

SHINAGAWA TECHNICAL REPORT

Shinagawa Refractories Australasia Pty. Ltd.
“New Generation Shotcrete Material for Alkali
Rich Areas of The Australian Market”

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品川技報

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**“New Generation Shotcrete Material for Alkali Rich Areas of
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Abstract

In the Australian refractory market, the main users of shotcrete materials are in the industrial (non steel) markets, particularly the cement and lime industry where resistance to alkali attack is required. Shinagawa Refractories Australasia has developed the NOVACRETE[®] range of shotcrete products with a focus on excellent installation characteristics across the range while maintaining the application specific formulations required in alkali rich environments.

1. Introduction

The shotcrete or wet gunning process has been well established in international refractory markets since the early 1990s^{1), 4)} and has merits due to considerations such as speed of installation, lower levels of wastage and safety concerns such as dust generation when compared to dry gunning equivalents^{1)~4)}. The installation procedure is the same as most standard wet gunning installations where a dry castable is mixed with water before being transported via a concrete pump to the work face where an accelerator is mixed with the castable in a high velocity air stream^{2), 3)}.

Shinagawa Refractories Australasia's NOVACRETE[®] range of products has been developed as a robust, user friendly product that is able to be easily installed. The current range that applies to the cement and lime industry include several products with each of these products having a certain role in the market place.

2. NOVACRETE[®] Products for Application in Cement and Lime Kilns

Rotary kilns in the cement industry in Australasia are traditionally lined with refractory brick, however there are areas of cement and lime manufacturing plants that are lined with monolithic refractories such as preheat towers, hoods, coolers and tertiary air ducts⁴⁾. These areas contain high levels of alkali that can cause loss of refractory linings by the process:

alkali vapour → penetration → solidification → spalling

Shinagawa Refractories Australasia's alkali resistant products give protection against

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Table 1 Comparison of NOVACRETE[®] products

Product		NOVACRETE [®] R2	NOVACRETE [®] R4	NOVACRETE [®] R9
Aggregate		Mullite / Andalusite	High alumina + SiC + ZrO ₂ •SiO ₂	Mullite + SiC + ZrO ₂ •SiO ₂
After heating at 110°C / 24 hrs	BD (kg/m ³)	2450	2860	2530
	MOR (MPa)	8	10	8
	CCS (MPa)	80	70	90
	PLC (%)	-0.1	-0.1	-0.1
After heating at 1000°C / 5hrs	BD (kg/m ³)	2350 – 2450	2750	2450
	MOR (MPa)	12	12	10
	CCS (MPa)	70	80	90
	PLC (%)	-0.4	-0.1	-0.3

the penetration of alkali vapour by creating a high viscosity glass on the surface layer of the refractory¹⁾ hence they are well suited to the environment while maintaining the good physical properties achieved by the use of low cement castables (LCCs).

The products that have been developed are NOVACRETE[®] R2, NOVACRETE[®] R4 and NOVACRETE[®] R9 and are aimed at being able to perform across all areas in these industries (Table 1). NOVACRETE[®] R2 is a 60% alumina material based on low iron, synthetic mullite aggregates and is designed for use in a wide range of industrial applications including those with a low alkali load. NOVACRETE[®] R4 is a premium grade alkali resistant material which is chemically also 60% alumina. It is formulated on high alumina aggregates with the addition of Silicon Carbide and Zirconia Silicate for increased resistance to alkali vapour penetration. The base aggregate choice also gives the material good abrasion resistance in environments such as cement and lime kiln preheat tower cyclones. NOVACRETE[®] R9 was developed to have the alkali resistance of NOVACRETE[®] R4 but is based on lower density aggregates. The end result is a product that has the same alkali resistance at 10% lower installed density.

