An Automated Reference-Free Rietveld-Method-Based X-Ray Diffraction Analysis of Cryolite Ratio

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Abstract

In most aluminum smelters, cryolite ratio (CR) is normally measured automatically using X-ray diffraction (XRD) quantitative phase analysis using calibration curves. However, two factors significantly reduce the accuracy of measuring CR by such methods. First, XRD analytical instruments need periodic calibration, which is performed using multiphase matrix reference materials of bath with a known quantitative phase composition. Creating such reference materials is a challenging task, because they should contain 4 – 6 fluoride phases, whose concentrations are accurately certified. Second, the calibrated methods do not consider variations of microcrystalline and atomic structure of phases in real solid bath samples. Thus, using reference-free full-profile Rietveld method instead of conventional XRD methods for measuring CR is advantageous for the process control because it does not use calibration and refines the crystal structure of bath samples. However, the Rietveld method is interactive and needs automation for implementing in the process control. If so, the method automatically refines preset approximate values of profile and structural parameters of the crystalline phases and then calculate CR from the quantitative phase composition. The problem is the preset of adequate approximate parameter values that are accurate enough to be refined automatically. We developed a new method to address this problem. The essence of the method is an automatic search of the initial approximate values by a genetic algorithm (GA) followed by the Rietveld refinement of the found values. The accuracy of the automatic analysis of CR performed for 24 branch reference materials of bath is characterized with a standard deviation of 0.035 and can be improved by further developments in GA.

Keywords: Cryolite ratio, Rietveld method, process control, x-ray diffraction phase analysis, bath composition.

1. Introduction

Electrolyte in aluminum electrolysis cells constantly suffers from the destabilization of its chemical composition, which shifts from the optimum. The optimal composition of bath is maintained by adding fluorides in a cell. The amount of fluorides is calculated in accordance with the results of periodically performed express quantitative analysis of solid bath samples. A number of methods are used for this purpose, such as chemical analysis (CA), X-ray diffraction analysis (XRD), X-ray fluorescence analysis (XRF), thermal analysis, etc. Normally, electrolyte is the melt of Na-Al-Ca-F-O, and sometimes KF, MgF_2 or LiF are added. The chemical elements exist in the melt in the form of complex ions, whose composition changes during the electrolysis cycle. As so, an integral characteristic of the bath composition is the cryolite ratio (CR) – the ratio of molar concentrations of sodium fluoride and aluminum fluoride (Equation (1)):

$$CR = \frac{C(NaF),mol.\%}{C(AlF_3),mol.\%} = \frac{2C(NaF),wt.\%}{C(AlF_3),wt.\%} \tag{1}$$

where:
C(NaF) Concentration of sodium fluoride in electrolyte, mol. % or wt. %
C(AlF_3) Concentration of aluminum fluoride in electrolyte, mol. % or wt. %.

Bath ratio (BR) is also used to characterize bath composition, given by Equation (2), or excess AlF_3, as expressed in Equation (3):

$$BR = \frac{1}{2}CR \tag{2}$$

$$AlF_3ex = C(AlF_3) - \frac{1}{3}C(NaF) \tag{3}$$

where:
C(NaF) Concentration of sodium fluoride in electrolyte, wt. %
C(AlF_3) Concentration of aluminum fluoride in electrolyte, wt. %

CR, BR and AlF_3ex all indicate similar information about the bath composition.

The express process control of the electrolyte composition is generally performed by X-ray diffraction quantitative phase analysis (QPA), which uses calibration curves [1 – 3]. The cryolite ratio is calculated according to Equation (1). The concentrations of NaF and AlF_3 are calculated using the results of the QPA of crystallized bath samples. The concentrations of phases listed in Table (1), in turn, are calculated from the measured intensities of their diffraction peaks. The optimal frequency of measuring the CR is once every two days, the accuracy of the analysis is Δ(p = 0.95) ~ 0.04 (that is, ± 0.04 at 95 % confidence level), and the optimal measurement time per sample is several minutes.

Table 1. The phase composition of typical industrial bath samples at the Russian aluminum smelters.

