracks occurred within the structure, the structure itself was relatively solid and tight. Chamotte low cement castables showed a little wear at 1150℃ or higher, whereas chamotte ordinary castables showed large wear. High alumina-dense gunning mix showed a little wear at around 1200℃, but the wear was less than that of chamotte low cement castables or ordinary castables. Silicone carbide castables and silicone carbide-dense gunning mix showed some wear at 1150℃ or higher, with especially large wear for the case of silicone carbide-dense gunning mix.

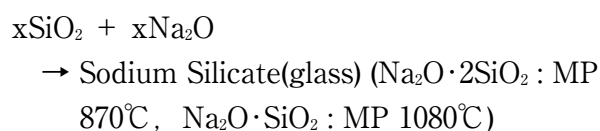
3. 3 Reactivity of individual refractory material

- i) Alumina bricks are comprised of corundum, α - Al_2O_3 , and alumina-low cement castables are comprised of mainly corundum, α - Al_2O_3 and a small amount of $\text{CaO} \cdot \text{Al}_2\text{O}_3$. These minerals show the following reaction when alkaline Na_2O penetrates²⁾.

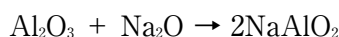
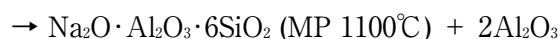
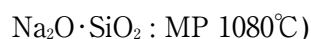
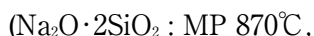


It is considered that when α - Al_2O_3 changes to β - Al_2O_3 which has larger crystal structures, the structure of refractory materials swells and easily cracks.

- ii) Chamotte bricks and castables are comprised of mullite ($3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$), cristobalite (SiO_2), quartz (SiO_2), etc. It is considered that these minerals show the following reaction when Na_2O penetrates³⁾.

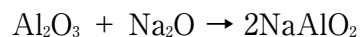
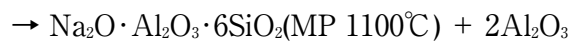
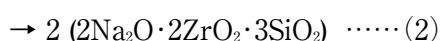
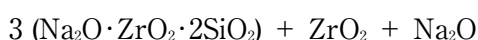


- (2) シャモット質のれんがとキャストブルの鋳物組成は、ムライト ($3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$), クリストバライト (SiO_2), 石英 (SiO_2) 等であり, Na_2O の侵入によって次式の反応が起こると考えられる³⁾。



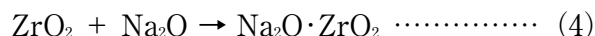
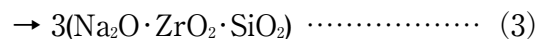
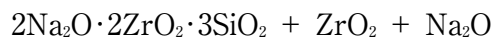
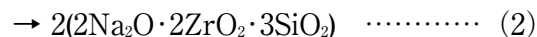
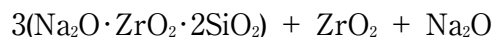
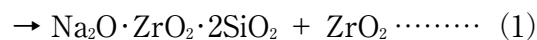
シャモット質耐火物は、一般に化学組成 SiO_2 および Al_2O_3 の含有量の相違によって、上記のいずれかの反応が起こりやすい。耐火材料の Na_2O による腐食は、耐火材料組織がSodium Silicate, $\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 6\text{SiO}_2$ (アルバイト) および NaAlSiO_4 (カーネギエイト) 等のアルカリ化合物の生成によって、溶損される場合や膨大し剥離損傷される場合が見られる。

- (3) ジルコン質耐火材料の鋳物組成は主にジルコン ($\text{ZrO}_2 \cdot \text{SiO}_2$) であり、次式のように Na_2O の侵入によって最初に $\text{Na}_2\text{O} \cdot \text{ZrO}_2 \cdot 2\text{SiO}_2$ と ZrO_2 に分解され、順次 (2), (3), (4) 式の反応が起こると考えられ⁴⁾, 耐火材料組織が崩壊していくものと考えられる。

