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SURVEY ON WORLDWIDE PREBAKED ANODE QUALITY

Raymond C. Perruchoud, Markus W. Meier and Werner K. Fischer
R&D Carbon Ltd.,P.O. Box 362, 3960 Sierre, Switzerland

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ABSTRACT

Anode quality data of 60 prebaked carbon plants were reviewed. The ranges and mode values of the means and of the variability of anode properties were determined and discussed. Some examples of distribution of properties are examined.

Causes of inferior or excellent anode quality figures were considered and their effects on the anode behavior and on pot performance are addressed. Interrelationships of thermal shock relevant properties are reported.

The bench mark anode quality that can be achieved in a modern plant using typical raw materials is also given.

ANODE PERFORMANCE

Technical Aspects

The carbon anodes experience severe thermal conditions in the pots. Thermal shock cracking, air burn and CO_2 burn behavior are decisively influenced by the anode characteristics but also by the pot conditions, as reviewed in Figure 1.

Besides these aspects, a good rodding of the stubs is a prerequisite for low tension drop but also to avoid burn-off, related to poor stub-carbon contacts, and broken butts due to a tight connection.

The geometry of anodes, the current intensity of the pots and the precision of the anode setting are important anode related parameters that will impact their behavior.

Even though the anodes are exposed to various conditions that are pot technology dependent, the intrinsic carbon quality will influence the overall electrolysis process.

Cost Aspects

The determination and knowledge of the levels of the anode properties (mean values and 2 σ variability) is of utmost importance to avoid anode failures causing a dramatic Al production cost increase.

Carbon anodes represent in average about 200 $/tAl in the production cost but in case of severe trouble, like carbon foam accumulation in the bath, losses up to 100 $/t Al can be experienced. This is related to lower current efficiency (up to 3 %), higher energy consumption, extra personal cost, shorter pot lifetime and of course higher carbon consumption.

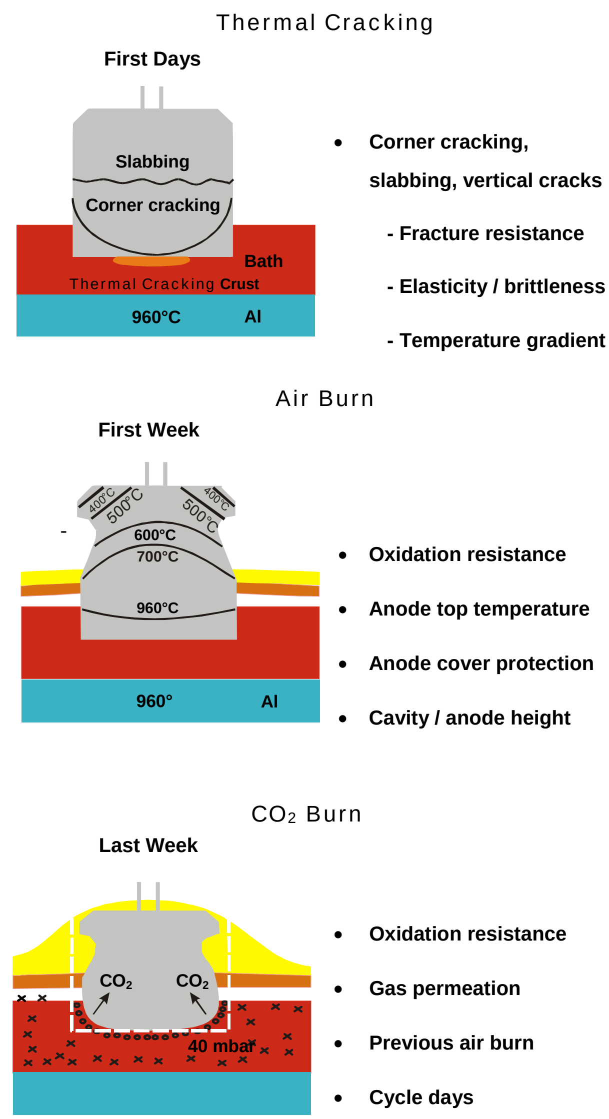

Figure 1 Prebaked anode behaviour in the pots

● Direct effect
○ Indirect effect

Pots \ Anodes	Sp. Electr. Resistance	Thermal Conductivity	Coeff. Therm. Expans.	Elasticity Modulus	Weibull Modulus	Fracture Energy	Air React. Loss + Dust	Co2 React. Loss + Dust	Permeability	P, Fe, Si, V, Ni	Sulfur	App. Density	Anode Height
Energy Consumption	●									○			
Thermal Loss		●											○
Thermal Shock		●	●	●	●	●							
Carbon Consumption		●					●	●	●		●	○	○
Current Efficiency		○					○	○	○	●		○	○
Metal Quality										●		○	○
Emission											●		

