

SHINAGAWA TECHNICAL REPORT

コークス炉用珪石れんが

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品川技報

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要 旨

コークス炉の建設・改修用の珪石れんがC.SC, C.SCD, C.SCDD, および積替え補修用珪石れんがHRS, C.FS-98について述べた。C.SC, C.SCD, C.SCDDはそれぞれドイツ規格のKN, KD, KSに対応するもので多くの建設に使用されている。HRSは急加熱しても割れ難い積替え補修用れんがで、多くの実績がある。C.FS-98は常温からほとんど熱膨張しないれんがで、今後実績を積み重ねて行く製品である。

Abstract

Silica bricks, C.SC, C.SCD and C.SCDD for coke oven construction or renovation and HRS and C.FS-98 for exchange repair are introduced. C.SC, C.SCD and C.SCDD correspond to the grades normalized in German standard (DIN) as KN, KD and KS, respectively. They have been widely applied to new coke oven constructions. HRS, with excellent thermal spalling resistance for hot exchange repair, has many successful results. The effectiveness of the extremely small thermal expansion from room temperature to high temperature of C.FS-98 will be validated in various commercial applications in the future. In this paper, characteristics of these silica bricks are described.

1. 緒言

本報では、コークス炉用珪石れんがとして、常温で実施される建設・改修用の材質と高温で実施される熱間補修用の材質について述べる。本書の総説に述べられているように、石炭乾留のための熱は炉壁の熱伝導で燃焼室から炭化室に供給されるため、炉壁の珪石れんがの熱伝導率は高い方が好ましい。また、炭化室炉壁のれんがは高い石炭膨張圧を受けていることに加え、石炭装入やコークス押し出しに伴う摩耗や剥離を生じる。これら

1. Introduction

Silica bricks for construction/renovation and hot repairs are described in this paper. As mentioned in a review article in this booklet, heat for coal coking is transmitted from the combustion chamber to the coking chamber through the oven wall by thermal conduction, thus, high thermal conductivity of the wall silica brick is desirable in terms of heat efficiency. In addition, in order to withstand the high coal-expansion pressure during coking as well as the abrasion

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に対し、当社は珪石れんがの低気孔率化を図って対応してきた。当社は、確立した技術を中国の中鋼集団耐火材料有限公司に委譲、高品質な珪石れんがC.SC, C.SCD, C.SCDDを供給しており、それぞれドイツ規格（DIN : Deutsches Institut für Normung）のKN, KD, KSに相当する。

一方、長年の使用で損傷が激しくなった炭化室はれんがの積替え補修が必要となる場合もある。コークスの需給はタイトな状態が続いているため、補修に際してはコークス炉の高い生産性を維持するため短期間での施工が求められ、かつ、補修部には高い信頼性が必要である。これに対して、熱間でれんがの積替えを行っても亀裂が入らず急速昇温可能で、さらに、使用中に組成と特性が珪石れんがに近づいていくことで高い信頼性を得ることができる熱間補修用れんがHRS（Hot Repair Silica）を開発し、各所で多くの実績がある。加えて、熱膨張がほぼゼロのれんがC.FS-98もラインナップしている。

2. 建設・改修用珪石れんが

珪石れんがは石英からなる天然の原料に石灰などの転位促進剤を加えて混練し、成形した後に1400℃程度で焼成して得られる。石英は焼成中にクリストバライトとトリジマイトに相転位し、こ

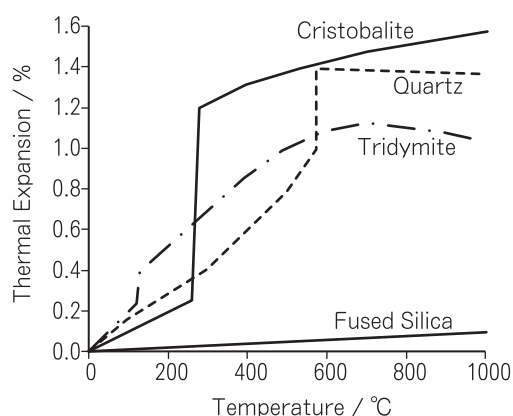


Fig.1 Thermal expansion behavior of minerals consisting of SiO_2 .

and peeling-off due to coal charging and coke discharging, high rigidity is required of the wall bricks. Therefore, we improved silica brick performance by reducing porosity. Our newly developed silica brick manufacturing technology was transferred to Chinese producer “Sinosteel Refractory Co., Ltd.” to manufacture high quality silica bricks C.SC, C.SCD and C.SCDD. These correspond to KN, KD and KS, which have been normalized in the German standard (DIN: Deutsches Institut für Normung), respectively.