3. Alkali Resistance Test Method

The products in this study were tested for resistance to alkali attack by Shinagawa Refractories Australasia standard cup test method. Samples were cut from gunned panels with the cup section formed by core drilling. The samples were prefired to the test temperature of 1100°C before being filled with the alkali salt reagent and a lid of the same refractory material being affixed with an air setting mortar. The samples were then fired to 1100°C and held at this temperature for a total of 48 hours before cooling to room temperature. The lid was removed and the sample inspected before being refilled with reagent, sealed and fired to 1100°C for a further 48 hours. On completion of the second cycle the samples were sectioned and photographed with observations made as to the condition of the materials.

4. Alkali Resistance Test Results

4. 1 Using potassium sulphate as the reagent

When samples were filled with Potassium Sulphate and fired to 1100°C the reagent was absorbed into the cup as seen in Fig. 1. The NOVACRETE® R2 sample showed some small cracks indicating that the vapour penetration had some effect. The NOVACRETE® R4 and NOVACRETE® R9 samples did not show any discontinuity in the samples after firing.



Fig. 1 Results of alkali cup testing at 1100°C with Potassium Sulphate reagent.

4. 2 Using sodium sulphate as the reagent

4. 2. 1 Firing at 950°C

Results shown in Fig. 2 show that for the NOVACRETE® R2, the salt was absorbed into the refractory material with no evidence of cracking or bowing of the sample. The NOVACRETE® R4 and NOVACRETE® R9 show containment of the alkali salt with some reaction layer in each of the samples with no evidence of cracking or bowing present in the samples.



Fig. 2 Results of alkali cup testing at 950°C with Sodium Sulphate reagent.



Fig. 3 Results of alkali cup testing at 1100°C with Sodium Sulphate reagent.

4. 2. 2 Firing at 1100°C

Results are shown in Fig. 3 and like the 950°C firings; there is absorption in the NOVACRETE® R2 sample with no disruption to the structure. The NOVACRETE® R4 and NOVACRETE® R9 samples also show containment of the reagent with a reaction layer larger than that of the samples fired to 950°C. This is expected as the reaction rate will increase as the firing temperature is increased.

4. 2. 3 Summary of results

From the results observed, the NOVACRETE® R2 is considered applicable for areas of zero or mild alkali conditions only as there is disruption of the sample in the Potassium Sulphate test. Varying the alkali conditions did vary the result with the Sodium Sulphate reagent causing no cracking or bowing.

The NOVACRETE® R4 and NOVACRETE® R9 did not display any disruption through cracking or bowing in any of the alkali cup testing conducted. These products are considered as Shinagawa Refractories Australasia's premium alkali resistant shotcrete grades for the cement and lime industry.

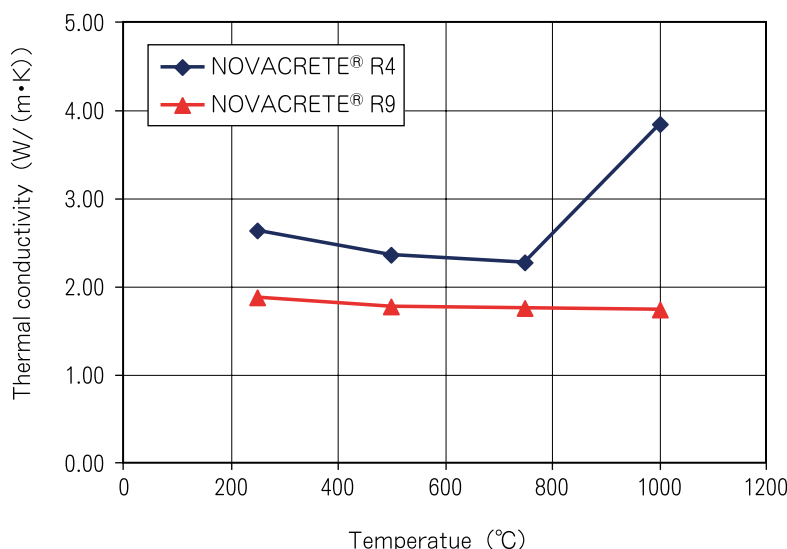


Fig. 4 Thermal conductivity of NOVACRETE® R4 and R9.