Table 1 Effects of anode properties on the electrolysis process

ANODE PROPERTIES

Relevance for the Electrolysis

Qualitatively the Table 1 below summarizes the relevance of the anode properties on the electrolysis parameters, from the energy consumption to the metal quality; more quantitative information on the thermal cracking (1) and on the carbon consumption (2, 3) are given elsewhere.

Prebaked Anode Testing

Routine quality control of carbon materials is today performed by most of the smelters. Equipment adapted to the testing of anode cores (diameter 50 mm) are available and the corresponding methods have been standardized for instance by the ISO TC 47 sub-committee 7 (4).

For carbon anodes, there are 11 standards (see Table 2) available, including one on the sampling (ISO 8007). A description of the measuring principles is given in (5).

The sampling rate is normally around 0.5 to 1.0 %. The cores are taken by a drilling machine mounted on the conveyor system that delivers the anodes to the rodding plant.

For a typical mid-size smelter, a 120m^2 laboratory with separate areas for sample preparation, reactivity furnaces and XRF spectrometer is appropriate. Two persons are sufficient to run the operations during the day shift. This anode laboratory is of course integrated to the coke, pitch, cathode quality testing and possibly to the other metal testing facilities for metal, alumina, bath materials.

WORLDWIDE ANODE QUALITY

Prebaked Carbon Plants

There are about 100 prebaked anode plants in the world including the 20 most significant smelters that we registered in China.

Basic information on the carbon plants features were collected and reported by K. Hulse (6) in 2000. A total of 60 carbon plants anode quality data covering the last decade period were compiled in this study including those previously evaluated by M. Meier (1).

Of course there are significant improvements made in paste plant and baking technology that positively influenced the anode quality development. But due to raw material quality deterioration the overall levels of anode properties have remained quite unchanged over the last decade.

Overview of Anode Properties

The results of the anode properties from the 60 carbon plants are summarized in Table 2.

The worldwide ranges of the mean and 2σ values are first given. The mode values obtained from analysis and interpretation of the frequency distribution are also shown. This gives additional information on the most frequent level of each property. The modes (i.e. the most likely values) are better indicators than the average values for properties that do not show a classical bell shape (Gauss) distribution, as it is the case for the sp. el. resistance data shown in the Figure 2.

Finally the bench mark values are listed. We considered for this purpose, values that can be achieved in a modern plant using typical raw materials and not the best one available. For instance for the coke we considered a typical US Gulf coast blend coke that anyhow represents practically half of the coke supply of the prebaked anode smelters examined here. For butts a 25 % recycling ratio was considered.

These bench mark values give interesting targets to be reached for any plant using typical raw materials. For some properties, like the means of flexural and compressive strength, we must keep in mind that they are not necessarily relevant for the thermal shock resistance of anodes. The real target is rather high Weibull modulus (7) obtained mainly with low 2σ of the flexural strength. This aspect will be re-discussed later.