On the other hand, severely damaged coking chambers require brick exchange repair. However, the tight supply and demand for coke situation, short repair time and high credibility of repaired chambers are required. Regarding this situation, we developed HRS (Hot Repair Silica) for hot repair which allows a quick heating up schedule due to its high thermal shock resistance. Additionally, changes in its mineralogical composition and physical properties, approaching that of traditional silica brick during high temperature operation, assures high quality of the repaired chambers. HRS has shown successful results in many coke oven repairs. In addition, we provide silica brick C.FS-98 which has extremely low thermal expansion. While only a few practical results have been obtained for C.FS-98 at this moment, suitable commercial application will be studied in the near future.

2. Silica Bricks for Construction and Renovation

Silica brick is manufactured by pressing a mixture of natural quartzite and lime, which functions as phase transformation accelerator, followed by burning at approximately 1400℃. During the burning process, quartz transforms to cristobalite and tridymite showing

これらの結晶相は高温での熱膨張が極めて小さいため (Fig.1)¹⁾, 珪石れんがは700℃以上でほとんど熱膨張しない特性を示すようになる。このため700℃以上で発生する熱応力は極めて小さく, 冷却されずに稼働し続けるコークス炉に適したれんがとして広く使用されている。一方, 700℃以下の熱膨張係数は大きく, 温度が低下すると割れやすい。ここで, Fig.2¹⁾に示すように, 石英のクリストバライトやトリジマイトへの相転位は大きな体積膨張を伴うことから, 珪石れんがに石英が残存していると高温で圧縮割れや壁の迫り出しを生じる危険性が懸念される。したがって, 珪石れんがの製造には焼成中の相転位を促進しつつ焼成後の冷却で割れを発生させないように, 高度な焼成管理技術が要求される。また, コークス炉建設には非常に多くの形状のれんがが使用されるため, それぞれの形状にあった成形技術と工程管理技術が求められる。

当社は国内で確立した珪石れんがの生産を多くの最新鋭の製造設備を有する中鋼集団耐火材料有限公司に委譲した。その際, れんがの製造技術のみならず製品検査, 梱包, 納期管理などのノウハウも提供した。それに基づいて両社の協力基盤を

a low thermal expansion coefficient at high temperature as shown in Fig.1¹⁾. This results in unique silica brick thermal expansion behavior in which the thermal expansion coefficient above 700℃ is small. Hence, it is suitable to coke oven which operates for many decade without cooling since little thermal stress initiation is expected above 700℃. Contrarily, silica brick is easy to spall below 700℃ due to large thermal expansion coefficient. As shown in Fig.2¹⁾, since considerable volume change occurs along with the crystal phase transformation from quartz to cristobalite or tridymite, compressive fracture and/or flexure of chamber wall may occur if residual quartz is included in the silica bricks. Thus, burning has to be carefully controlled in the silica brick manufacturing process so as to complete the crystal phase transformation as well as prevent cracking during cooling. Furthermore, since coke oven construction requires numerous kinds of shapes, individually suited molding technology and careful manufacturing process control technology are necessary.

We transferred the newly developed silica brick manufacturing technology as well as know-how for inspection, packing, delivery control, etc, to the Chinese company Sinosteel Refractory Co., Ltd. which owns many state-of-the-art manufacturing facilities. A high quality silica brick supplying system has been established through this technology transfer