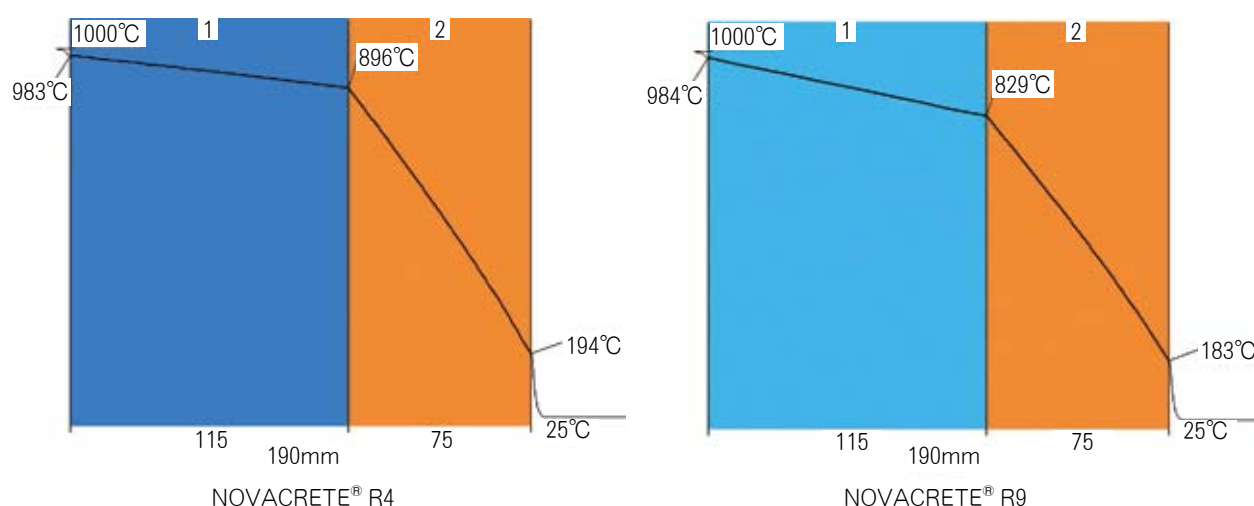
5. Influence of Density on Properties and Performance

Both NOVACRETE® R4 and NOVACRETE® R9 share the same system to generate alkali resistance, however the NOVACRETE® R4 is based on high alumina matrix and the NOVACRETE® R9 is based on a preformed Mullite matrix. The end result is a density difference of approximately 10% meaning a decrease in the material required to be ordered by the end customer while maintaining similar physical properties and performance in alkali environments.

Not only is there a benefit in density and material requirements, the NOVACRETE® R9 has a decreased thermal conductivity compared to NOVACRETE® R4 due to the inherent thermal conductivity of the main aggregates in the products. This difference in thermal conductivity between the products is seen in Fig. 4. In a standard configuration of inside temperature of 1000°C with a lining configuration of 75mm 1200°C grade lightweight refractory as backup layer and 115mm layer of dense hot face refractory, the effect on shell temperature can be seen in Fig. 5. The end result is a lower shell temperature and heat loss and as previously noted a lower lining weight.

6. Installation of NOVACRETE® Products

NOVACRETE® products are designed with the aim to make the product as easy as possible for the contractor to install. The products are robust enough to withstand the slight variances in water addition that is the case on a lot of sites and are able to be installed through a range of equipment types such as small and large pan mixers and small and large concrete pumps. Careful design in particle size has led to products that are able to be transported very long distances both vertically and horizontally in steel pipe work with vertical pumping distances approaching 100m being achieved. Control of



	NOVACRETE® R4	NOVACRETE® R9
Interface Temp °C	896	829
Outside Temp °C	193	183
Heat Loss W/m ²	2607	2364
Heat Storage MJ/m ²	362	312
Lining weight kg/m ²	391	358

Fig. 5 Effect of lower density and thermal conductivity on shell temperatures.