Property		Unit	Standard	Worldwide Range		Worldwide Mode		Bench Mark	
				Mean	2σ	Mean	2σ	Mean	2σ
Apparent density		kg/dm^3	ISO 12985-1	1.50 - 1.62	0.015 - 0.060	1.57	0.03	1.60	0.015
Sp. electr. resistance		μΩm	ISO 11713	51 - 74	2 - 20	56	5	53	2
Flexural strength		MPa	ISO 12986-1	4 - 14	2 - 7	11	4	13	2
Compressive strength		MPa	ISO 18515	30 - 65	8 - 20	51	12	52	10
Static elasticity modulus		GPa	RDC-144*	3.0 - 6.5	1 - 2	5.1	1.2	5.2	1.0
Thermal expansion		$10^{-6}K^{-1}$	RDC-158*	3.6 - 4.6	0.2 - 0.6	4.1	0.4	4.2	0.3
Fracture energy		J/m^2	RDC-184*	100 - 260	40 - 80	210	70	240	60
Weibull modulus		-	-	2 - 12	-	8	-	12	-
Thermal conductivity		W/mK	ISO 12987	3 - 5	0.4 - 2.0	3.8	0.8	4.2	0.5
Xylene density		kg/dm^3	ISO 9088	2.05 - 2.10	0.012 - 0.040	2.075	0.022	2.085	0.014
Air Permeability		nPm	ISO 15906	0.3 - 4.0	0.3 - 8	1.0	1.4	0.5	0.3
CO2 Reactivity	**Residue**	%	ISO 12988-1	75 - 96	1 - 20	92	4	94	2
	Dust	%		0 - 10	0 - 10	2	3	1	1
	Loss	%		4 - 15	2 - 8	6	4	5	1
Air Reactivity	**Residue**	%	ISO 12989-1	55 - 95	4 - 18	68	12	80	10
	Dust	%		1 - 12	1 - 12	6	5	3	4
	Loss	%		4 - 35	4 - 15	26	9	15	6
Sulfur		%	ISO 12980	0.8 - 3.0	0.1 - 0.6	2.2	0.3	2.2	0.1
Vanadium		ppm	ISO 12980	30 - 350	5 - 60	220	20	200	10
Nickel		ppm	ISO 12980	70 - 220	5 - 20	130	10	130	10
Sodium		ppm	ISO 12980	100 - 1000	50 - 800	250	200	150	100
Iron		ppm	ISO 12980	100 - 800	50 - 1000	400	200	300	150
Silicon		ppm	ISO 12980	50 - 300	50 - 300	150	150	100	100
Phosphorus		ppm	ISO 12980	1 - 30	1 - 10	5	2	2	1

* R&D Carbon Ltd. Equipment number

Table 2 Worldwide prebaked anode characteristics

In any case bench mark properties (mean and 2σ) can be obtained in plants having, among other things

- efficient butts cleaning
- powerful heating (dry aggregate/ paste) system
- appropriate paste mixing and cooling units
- good forming machines
- modern baking furnaces

For each step of the manufacturing chain a design that guarantees a natural consistency together with an on-line process control are the pre-requisite for obtaining bench mark anode quality.

Distribution of some Key Properties

In Figure 2 six key properties distributions are shown and interpreted below.

The baked apparent density reached a level above 1.60 kg/dm^3 in 8 plants that all processed dense cokes with high percentage of recycled butts and all used powerful kneaders and forming machines (press or vibrator).

The lowest density levels were noticed for plants with poor mixing ability (mainly batch mixers) with too low mixing temperature, as no paste cooler was available.

High sp. electrical resistance (SER) level above 62 μΩm was associated with too high forming temperature levels (no cooler) and, probably, with poor heat-up rate temperature control during baking. Both conditions are known to lead to crack formations within the carbon block. The fact that a high SER value is associated with a low flexural strength level confirms this explanation.