Phase	Chemical Formula	Concentration range, wt. %	CR Range
Cryolite	Na_3AlF_6	0 – 90	> 1.67
Chiolite	$Na_5Al_3F_{14}$	0 – 85	< 3.0
Sodium fluoride	NaF	0 – 5	> 3.0
Ca-cryolite 1	$NaCaAlF_6$	0 – 15	< 3.0
Ca-cryolite 2	$Na_2Ca_3Al_2F_{14}$	0 – 20	< 2.95
Fluorite	CaF_2	0 – 9	> 2.45
Weberite	Na_2MgAlF_7	0 – 15	< 2.85
Neiborite	$NaMgF_3$	0 – 6	> 2.5
α–, β–, γ– alumina	Al_2O_3	2 – 5	

However, two factors significantly reduce the accuracy of measuring CR using calibration curves. First, XRD analytical instruments need periodic calibration, which is performed using multiphase matrix reference materials of bath with a known quantitative phase composition [4, 5]. Creating such reference materials is a challenging task because they should contain 4 – 6 fluoride phases, whose concentrations are accurately certified. Second, the calibrated methods do not consider variations of microcrystalline and atomic structure of phases in real solid bath samples. Thus, using reference-free full-profile Rietveld method [6] instead of conventional XRD methods for measuring CR is advantageous for process control because first the use of calibration is avoided and second the crystal structure of bath samples is refined.

The essence of the Rietveld method is the modeling of an experimental powder pattern of a sample as the sum of calculated specific powder patterns of phases that are present in the sample. The inputs for the calculation are: crystal structures of the phases, which are taken from structural databases; and refinable models of diffraction profile and phases' microcrystallinity and texture. Both profile and structural parameters of the phases are refined during modelling by the built-in least squares method (LSM). Phase concentrations are calculated from the scale factors of their powder patterns, which are obtained as a result of the modelling. At the final step, elemental composition and technological parameters of the bath sample are calculated from the phase concentrations.

It was experimentally demonstrated in previous works, for example in [7] and [8], that the Rietveld method can provide technologically required accuracy for measuring CR. The problem is the preset of adequate approximate parameter values that are accurate enough to be refined automatically. Several quite successful attempts to automate the Rietveld method were made in recent years [9], [10]. The authors of [10] emphasize that the results can be used to predict the liquidus temperature and bath superheat. However, they are disadvantaged with respect to the calibrated methods in achieved accuracy and the extent of automation. The reason is that it is necessary to consider physicochemical characteristics of the AlF_3-NaF-CaF_2 while performing the automated analysis of bath by the Rietveld method. The most significant ones are as follows:

- An incomplete transition between the two calcium-containing cryolites during sampling;
- An incomplete polymorphous transition of cryolite;
- The assertion of MgF_2 (up to 1 wt.%) in bath. This happens because MgF_2 gets in bath with alumina and neglecting this fact can make measuring CR less accurate by 0.01 – 0.02.

While studying how trinary fluorides form by high-temperature XRD and TA [11], we established that one can consider the system as a quasi-binary cross section CaF_2-$NaAlF_4$, and the invariant equilibrium CaF_2 – $NaCaAlF_6$ – $Na_2Ca_3Al_2F_{14}$ – ($NaAlF_4$) exists at 745 - 750 °C. The specifics of the system are that the phase $NaAlF_4$ is metastable under standard conditions. At temperatures under the equilibrium temperature, $Na_2Ca_3Al_2F_{14}$ is stable; and over the equilibrium temperature, $NaCaAlF_6$ is stable. $NaCaAlF_6$, which exists in rapidly chilled samples, turns into $Na_2Ca_3Al_2F_{14}$ at 640 °C. Quantification of the calcium-containing cryolites is methodically problematic because of the incomplete transition and partial crystallinity of $NaCaAlF_6$, which are the results of the sampling. This reduces the accuracy of measuring CR. In the case of using the calibrated methods, this problem is partially solved by applying a correction to the total concentration of CaF_2, which is calculated using quantitative XRF data on calcium. However, there is no such opportunity in the case of using the classical Rietveld method. Another problem is that, at the room temperature, cryolite has monoclinic crystal lattice that undergoes a gradual second-order transition to the tetragonal type at 500 °C.