Fig. 6 Installation of NOVACRETE® product.

the chemical reactions in the calcium aluminate bonded system gives working times that enable long installation periods between cleaning of equipment. This allows contractors to schedule breaks in the installation work, such as meal breaks and adjustment of formwork to be completed with less risk of the refractory hardening in the pipe work. Fig. 6 shows the typical installation conditions of a NOVACRETE® product showing the normal characteristics of a shotcrete installation of low dust and rebound.

7. Conclusion

Installation of refractories by wet gunning also known as the shotcrete method gives the benefits of low dust, low rebound and potential for fast installation rates when compared to dry gunning of low cement refractories. Shinagawa Refractories Australasia has developed a range of NOVACRETE[®] products specifically for mild and high alkali environments seen in the cement and lime industries with good alkali resistance achieved in the tests conducted across a range of temperatures and alkali reagents.

References

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耐アルカリ性に優れた次世代ショットクリート材 (豪州市場向け)

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要 旨

豪州の耐火物市場においてショットクリート材は非鉄鋼産業、特に耐アルカリ性の要求が強いセメント産業や石灰産業で多く使用されている。Shinagawa Refractories Australasia (以下、SRA) は、耐アルカリ性に優れ、施工性が良好なショットクリート材 NOVACRETE[®]を開発した。

1. はじめに

ショットクリート(新湿式吹付け)工法は乾式吹付け工法と比較して、施工速度が速い、リバウンドロス(廃棄物発生量)が少ない、施工時の粉塵発生量が少ない等の優位性があり、1990年代初頭から世界中で適用されている^{1)~4)}。施工方法は一般的な湿式吹付け工法と同様であり、混練したキャストブルをポンプで圧送し、硬化促進剤を圧縮空気とともに添加し吹付けを行う^{2),3)}。

SRAのショットクリート材 NOVACRETE[®](ノバクリート)は施工性を重視しており、作業者にやさしい製品として開発された。現在の主な適用分野はセメントおよび石灰産業であり、同市場において欠かせない製品となっている。

2. セメントおよび石灰用キルン向けNOVACRETE[®]

豪州のセメントロータリーキルンは耐火レンガがライニングされているが、セメントや石灰の製造工場のプレヒーターやフード、クーラーやエアダクトといった部位には不定形耐火物が使用されている⁴⁾。このような部位は高アルカリ環境となるため、以下のプロセスで耐火物の損耗が起こる。

アルカリ蒸気 → 耐火物への侵入 → 耐火物中での沈積 → スポーリング

SRAの耐アルカリ性キャストブルは表面が高粘性のガラス層で覆われるためアルカリ蒸気に強く¹⁾、また低セメント化によって良好な物理特性も維持しているため、上述した高アルカリ環境下の使用に適している。

NOVACRETE[®] R2, R4, R9はこれらのキャストブルをベースとして製品化されており、セメントおよび石灰用キルンのあらゆる部位に適用できる(Table 1)。NOVACRETE[®] R2は合成ムライト骨材をベースとした低Feの $\text{Al}_2\text{O}_3=60\%$ 材質であり、アルカリの影響が比較的小さい部位への適用を目的とした材料設計となっている。NOVACRETE[®] R4は $\text{Al}_2\text{O}_3=60\%$ の高品位材質であり、高純度アルミナ骨材をベースとして、アルカリ浸潤に対する抵抗力を高めるため炭化珪素とジルコンが添加されている。また、ベースとなる高純度アルミナ骨材はセメント、

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石灰キルンのプレヒーターサイクロン部のような使用環境における耐摩耗性向上にも寄与している。NOVACRETE[®] R9は軽量材質であり、R4と同等の耐アルカリ性を有しながら、施工体の嵩比重はR4よりも10%軽い。

3. 耐アルカリ性の試験方法

本検討では社内ルツボ試験規格に準じたアルカリ侵食試験を行った。試料はパネルに吹付けた材料をコアボーリングにより加工した。試料を1100℃で事前焼成した後、内部にアルカリ塩試薬を詰め込み、試料と同材質の蓋と気硬性モルタルにて封をした。その後1100℃で48時間加熱した後、冷却、開封して試料を観察し、再びアルカリ塩試薬を詰め込み、さらに1100℃で48時間保持した。2サイクル目を終えた後、試料を切断して状態を観察し写真撮影した。