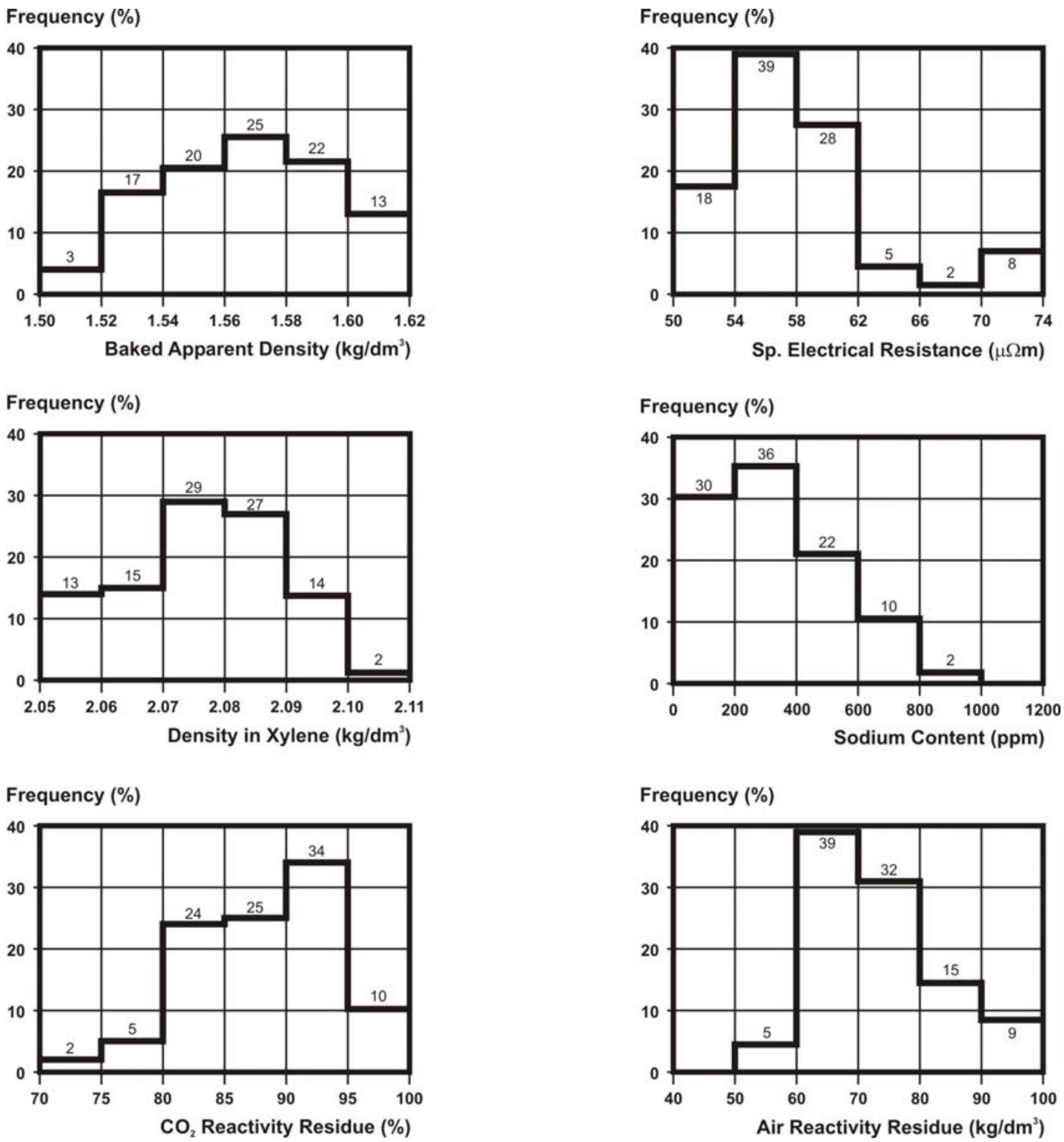

Figure 2 Frequency distribution of key anode properties: mean values of 60 anode plants

Concerning the baking conditions it is interesting to observe that the heat-treatment of anodes varies quite significantly as the xylene density of anodes ranges by more than 0.05 kg/dm^3. Even though there is a bias due to the coke xylene density scatter, we do believe that more than half of the xylene density range is related to the final baking temperature differences. We can estimate that the range of the average baking temperature is higher than 150°C.

The butts cleaning process is appropriately mastered by about half of the plants where carbon anodes show a content of sodium below 300 ppm. At a rate of 25 % of butts recycling this means that the sodium content in the crushed recycled butts was below 1000 ppm. However the bench mark is as low as 300 ppm (8) of sodium in the crushed butts resulting in less than 100 ppm sodium contamination level in the anodes.

Sodium, vanadium and sulfur content (9) together with the baking degree are the main parameters that influence the reactivity figures. The CO_2 reactivity residue is above 90 % for practically half of the plants but another half ranges in the eighty percent. Poorer values are systematically encountered for plants with poor butts cleaning and poor baking operations using low sulfur sodium sensitive cokes.

For the air reactivity, poor values in the fifty percent are related to the same problems but for plants using high V cokes. For cokes with 300 ppm V content the best plants nevertheless achieve values in the mid-seventies, while with typical Gulf coast, coke values in the eighties are still possible. The best levels are systematically found in plants using low vanadium coke having good butts cleaning and appropriate baking conditions (10).