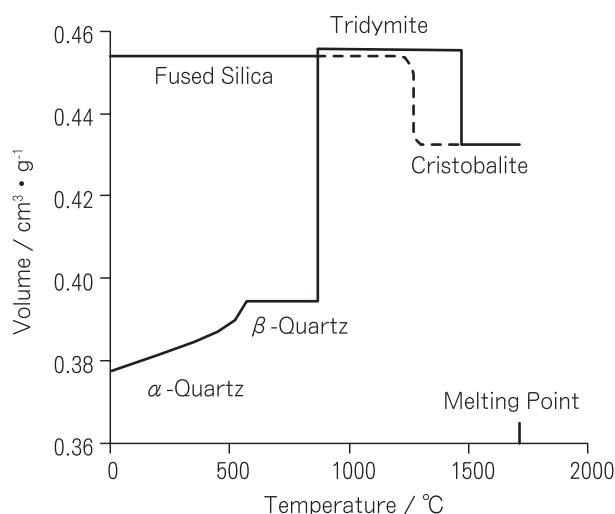


Fig.2 Changes in crystal species and volume as a function of temperature¹⁾.

Table 1 Typical properties of silica bricks for coke ovens

Brand	C.SC	C.SCD	C.SCDD
Corresponding DIN	KN	KD	KS
Apparent Porosity / %	21	19	17
Apparent Specific Gravity / -	2.32	2.32	2.32
Cold Crushing Strength / MPa	40	50	65
Chemical Composition / mass%			
SiO ₂	94.5	95.5	95.3
Fe ₂ O ₃	0.8	0.6	0.7



Fig.3 External appearance of silica brick.

構築，高品質珪石れんがの供給体制を確立している。

Table 1にコークス炉用珪石れんがの品質を，Fig.3にれんがの写真を示す。C.SCはDINのKNに相当する標準品でコークス炉用として広く用いることができる。C.SCDはDINのKDに相当する熱伝導率の高い低気孔率品で炭化室の壁の主流となっている。C.SCDDはDINのKSに相当するもので，さらに気孔率を低減させた高密度品である。

当社が供給する珪石れんがは，中鋼集団耐火材料有限公司で厳しく品質管理されており（Fig.4），規格を十分満足した製品を安定的に製造している。コークス炉の建設のように多量のれんがを製造する場合，成形用プレス機の金型が摩耗することで徐々に寸法が大きくなり，その結果れんがの寸法が公差内で大きい側に偏る場合がある。寸法が大きい側に偏ると築炉時にれんがの切断加工を行う必要が生じロスが大きくなるが，小さい側に偏った場合モルタルで調整が可能である。そこで，寸法を高い精度で管理した上で小さい側に偏らせた偏公差で製造することが有効である。中鋼集団耐火材料有限公司は，そのような要求にもきめ細かく対応してきた（Fig.5）。

また，コンテナ内でのれんがの角欠けなどに配慮した梱包も実施している。れんがを保管する十



Fig.4 Inspection of silica brick at Sinosteel Refractory Co., Ltd.

and tight partnership.

Table 1 and Fig.3 show the typical properties and external appearances of the silica bricks, respectively. C.SC is a standard type brick corresponding to KN which is normalized according to DIN. It is widely applicable to the coke oven. Dense brick C.SCD, which corresponds to KD normalized according to DIN, exhibits high thermal conductivity and low porosity. It is our main brand for the coking chamber wall. The lowest porosity super dense brick C.SCDD corresponds to KS normalized according to DIN.

The quality of our silica bricks is strictly controlled at Sinosteel Refractory Co., Ltd. as indicated in Fig.4, thus, we can stably provide silica bricks which fully satisfy the requirements of the industrial standards. Generally, production of a huge number of bricks, which is needed for coke oven construction, tends to induce larger uneven deviation of geometrical dimensions because of pressing mold abrasion. Although positive deviation in brick dimension requires brick cutting which increases the work load, gaps caused by negatively deviated brick can be adjusted by joint mortar. Hence, accurate control of the brick dimensions which deviate negatively is effective for construction work efficiency. Sinosteel Refractory Co., Ltd. thus responded to requirements such as those