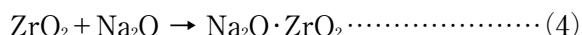
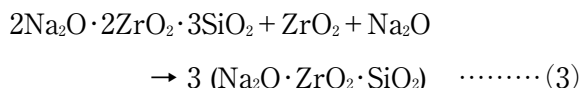


Chamotte refractory materials tend to show either of the above reactions depending generally on differences in the chemical proportions of SiO_2 and Al_2O_3 . In the corrosion of refractory materials by Na_2O , the structure of refractory materials sometimes becomes worn, or becomes swollen or peeled off, and damaged due to the formation of alkali compounds such as sodium silicate, $\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 6\text{SiO}_2$ (Albite) and NaAlSiO_4 (Carnegieite).

- iii) Zirconia refractory materials are mainly comprised of zircon ($\text{ZrO}_2 \cdot \text{SiO}_2$). It is considered that this mineral first decomposes to $\text{Na}_2\text{O} \cdot \text{ZrO}_2 \cdot 2\text{SiO}_2$ and ZrO_2 then the reactions of Eq. (2), (3) and (4) occur sequentially when Na_2O penetrates⁴⁾, and finally the structure of the refractory materials disintegrates.

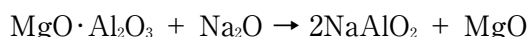


It is estimated that zirconia refractory materials produce alkali compounds according to the reaction described in Eq. (4), then crack in the structure due to the dislocation of crystals, and are finally peeled off.

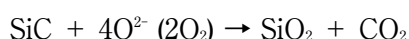


ジルコニア質耐火材料は、(4) 式の反応によってアルカリ化合物を生じ、結晶の転移等により組織に亀裂を生じて剥離するものと推定される。

- (4) スピネル質耐火材料の主鉱物組成はスピネル ($\text{MgO} \cdot \text{Al}_2\text{O}_3$) であり、 Na_2O が侵入すると次式のようにスピネルが分解されアルミン酸ソーダ化合物を生成し、耐火材料組織が膨大し、亀裂・剥離により損傷されるものと考えられる。

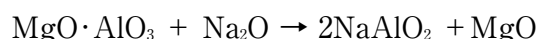


- (5) 炭化珪素質耐火材料は、 Na_2CO_3 、 Na_2O が分解して発生する活性な酸素が SiC を酸化し、次式の反応を生じて溶損が進行するものと考えられる。

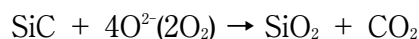


- (6) 塩基性耐火材料の中で一般に高純度マグネシアクリンカーやクロム鉱を使用している耐火材料は、アルカリ化合物が生成されにくく、アルカリの腐食に対しては強い。しかし、フォルステライト ($2\text{MgO} \cdot \text{SiO}_2$) やモンチセライト ($\text{CaO} \cdot \text{MgO} \cdot \text{SiO}_2$) 等が存在すると、次式のようなアルカリ化合物を生成し、溶損や組織の膨大による剥離損傷が発生しやすいと考えられる⁵⁾。なお、塩基性耐火物は一般に熱膨張率が大きく、熱スポーリングが発生しやすい。

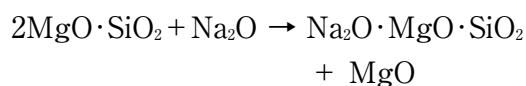
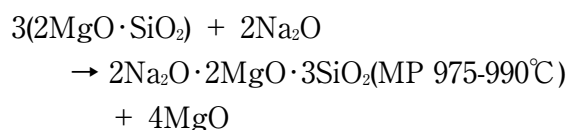
- iv) Spinel refractory materials are comprised of spinel ($\text{MgO} \cdot \text{Al}_2\text{O}_3$). It is considered that when Na_2O penetrates, this spinel first decomposes as following reaction and sodium aluminate compounds are produced, and then the refractory materials become swollen and damaged by cracks and peeling.