Consistency of Properties

The consistency figures of the anodes produced in the 60 plants are quite different, as shown in Table 2 under the 2σ range column. Their distribution can be plotted as simple frequency histogram of the 2σ, like for the flexural strength or xylene density in Figure 3, when the variability is not basically dependent on the level of the property. One fifth of the plants only have a satisfactory control of the variability of the anode flexural strength below 3 MPa. In about 20 % of the plants, the scatter of this property was two to three times higher due to the presence of horizontal cracks. In this case slabbing of anodes in the pots was reported as a major cause of ahead of schedule anode changes.

For the xylene density half of the plants produce anodes with 2σ between 0.015 and 0.025 kg/dm^3 but for more than 20 % of them the scatter of xylene density exceeds 0.03 kg/dm^3, which impacts negatively the dusting propensity of anodes in the pots related to under-baked anodes (11).

The variability of some anode properties is not independent of their levels. In this case it is more appropriate to consider the 2σ values as a function of the mean values, as shown for the air permeability and the CO_2 reactivity residue in Figure 3.

The quality of the control of the plant operations has an impact on given properties. Best and worst plant control can be estimated from this type of graphs. The typical relationship observed for the majority of plants can be also determined as shown by the mode straight-line in Figure 3. For instance, for the CO_2 reactivity residue a 2σ of 10 % should be at least reached for a mean level of 80%. This can be expressed mathematically by the following relationship:

$$2\sigma \leq \frac{100 - \text{RR mean}}{2}$$

A bench mark consistency, given by the straight line labeled as "best plant", would be twice as low. This type of additional information on the consistency allows assessing any needs of process control improvements for a given plant.

Relationships of Properties

It is beyond the scope of this paper to address multiple regression analysis of key anode properties that will allow identifying for any plant the sources of a given inferior anode quality.

Nevertheless there are simple relationships that are worthwhile to be mentioned, like the one we found between the compressive strength (CS) and the elasticity modulus (Figure 4a). An increase of the compressive strength, by higher pitching or better mixing or forming intensity, leads automatically to higher anode inelasticity and therefore to higher stored energy in the carbon body when the block is immersed in the bath.