The process goes backwards during the sample cooling, and in the case of fast cooling the transition can be incomplete [12]. The AlF_6 octahedrons of the cryolite crystal structure change orientation from inclined to vertical and back, and the powder pattern changes respectively. Such structural details can be refined during an interactive Rietveld refinement by a specialist. However, automated versions of the Rietveld method do not allow refining this change because there is no automated methodology of choosing initial values of structural parameters, which differ from sample to sample. We have established that the incomplete transition can cause the variations of the cryolite's diffraction peak intensity up to 5 rel. %. This, in turn, can reduce the accuracy of measuring CR by about 0.02.

To address the above-mentioned problems, we suggest applying a self-configuring genetic algorithm (SGA) with a built-in Rietveld method. The SGA provides a completely automated analysis of bath chemical composition and does not need preconfiguring. In the present paper, we provide the results of the application of the SGA to the analysis of CR in branch matrix reference materials of calcium-magnesium-bath.

2. The Method of Genetic Self-Configuring Algorithm

The essence of the QPA by the Rietveld method is an iterative minimization of the difference between an experimental powder pattern and the calculated one by the LSM:

$$\Phi(\bar{P}_{k+1}) = \sum_i w_i \left(Yo(2\Theta_i) - Yc(\bar{P}_k + \Delta\bar{P}_k, 2\Theta_i)\right)^2 \to 0 \tag{4}$$

where:

Yo, Yc	Experimental and calculated intensities at the position $2\theta_i$, respectively;
w_i	Weight coefficient
Pk	Vector of profile, microstructural, and structural parameter values at iteration k
ΔPk	Parameter increments calculated by the LSM; the initial approximations are set at k = 0.

If the sample does not contain an amorphous phase, the concentrations are calculated according to the following equation:

$$C_a = S_a Z_a M_a V_a / \sum_{j=1}^{N} S_j Z_j M_j V_j \tag{5}$$

where:

S_a	Scale factor of a phase *a,* which is obtained from the calculated powder pattern *Yca,*
V_a	Cell volume
Z_a	Number of structural units per cell
M_a	Molecular weight of a phase *a*
N	Number of crystalline phases in the sample.

If an amorphous phase is present in the sample, the QPA uses an internal standard [6].

Genetic algorithms (GA) [13] are based on the principles of the Darwin theory, namely populations consisting of many individuals evolve according to preset selection rules to the state of the best fitness. The efficiency of the GA optimization depends on the choice of genetic operators, such as selection, crossover, mutation and substitution. However, the settings for an effective algorithm which ensure that acceptable results are obtained within the shortest possible time can be different for different problems. To address this issue, we suggest applying a genetic algorithm which we have developed to set the initial values of the parameters for each sample automatically [14]. This approach provides high accuracy of measuring the cryolite ratio, but it is not yet fully applicable to the process control. This is because the algorithm must be configured as well. Therefore, procedures of dynamic self-adapting and self-configuring of algorithm settings seem to be perspective [15 – 16]. Self-configuring is an automated choice of effective genetic operators from a given set during an algorithmic run while solving the problem at hand. The configuration of operators is determined stochastically based on the probability of an operator to be used for generating a new solution. These probabilities are calculated according to their success in previous stages. The deployment probability of the most successful operator, the one that gave the best solutions on the previous generation, is increased, whereas the probabilities of other operators are decreased. This makes possible the automated choice of the best configuration of operators for increasing algorithm productivity.

The refinable part of P composes of parametrical strings that play the role of individuals that are evolutionarily optimized by a GA. The full set of parameters P, which includes both refinable and fixed parameters, describes a trial model of multiphase sample characteristics. In the case of the evolutionary QPA, a range must be defined within which possible values of refinable parameters fall. The best values found within the range by the GA are then refined by the Rietveld method. A QPA feature is that it allows the GA to conduct the search for appropriate initial values of parameters within a wide range. For example, the crystal structures of phases having been found in a sample may be used to set initial values of refinable structural parameters. Crystal structures are normally taken from crystal structure databases. In this case, the atomic coordinates of general crystallographic positions may be chosen as refinable parameters. In addition, the occupation of the positions may be refined for solid solutions. Thus, the range limits the variation of both atomic coordinates and occupation coefficients.