4. 耐アルカリ試験結果

4. 1 硫酸カリウム試薬を用いた結果

試験結果をFig. 1に示す。試料に硫酸カリウム試薬を充填して1100℃加熱すると、試薬は試料に吸収された。NOVACRETE[®] R2では浸潤した蒸気がある程度は影響したことを示す小さな亀裂が認められた。それに対してNOVACRETE[®] R4とR9には亀裂が全く認められなかった。

4. 2 硫酸ナトリウム試薬を用いた結果

4. 2. 1 950℃加熱

試験結果をFig. 2に示す。NOVACRETE[®] R2では試薬が吸収されたものの、亀裂や変形などは認められなかった。NOVACRETE[®] R4とR9では試薬との反応層が認められたが、亀裂や変形などは認められなかった。

4. 2. 2 1100℃加熱

試験結果をFig. 3に示す。950℃加熱と同様の結果を示しており、NOVACRETE[®] R2は試薬が吸収されたものの、亀裂や変形が認められなかった。NOVACRETE[®] R4とR9は950℃の試験結果と比較して反応層が拡大していた。これは温度上昇にともなう反応速度の増加によるものと考えられる。

4. 2. 3 実験結果のまとめ

NOVACRETE[®] R2は硫酸カリウムを用いた試験で試料に損傷が認められたため、アルカリの影響が中程度以下の条件に適していると考えられる。ただし、アルカリ条件によって結果も異なり、硫酸ナトリウムを用いた試験では亀裂も変形も生じなかった。

NOVACRETE[®] R4とR9はどの条件においても亀裂や変形などは認められなかったため、セメントや石灰産業向けの製品として高い耐アルカリ性を有していると考えられる。

5. 品質特性と耐用に及ぼす嵩比重の影響

NOVACRETE[®] R4とNOVACRETE[®] R9では耐アルカリ性を付与する材料設計は同じであるが、R4が高アルミナ組成ベースであるのに対して、NOVACRETE[®] R9はムライトベースである。そのためR9はR4よりも約10%軽量であり、施工所要量の低減に寄与している。

また、主骨材の違いによってR9はR4と比較して熱伝導率が低い。R9とR4の熱伝導率をFig. 4に示す。炉内温度を1000℃として稼働面側に115mmの耐火物（R9またはR4）、背面側に75mmの軽量耐火物（最高使用温度1200℃）をライニングした場合の鉄皮温度へ与える影響をFig. 5

に示す。熱計算結果からR9を適用した場合、鉄皮温度が低くなり、R4と比較して熱ロス抑制効果が高いことが分る。

6. NOVACRETE®の施工

NOVACRETE®はできるかぎり簡便な施工を実現するために設計された製品であり、施工水分量の些細な変動に対しても安定であることから、ミキサーの大小やコンクリートポンプの能力にかかわらず様々な場所で施工可能である。製品粒度の最適化により、ポンプ圧送にて100mにおよぶ鉄管でも垂直・水平方向によらず長距離搬送が可能である。また硬化時間の制御によって配管中での硬化リスクが低いため、作業中の休憩時間や型枠の調整時間および施工機器の清掃までの可使時間を十分確保すること可能である。Fig. 6にNOVACRETE®を用いた一般的な施工の様子を示す。図からショットクリート工法は粉塵が少なく、リバウンドも少ない施工法であることがわかる。

7. 結論

低セメント耐火物の乾式吹付け工法と比較して、ショットクリート工法は粉塵の発生やリバウンドロスが少なく、短時間で施工可能な湿式吹付け方法である。SRAではセメント産業や石灰産業のような中～高アルカリ環境での使用に適したショットクリート材 NOVACRETE®を開発した。これらの製品は、さまざまな試験の結果、優れた耐アルカリ性を有していることを確認している。