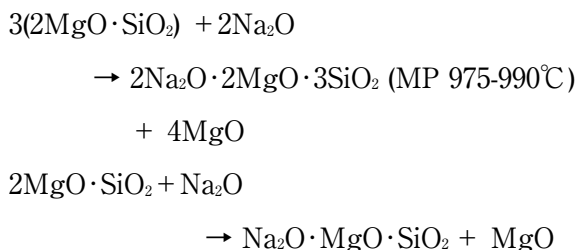


- v) In silicone carbide refractory materials, it is considered that SiC is oxidized by active oxygen produced by the decomposition of Na_2CO_3 and Na_2O , then the following reactions occur and wear progresses.



- vi) In basic refractory materials, those refractory materials using high purity magnesia clinker or chromium ore hardly produce alkali compounds in general, and show strong resistance to alkaline corrosion. However, when forsterite ($2\text{MgO} \cdot \text{SiO}_2$) or monticellite ($\text{CaO} \cdot \text{MgO} \cdot \text{SiO}_2$) exists, alkaline compounds shown in the equation below can be produced and cause wear or peeling damage by the swelling of the structure⁵⁾. Basic refractory materials have large thermal expansion coefficients in general, and easily cause thermal spalling.





3. 4 各耐火材料とNa₂Oとの反応性についてのまとめ

代表的な耐火材料についてアルカリNa₂Oとの反応試験を実施した結果、以下のことが判明した。

- (1) Na₂CO₃, Na₂Oに対してはSiO₂成分の多い材質やSiC材質は損傷が大きい。
- (2) 塩基性耐火材料および高密度アルミナ質れんがは損傷が軽微であり、高密度シャモット質も比較的損傷が少ない。
- (3) 当社耐火れんがの耐アルカリ性
DIRCO-7C > DRL-100F > ZCN > BFD
> SP-10P > ZBK-L
- (4) 当社不定形耐火物の耐アルカリ性
SNG-A601 > CST-N51 > CST-A81 ≒ CN-150
≒ CS-145 > SNG-S851

4. Na₂O, K₂O, NaClとの反応試験

バイオマス廃棄物についてはNa, Kを多く含んでいるものがあるが、同時に燃焼する廃棄物の中には廃プラスチック等のようにClを多く含んでいるものも予想され、燃焼中にNa, Kと反応してアルカリ塩のNaClやKClになる可能性もある。実際の焼却炉においてNaCl等として確認されたこともある。そこで、Na₂O, K₂O, NaClの腐食性を確認するため、ハイアルミナ質およびシャモット質のれんが、キャストブルについて反応試験を実施した。

4. 1 腐食状況

Na₂O, K₂O, NaClとの反応試験結果をFig. 4,

3. 4 Summary of the reactivity of individual refractory material with Na₂O

From a reaction test of typical refractory materials with alkaline Na₂O, the following results were obtained.

- i) Refractory materials with a larger amount of SiO₂ component or SiC materials suffer greater damage by Na₂CO₃ and Na₂O.
- ii) Basic refractory materials and dense alumina bricks suffer slight damage, and dense chamotte refractory materials also suffer relatively minor damage.
- iii) The alkaline resistance of refractory brick products of Shinagawa Refractories Co., Ltd. is given by:
DIRCO-7C > DRL-100F > ZCN > BFD >
SP-10P > ZBK-L
- iv) The alkaline resistance of monolithic refractory products of Shinagawa Refractories Co., Ltd. is given by:
SNG-A601 > CST-N51 > CST-A81
≒ CN-150 ≒ CS-145 > SNG-S851

4. Reaction Test with Na₂O, K₂O and NaCl

Biomass wastes sometimes contain large amounts of Na and K, and waste materials which are combusted together might also contain waste plastics which have a larger Cl component. Therefore, alkaline salts such as NaCl or KCl can be produced through the reaction with Na or K during the combustion processes. Indeed, NaCl and other substances have been confirmed in an actual incineration plant. In order to confirm the corrosiveness of Na₂O, K₂O and NaCl, reaction tests were performed on high alumina and chamotte brick materials and castable materials.

4. 1 State of corrosion

Figs. 4 and 5 show the results of the reaction test with Na₂O, K₂O and NaCl.