Narrow search ranges pose a problem for the evolutionary full-profile QPA. In such cases, the values of the R-factor vary unsatisfactorily. Therefore, it becomes an unreliable selection criterion. To improve the sensitivity of the criterion, we suggest adding bias between the measured sample's elemental composition and the composition calculated from the phase concentrations:

$$R_p = 100 \cdot \left\{(1 - w_{ch}) \cdot \sqrt{\frac{\sum_i w_i \cdot [Yo_i - Yc_i(\bar{P})]^2}{\sum_i w_i \cdot (Yo_i)^2}} + w_{ch} \cdot \frac{\sum_t w_t \cdot [\sum_\alpha p_{t\alpha} \cdot \frac{S_\alpha Z_\alpha M_\alpha V_\alpha}{\sum_\alpha S_\alpha Z_\alpha M_\alpha V_\alpha} - C_t^{ch}]^2}{\sum_t w_t \cdot (C_t^{ch})^2}\right\} \tag{6}$$

where:

C_t^{ch}	Concentration of an element *t* measured by chemical analysis
P_{ta}	Mass fraction of an element *t* in phase *a*
W_{ch}	Weight contribution of the chemical data in R_{wp} (normally 0.5).

In terms of bath composition analysis, the fitting function in Equation (6) combines quantitative XRF data on CaF_2 and MgF_2 with diffraction data, thus reduces the influence of the mentioned physicochemical problems. The combination of the suggested variant of the full-profile Rietveld method with the parallel SGA provides an automated QPA.

3. Experimental Procedure

As the model objects, we had chosen 24 branch reference materials used at five Russian aluminum smelters [5]. The objects had been chosen for the following reasons. Firstly, they were made from real industrial baths taken from different aluminum smelters. Therefore, they were entirely consistent with all the features of real crystallized bath samples, such as composition, impurities, and microstructure. Secondly, the balance between the chemical and phase composition of the reference samples is fully guaranteed by the correspondence among the results obtained by the different analytical methods used for the certification. The mean uncertainty of the certified CR values was 0.008. Thirdly, the quantitative phase composition significantly varies from sample to sample and covers the range of cryolite ratios from 1.9 to 3.

The powder patterns were obtained with a Shimadzu-7000 powder diffractometer with scintillator detector using CuKα radiation in the range $10 < 2\Theta < 90$; the exposition step was 0.01. The structural models were taken from the Inorganic crystal structure database (ICSD) [17]. We compiled a standard excessive list of contained phases, which is provided in Table 2, for each sample. The nineteen parameters listed in Table 2 were refined for the chosen phases. In cases when a phase was absent in a sample, its scale factor and the concentration were set to zero. The SGA was run three times for each sample. As the QPA result, we accepted the arithmetic mean of the phase concentrations that were established over three runs. The analysis of each sample lasted about 15 minutes.

Table 2. Parameters that were refined by the self-configuring genetic algorithm (SGA) for the bath reference materials.

Phase	List of Refinable Parameters
Na_3AlF_6	*S, a, b, c, β, U, W, Eta0, Asym1*, atomic coordinates (12 positions), correction of the intensities for preferred orientation along *hkl* [220] and [112] by the March-Dollase model
$Na_5Al_3F_{14}$	*S, a, c, U, W, Eta0, Asym1*, atomic coordinates (9 positions)
$NaCaAlF_6$	*S, a, b, c, β, U, W, Eta0, Asym1*
$Na_2Ca_3Al_2F_{14}$	*S, a, U, W, Eta0, Asym1*
CaF_2	*S, a, U, W, Eta0, Asym1*
Na_2MgAlF_7	*S, a, b, c, U, W, Eta0, Asym1*
$NaMgF_3$	*S, a, b, c, U, W, Eta0, Asym1*
α-Al_2O_3	*S, a, b, U, W, Eta0, Asym1*
γ-Al_2O_3	*S, a, U, W, Eta0, Asym1*

where:

S	Scale factor
a, b, c, β	Unit cell parameters
U, W	Peak FWHM by Pseudo-Voigt
Eta0	Peak shape parameter
Asym1	Peak asymmetry parameter.

Research laboratories at aluminum smelters are equipped with combined XRD-XRF instruments. Normally, the instruments combine an X-ray diffractometer with a fixed X-ray fluorescence channel that provides the quantification of calcium and magnesium. For this reason, we used concentrations of these two elements to calculate the R-factor according to Equation (6).