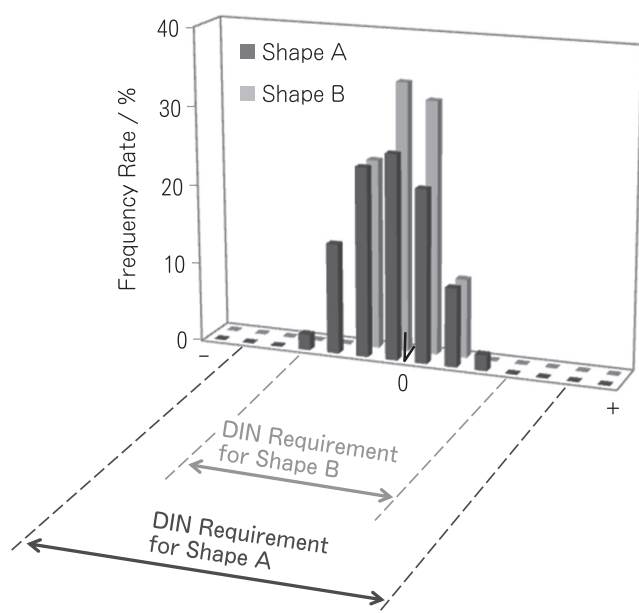


Fig.5 Deviations in geometrical dimensions of silica bricks manufactured at Sinosteel Refractory Co., Ltd.

分な倉庫が確保できない場合、築炉による倉庫在庫の減少に合わせてきめ細かい製造～出荷管理が必要であり、中鋼集団耐火材料有限公司と当社の緊密な連携でそれに対応している。

3. 熱間積替え補修用れんが

コークス炉は稼働を開始すると燃焼を止めることがなく温度の変動は小さいが、炭化室の両端(端フリュー)はコークス押し出しの度に開放され温度が低下するため、れんがの損傷が大きい。そのため、比較的早い段階から吹き付けや溶射によって補修されるが、損傷が激しくなるとれんがの積替えが行われる。積替えは対象の燃焼室に築炉工が入って行われるため、温度を低下させる必要がある。一方、積替えのために炭化室全体を冷却すると、炭化室の中央部まで低温に曝されれんがが大きく損傷する。そのため、積替え範囲の作業環境保護とその他の範囲の温度維持を目的に、注意深く断熱される。Fig.6は6フリューまでの積替えの例である。積替え部奥の炭化室内に遮熱壁を設置し既存れんが表面を断熱パネルで保温して熱間

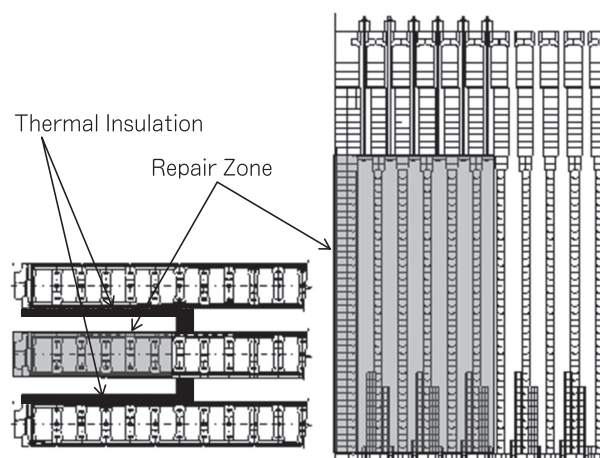


Fig.6 Example of end-flue repair.

indicated in Fig.5.

In addition, careful packing in order to prevent edge defects, which tends to occur in the container, is possible. Close cooperation between Sinosteel Refractory Co., Ltd. and us allows intensive control of production and shipment particularly for the construction site without sufficient warehouse.

3. Silica Brick for Hot Exchange Repair

While temperature variation of coke ovens is small since they operate continuously without cooling, both ends of the coking chamber (end flue) are cooled during the open-door pushing-out process, resulting in brick deterioration. Therefore, end flues are repaired by gunning and/or ceramic welding from early stages of coke oven operation. For severely damaged walls, however, brick exchange repair is carried out. In most cases, repair bricks are manually installed by brick layers, thus, provision of human tolerable temperatures is necessary. On the other hand, whole chamber cooling seriously damages the bricks in the central area. Thus, careful thermal insulation is required for both purposes, i.e., conservation of low temperature for masonry and high temperature

Table 2 Typical properties of HRS

		HRS
Chemical Composition / mass %	SiO ₂	96.5
	CaO	1.5
	Fe ₂ O ₃	0.5
Apparent Porosity / %		17.0
Bulk Density / g·cm ⁻³		1.85
Cold Crushing Strength / MPa		25.0

Table 3 Results of rapid heat experiment

	HRS	Ordinary Silica Brick
RT⇒200℃	○	○
RT⇒300℃	○	×
RT⇒400℃	○	×
RT⇒500℃	○	×
RT⇒600℃	×	×
100℃⇒600℃	○	×

○ : No crack was observed.
 × : Cracks were observed.