Fig. 5に示す。

4. 2 まとめ

ハIALミナ質およびシャモット質の耐火材料とアルカリ塩 Na_2CO_3 , K_2CO_3 , NaCl との反応試験を実施した結果、以下のことが判明した。

- (1) Na_2O (or K_2O) – Al_2O_3 – SiO_2 系反応化合物の生成が見られた。供試耐火材料は明らかにアルカリ塩と反応して低融物を生成し、損傷された。
- (2) NaCl と供試耐火材料との反応化合物は認められず、耐火材料中に NaCl として浸透しているだけであった。
- (3) アルカリ塩が供試耐火材料に与える腐食性は以下であった。



4. 2 Summary

The reaction test of high alumina and chamotte refractory materials with alkaline salt, Na_2CO_3 , K_2CO_3 and NaCl , revealed the following results.

- i) Reaction compounds of Na_2O (or K_2O) · Al_2O_3 · SiO_2 were produced. Refractory materials used for the test produced substances with low melting temperature through the apparent reaction with alkaline salt and were damaged.
- ii) No reaction compounds of NaCl with reaction materials used for the test were confirmed, and only the NaCl that penetrated into the refractory materials was observed.
- iii) The corrosiveness of alkaline salt against refractory materials used for the test was as follows:

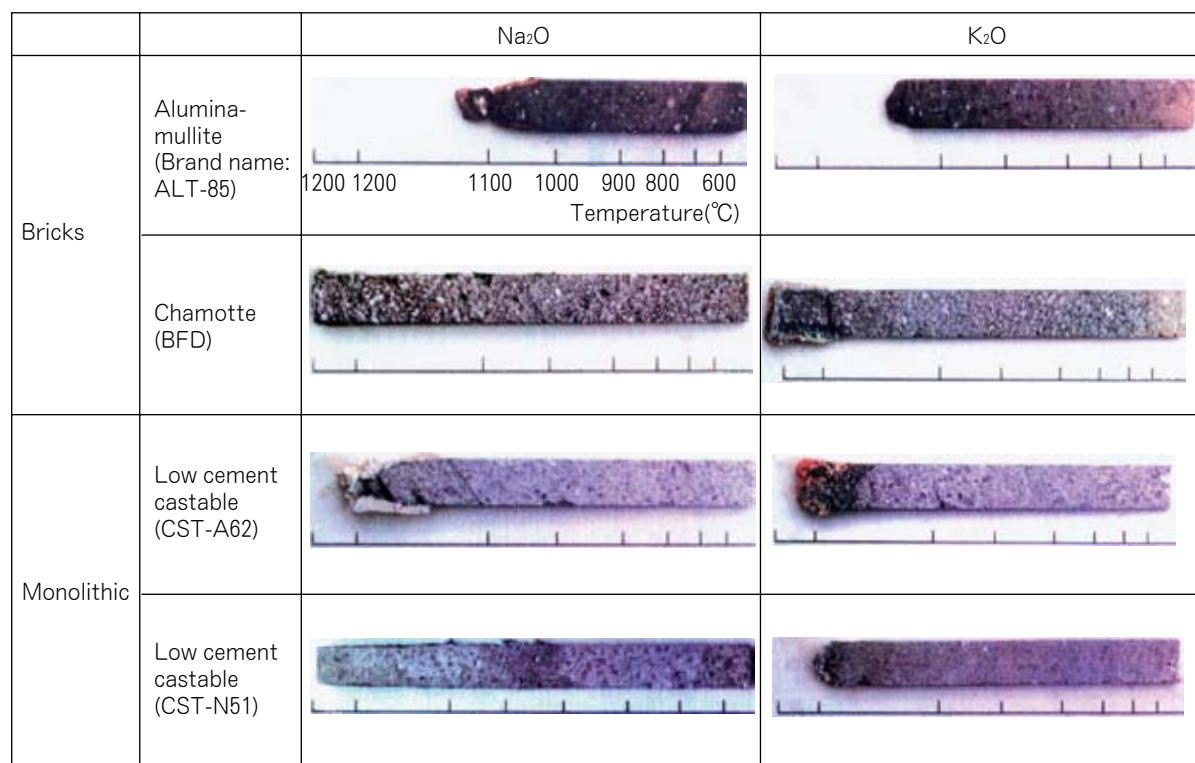


Fig. 4 Bricks and monolithic refractories after chemical reaction test with Na_2O or K_2O agents.