We preset the following genetic operators for the SGA:

1. Tournament selection among 3, 5, 7, 9 trial models, range selection;
2. Two-point crossover, three-point crossover, uniform crossover;
3. Low-level mutation, average-level mutation, high-level mutation, with three standard deviations each.

4. Results and Discussion

Figure 1 shows how the parallel SGA typically converges during the search for the profile and structural parameters. The graph was plotted during the running of the full-profile QPA of a bath reference material. The x-axis shows the number of the generation, whilst the y-axis provides the best corresponding R-factor value that was found among the population at the managing unit. The solution was found at the eightieth generation.

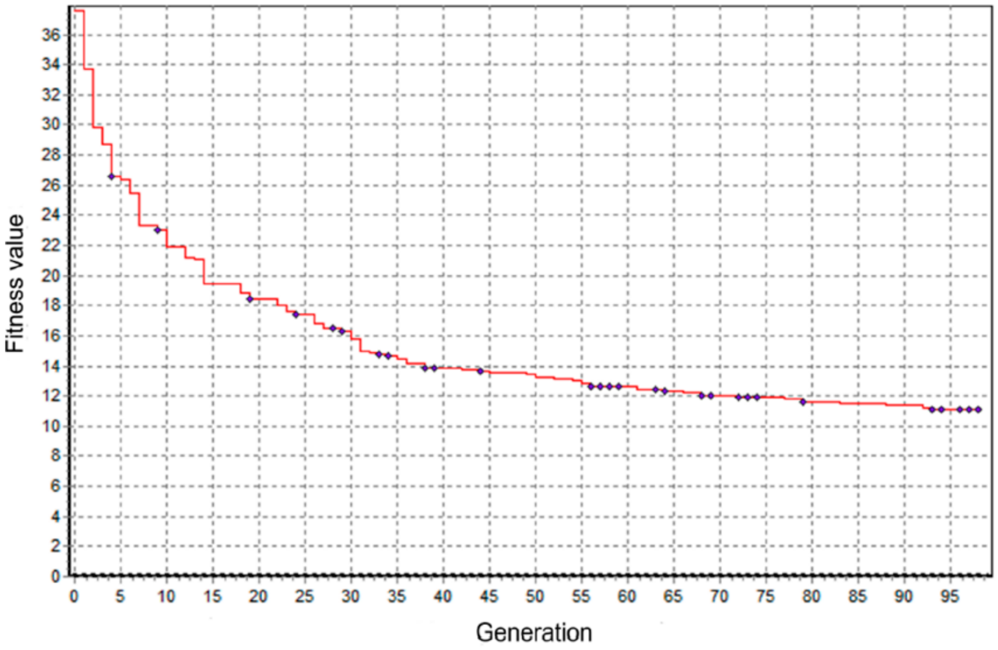

Figure 1. A typical graph of how the SGA converges when analyzing a bath sample.

Figure 2 depicts the experimental powder pattern of the analyzed bath reference sample and the profile that was calculated after the Rietveld refinement. The value of the profile R-factor, which characterizes the difference between the profiles, is 8.6 %.