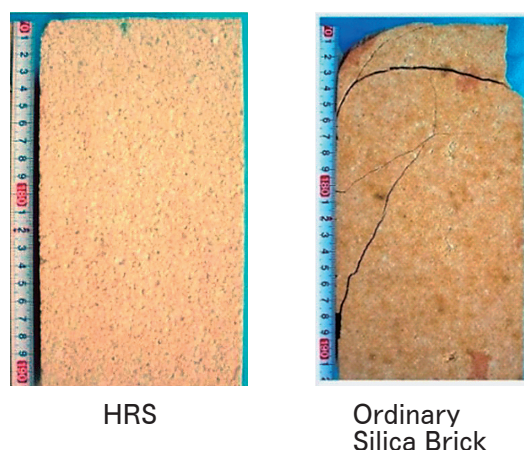


Fig.7 External appearances of silica bricks after rapid heating at 500℃.

積替え補修が行われた。

当社は2種類の積替え補修用れんがを供給している。一つはHRSで、珪石れんがをベースに熱膨張を低減することにより耐熱衝撃性を付与したものである。Table 2, 3にHRSの代表品質と各温度で急加熱した後の亀裂の観察結果を、Fig.7に500℃で急加熱した後の外観を示す。急加熱試験は所定温度に保持した電気炉に340×120×100mm形状のれんがを挿入し、亀裂発生の有無を目視確認した。Fig.7に明らかなように、通常珪石れんがは急加熱により激しく割れるが、HRSは割れを生じない。実窯の修理において、通常珪石れんがはれんが積み時点で割れを生じる場合があり、その時点で割れなくても施工後の昇温を緩やかに、例えば1カ月程度かけて、行う必要がある。これに対してHRSはれんが積み時に割れない

for the remaining chamber wall. Fig.6 gives an example of the thermal insulation system for brick exchange repair from the end flue to the 6th flue. A thermal insulation wall was installed in order to divide space into two sections; repair area and untouched area, and thermal insulation panels covered the adjacent chamber wall.

We provide two types of silica bricks for hot exchanging repair. One is HRS which exhibits excellent thermal shock resistance, which has been achieved by reducing the thermal expansion coefficient of regular silica brick. Table 2 and 3 summarize the typical properties and results of thermal shock test for the silica bricks, respectively. The thermal shock test was performed by inserting of 340×120×100mm samples into an electric furnace of which the in-furnace temperature was controlled at certain temperatures followed by inspection for crack initiation. As is obvious in Fig.7, No cracks were observed for HRS while ordinal silica brick exhibited sever spalling. Ordinal silica brick is sometimes broken during brick laying during repairs. If no spalling occurs during brick laying, a moderate heating up schedule, i.e. one month, is required in order to prevent thermal spalling. On the contrary, the shortest heating up time for walls repaired by HRS, which is never broken or cracked during brick laying, is two days.

In addition, long term stability of walls repaired by HRS is expected. The mineralogical

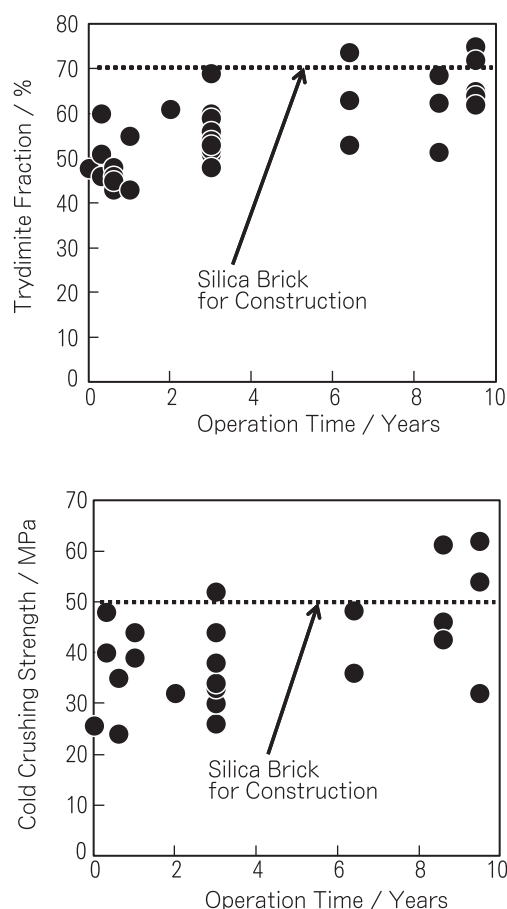


Fig.8 Changes in tridymite fraction and cold crushing strength of HRS in commercial application as a function of operation time.