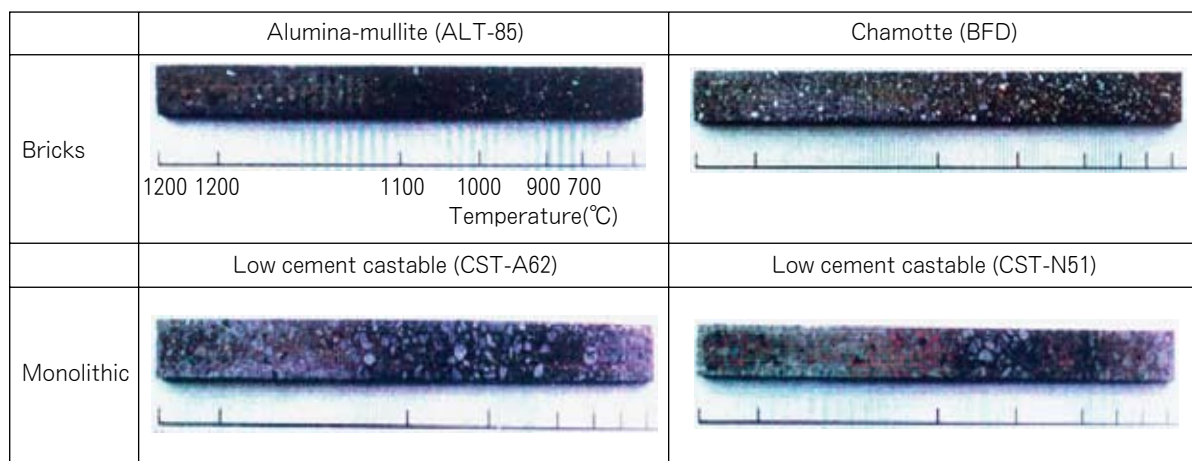


Fig. 5 Bricks and monolithic refractories after chemical reaction test with NaCl agents.

5. 実際のゴミ焼却灰との反応試験

前述の反応試験ではアルカリ塩のみによる腐食状況を確認した。ここでは、実際に処理されているゴミ焼却灰の中で、アルカリ成分が比較的多いものと少ないものによる耐火材料の腐食状況を示す。

5.1 試験方法

使用した焼却灰の化学成分をTable 5に示す。試験に供した耐火レンガの品質をTable 6に示す。今回は実際の灰溶融炉に適用される耐火レンガを選択して試験を行った。加熱条件は反応を加

5. Reaction Test with Actual Incineration Fly Ash of Wastes

The reaction test described above confirmed the state of corrosion caused only by alkaline salt. Therefore, a test was conducted using actually processed incineration fly ash of wastes, and the state of corrosion was compared between refractory products with relatively low or high amounts of alkaline components.

5.1 Test method

Table 5 shows the chemical composition of the incineration fly ash used for the test, and Table 6 shows the quality of the refractory brick products used. These brick products were selected from those used for actual ash melting furnaces. Test specimens were heated at 1300°C and held for 2 hours to accelerate the reaction. However, other conditions of the test were determined according to the previous alkaline reaction test.