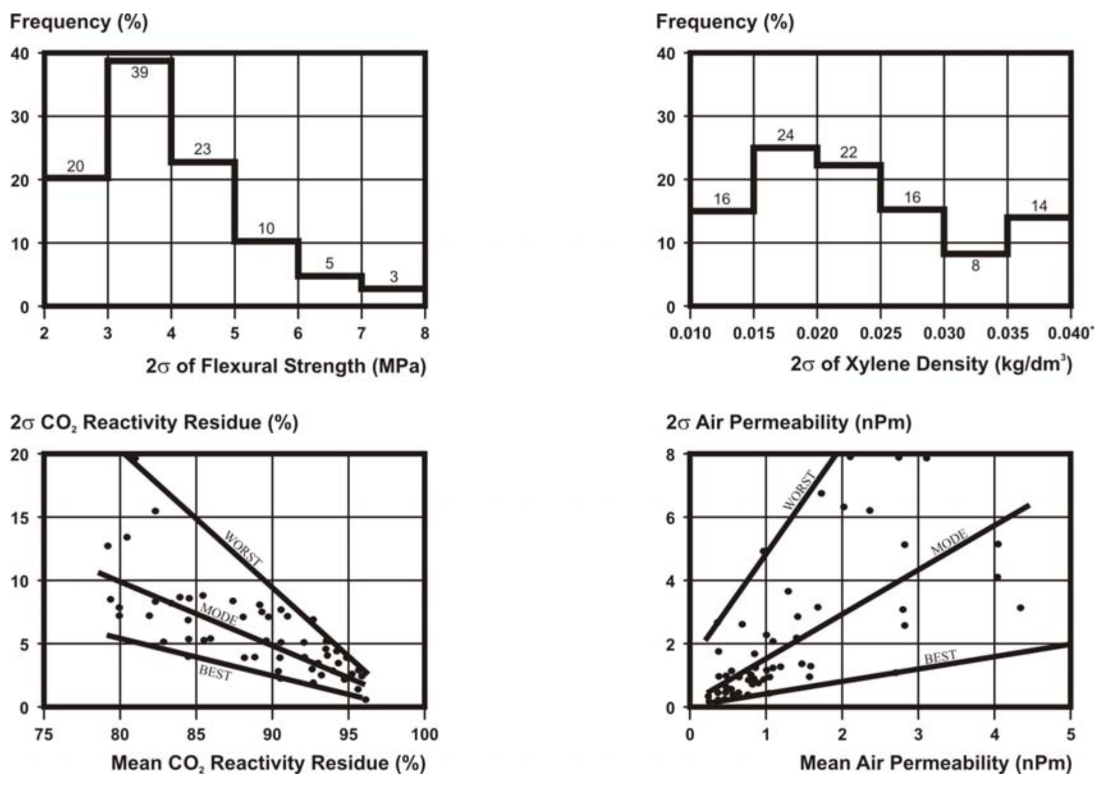

Figure 3 Consistency of some anode properties: 2 σ distributions and 2 σ vs. means

When the increase of compressive strength and of the inelasticity is concomitant with a proportional increase of the flexural strength (FS), as it is the case for the "best plant" line (Figure 4b), there is a reasonable chance that the brittleness of anodes is not deteriorated. For the worst plants however, with a ratio of CS/FS of 12 instead of 4, there is no doubt that the survival probability of the blocks to thermal shock will be quite poor.

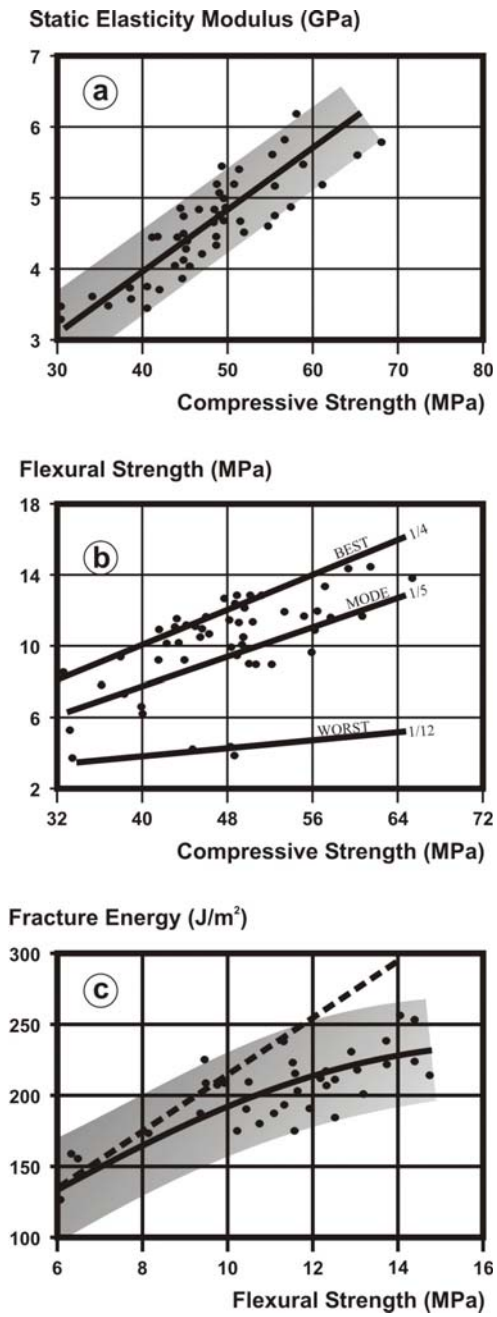

Figure 4 Interrelationship of some mechanical properties

To master thermal shock issue a resistance to crack propagation is ultimately needed. The Figure 4c shows that increasing the flexural strength level is not the ultimate answer to achieve this as the fracture energy level does not increase proportionally (dotted line), while the inelasticity will do inevitably.

CONCLUSIONS

The pieces of information presented in this paper are helpful to the carbon plants running routine quality control on their anodes. Worldwide range, mode and bench mark values can be used to critically assess the performance of the plant equipment but also of the process control systems.

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