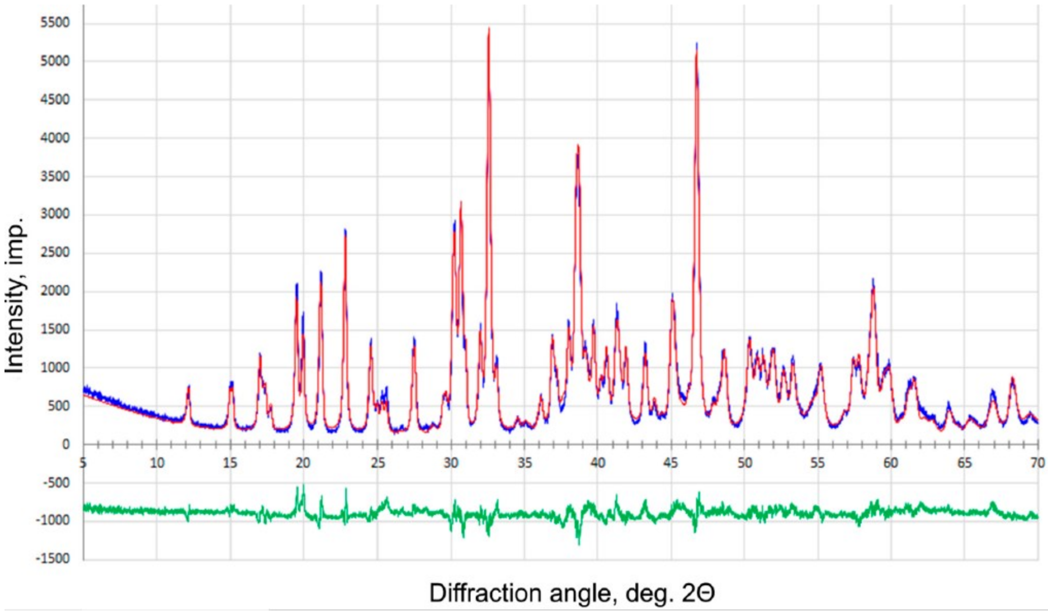

Figure 2. The model powder diffraction pattern calculated by the SGA (in red) and the experimental powder diffraction pattern (in blue) of a bath sample. The green line shows the difference between the profiles.

We propose the correspondence between the certified and calculated values of the cryolite ratio as the quality criterion for results of the evolutionary full-profile QPA. The cryolite ratios were calculated according to the Equation (1). Figure 3 shows the correspondence between the certified and calculated values of the cryolite ratio.

Figure 3 also provides the linear regression (y = a + bx) and the standard deviation, which numerically characterize the correspondence. Therefore, the bias of b from 1 characterizes the systematic error of the results, while the standard deviation describes the random error.

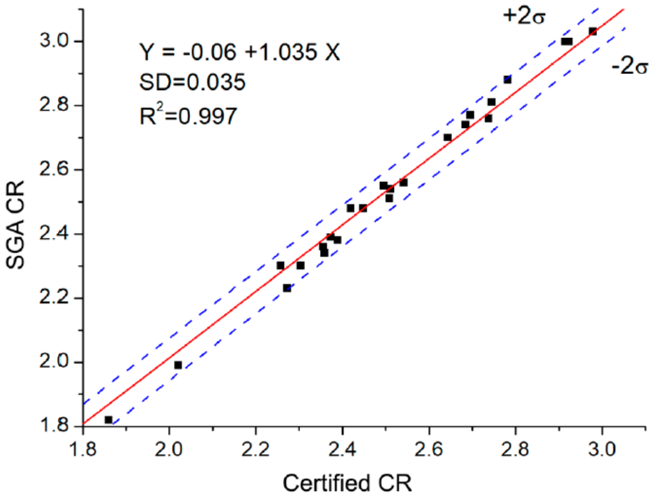

Figure 3. The correspondence between the calculated and certified CR values for the branch reference materials. Certified CR is the certified values; SGA CR is the calculated values; SD is the standard deviation.

The calculated values match the certified values with an accuracy of SD = 0.035, and all the results fall within the 95 % confidence interval. The linear regression equation is close to the $y = x$ form because the coefficient a is statistically insignificant. However, b is 1.035, which is greater than b in the linear model ($b = 1$). This indicates that the results of the evolutionary full-profile QPA are slightly overestimated. An analysis shows that this systematic error is caused by the overestimation of the Na_3AlF_6 concentration. This fact proves that the automated Rietveld method that uses SGA data refines the structure of this phase ineffectively. It appears that the structure distorts due to the incomplete transition of the Na_3AlF_6 high-temperature modification to the low-temperature modification. Such an effect is a result of the nonequilibrium crystallization of bath samples, which is caused by a specific sampling procedure being used at aluminum smelters. In addition, the structural distortion inflates the standard deviation of the results.

5. Conclusion

The achieved accuracy of the automated reference-free analysis of CR by the SGA are close enough to the actual accuracy of measuring CR at the RUSAL smelters. On the other hand, an interactive Rietveld analysis of the reference sample set provides SD = 0.015 [5]. Therefore, to effectively scale the SGA analysis for express process control and replace currently used calibrated method with it, the following measures should be taken: Eliminating of the systematic error, improving the accuracy and shrinking the analysis time by 2 to 3 times. However, the last task is not critical, because nowadays powder diffractometers acquire full profile in about 3 - 5 minutes. Moreover, a group of 2 – 4 PCs can be used for the mass analysis of CR. We believe that all this can be achieved by optimizing SGA and its software.

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