5.2 Results

Fig. 6 shows the results of the reaction test. The amount of corrosion of test specimens was larger in the case of incineration fly ash with larger alkaline component. Among these largely corroded materials, the amount

Table 5 Chemical composition of incineration fly ash

	Fly ash A	Fly ash B
Chemical composition	Content (mass%)	Content(mass%)
SiO ₂	0.7	27.8
Al ₂ O ₃	0.4	12.8
CaO	10.8	23.6
MgO	0.2	2.8
Na ₂ O	16.7	2.1
K ₂ O	15.8	0.6
SO ₃	10.0	2.4
Cl	46.5	7.4
lg.Loss	6.8	20.1

Table 6 Sample bricks

	Alumina-Silicon carbide	Middle alumina	High alumina	Alumina-Chrome
Brand name	SCX-A40	MLM-55F	DRL-90S	DRL-100FCZ
Chemical composition (mass%)				
Al ₂ O ₃	55.2	60.6	91.0	78.7
SiO ₂	11.4	38.5	7.9	5.4
SiC	35.6			
Cr ₂ O ₃				16.9
ZrO ₂				3.9
Apparent porosity(%)	11.0	15.5	16.0	15.5

速するため、1300℃で2時間保持する条件で実施したが、その他は前項のアルカリ反応試験方法に準じて実施した。

5. 2 結果

Fig. 6に反応試験結果を示す。アルカリ成分の多い焼却灰を用いた方が、供試材料の腐食の程度が相対的に大きかった。その中で、アルミナ-炭化珪素質れんがや中アルミナ質れんがの腐食がやや目立った。しかし、実際の焼却灰にはアルカリ以外の成分も多く含まれているので、アルカリのみを用いた試験よりも腐食の程度は小さいと考えられる。

6. 結言

リサイクルエネルギーとしてバイオマス廃棄物の活用が期待されるが、バイオマス廃棄物にはNa, Kを多く含んでいるものがある。このNa, Kが高温炉壁として使用される耐火材料に及ぼす腐食の影響を評価した。その結果、耐腐食性の点で適切な耐火材料を選択する指針が得られた。

しかし、バイオマス廃棄物エネルギーを利用する燃焼炉について、個々に適切な耐火材料を選択するには、下記の検討項目も実施する必要がある。

(1) バイオマス廃棄物等の実際の燃焼灰の調査と耐火材料との反応性の検討。

of corrosion of alumina-silicone carbide brick products and middle alumina brick products was particularly high. However, in actual incineration plants, the amount of corrosion could be smaller than this test result which used only alkaline substances, since the incineration fly ash used in actual incineration plants also contain other non-alkaline components in large amounts.

6. Conclusions

Biomass wastes are expected to be effectively recycled to produce energy. However, biomass wastes sometimes contain large amounts of Na and K. The effect of corrosion by Na and K on refractory materials which are used for high-temperature furnaces was studied, and a valuable guideline was obtained for selecting optimum refractory materials in terms of corrosion resistance.

However, in order to select optimum refractory materials for combustion furnaces assuming that biomass wastes are recycled to produce energy, the following issues must also be studied:

- i) Actual incineration fly ash of biomass wastes, and its reactivity with refractory materials,
- ii) The structure and operating conditions of

Brand name	Ash A	Ash B
SCX-A40		
MLM-55F		
DRL-90S		
DRL-100FCZ		

Fig. 6 Cross section of samples after chemical reaction test under the condition of 1300°C-2h with fly ash generated in actual furnace.

- (2) 利用しようとする炉の構造と操業条件からの検討。
- (3) 溶損，膨大・剥離，スポーリングなどの使用条件に応じた損傷形態の推定。
- (4) 施工方法，コストの検討。

- the furnace in which refractory materials are used,
- iii) Possible types of damage such as melting, swelling and peeling and spalling, corresponding to actual usage conditions, and
- iv) Method and cost of installing refractory materials.

References

- 1) Takashi Katsura : Bunseki [10] 648～655, 1979
- 2) Akira Yamaguchi and Etsuro Kato : Yogyo-Kyokai-Shi 83 [10] 485～490, 1975
- 3) Susumu Okawara and Akira Yamaguchi : Yogyo-Kyokai-Shi 77 [6] 208～216, 1969
- 4) Akira Yamaguchi : Yogyo-Kyokai-Shi 79 [4] 124～131, 1971
- 5) Akira Yamaguchi : Yogyo-Kyokai-Shi 78 [7] 237～249, 1970