のみでなく、施工後、最短2日間で昇温して立ち上げた実績がある。

このような急加熱に強い特性に加えて、HRSは実窯で長期間使用されることで組成が変化し、組成や特性が珪石れんがに近づいていくという特徴がある。Fig.8にHRSれんがの使用年数とトリジマイト量、圧縮強度の変化を示す。HRSは実窯で稼働中にその組成や特性が、建設用の珪石れんがに近づいていることがわかる。

もう一方の熱間積替え補修用れんがは、無膨張れんがである。Table 4に無膨張れんがC.FS-98の代表品質を、Fig.9にC.SCD、HRS、C.FS-98の熱膨張曲線を示す。無膨張れんがは中鋼集団耐火材料有限公司で製造している。無膨張であるため、

Table 4 Typical properties of C.FS-98

		C.FS-98
Chemical Composition / mass %	SiO ₂	99
	Al ₂ O ₃	0.1
	Fe ₂ O ₃	0.1
Apparent Porosity / %		16
Bulk Density / g・cm ⁻³		1.86
Cold Crushing Strength / MPa		44

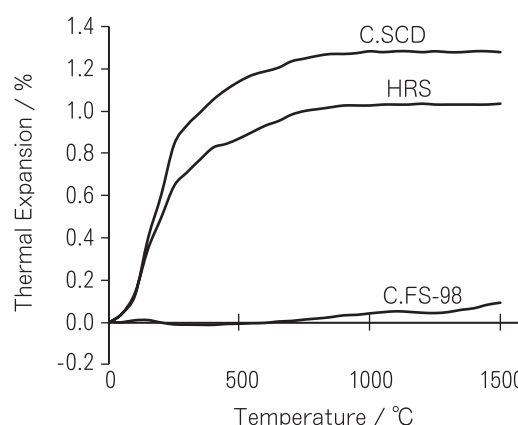


Fig.9 Thermal expansion curves of silica bricks.

composition and physical properties of the HRS approach to those of silica brick for construction over long term oven operation as shown in Fig.8, which indicates changes in the trydymite fraction and compressive strength as a function of time. This is evidence of the stableness of walls repaired by HRS.

The other silica brick for hot exchange repair is zero-thermal expansion brick. Table 4 shows the typical properties of zero-thermal expansion brick, C.FS-98 and Fig.9 summarizes thermal expansion curves of C.SCD, HRS and C.FS-98. C.FS-98 is manufactured by Sinosteel Refractory Co., Ltd. Due to its expansion-free property, no consideration for expansion absorption is necessary, resulting in easy brickwork design. Suitable application of the C.FS-98 will be examined and validated in commercially operated coke ovens in the near future.

膨張代を考慮する必要がなく，補修時の設計が簡便に行えることから，今後実窯での実績を積み重ねて行く。

4. 結論

当社はコークス炉の建設・改修用の珪石れんがとして工業規格を十分満足しているC.SC, C.SCD, C.SCDDを，積替え補修用として多くの実績のあるHRSと無膨張れんがC.FS-98を供給しており，いずれも厳しく管理された工場で製造されている。それぞれのれんがは特徴的な高温特性を示し，目的に応じた最適な材質選択が可能である。

4. Conclusion

We provide silica bricks for coke oven construction/renovation and for hot exchange repair. C.SC, C.SCD and C.SCDD are bricks for construction/renovation which fully satisfy industrial standards. For hot exchange repair, our successfully applied HRS and zero expansion C.FS-98 are available. These bricks are manufactured through a strictly controlled process. According to the unique high temperature properties of these bricks, suitable bricks can be selected for different requirements.

References

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