LABORATORY INVESTIGATION OF PCDD/Fs AND DIOXIN-LIKE COMPOUNDS FORMATION DURING CHLOR-ALKALI PROCESS

Teru Yamamoto, Kazuo Higashino, Takeshi Ohura*, Takashi Amagai*, Hiroaki Takemori**, Takumi Takasuga **, Yuko Sasaki

The Tokyo Metropolitan Research Institute for Environmental Protection, 1-7-5 Sinsuna Koto-ku Tokyo 136-0075, Japan, *University of Shizuoka, 52-1Yada Shizuoka 422-8526, Japan, **Shimadzu Techno-Research INC. Nakagyo-ku Kyoto 604-8436, Japan

Abstract
We examined polychlorinated dibenzo-*p*-dioxin, polychlorinated dibenzofuran (PCDD/Fs) and dioxin-like compounds formation during brine electrolysis with pitch used as the binding agent of graphite electrode. Graphite electrode was used in the past as an industrial process of chlorine production. The level of PCDFs was up to 1,800,000pg/L (28,000pg-TEQ/L) in brine electrolysis with pitch. This value corresponds approximately to 150μg/g-pitch (4.4μg-TEQ/g-pitch). It was obvious that specific homologue/congener patterns of PCDF from lower to higher components were apparently formed according to electrolytic conditions such as temperature, current density and also pitch form. Amounts of PCDF formation per unit concentration of pitch were 10,000-100,000ng/g-pitch. Additionally, high levels of chlorinated polycyclic aromatic hydrocarbons (Cl-PAHs), which were dioxin-like compounds, were also detected in the above anolyte samples of brine electrolysis. Furthermore, concentrations of Cl-PAHs and the ratio of Cl-PAHs to dioxins varied according to the electrolysis process performed. These results can support the assumption that brine electrolysis by graphite electrode abundantly contained pitch in the past might have been a significantly potential source of Cl-PAHs as well as PCDFs contamination.

Introduction
Polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/Fs) and other persistent organic pollutants (POPs) emitted probably from contemporary and/or historical sources have been remaining the global problem[1-3]. Contamination discovered in soils and sediments has been particularly not also increasing the environment and human risk, but may substantially disturb the effective and valuable uses of ground. Since 2000s, several severe affairs identified PCDFs as major contaminants were revealed from canal sediments and soils in Tokyo[4]. Our recent study indicated that chlorine disinfection to sediment/soil for the purpose of reducing the hygienic risks getting pathogenic virus and bacteria might lead to form high level of PCDF contamination[5]. Since there are some cases for soil improvement/adjustment, chemical pest control and chemical treatment before backfill reuse of dredged sediment/soil are widely used as an effective countermeasures, widespread chlorine usual in open environment may be responsible for contemporary potential sources of PCDFs. Specific congener pattern dominated in dioxin have been also observed in pulp bleaching processes and even the water purifying process of drinking water operating chlorine process[6-9]. Similar pattern have also been identified in graphite electrode sludge samples taken in the soil around chlor-alkali factories[10-15]. Other investigation performed in regard to the soil contained high concentrations of PCDFs in the past factory site in Tokyo just demonstrated that the contamination might originate from chlor-alkali process to produce chlorine from NaCl operated in the past located on its ground. The origin of PCDFs related to chlor-alkali process might be dibenzofuran and polycyclic aromatic hydrocarbons (PAHs) contained in coal tar pitch as binding agent of graphite electrode[16]. Previous study has been reported PCDF formation by chlorination of PAHs in rubber material of electrolytic cell[16]. In addition, it has been reported that high levels of Cl-PAHs such as polychlorinated naphthalenes and other compounds were contained in contaminated soils taken at the past factory sites using electrolysis process[17-18]. The chlor-alkali plants in many countries included Japan have already adopted titanium electrode instead of graphite electrode since 1980s. Therefore, the purpose of this study is to confirm specific PCDFs and dioxin-like compounds formation during typical and historical chlorine process.

Materials and Methods
The laboratory unit of brine electrolysis by flow cell system is shown in Fig.1. The apparatus consisted of the

electrolytic cell, anode/cathode feeder and circulating water system to supply solution was installed in a exhaust chamber. Inside the electrolytic cell, artificial graphite electrode or titanium electrode used as anode and SUS304 as cathode were separated two compartments by ion-exchange membrane made by perfluorosulfonic acid-based films. Graphite electrode fixed in anode cell was used as in the past typically industrial chlor-alkali processes. Saturated brine solution supplied to anode cell made chlorine ion form chlorine, and hypochlorous acid and hydrochloric acid were also formed depending on pH and temperature condition of anolyte. There was also some sodium hydroxide formed by the reaction of sodium ions passing through the separator with hydroxyl ion. Gaseous chlorine formed from anode cell was removed by Cl_2 recovery system. Full scale of experimental apparatus of brine electrolysis is 1.6m×0.6m×1.1m (L × W × H) size.

Table 1 summarizes experimental conditions and parameters in this operation. Electrolysis was performed in acid during the operation. After dechlorination, the anolyte solution included suspended solid was extracted by Empore disk (C18 octadecyl). These were put together and extracted over 16h with toluene by Soxhlet extraction. Congener specific analysis of MoCDD/F-OCDD/F was carried out using HRGC/HRMS (Agilent HP6890 and JMS-700) operated at resolution 10,000. The analytical procedure of TeCDD/F-OCDD/F was approximately according to the above. MoCDD/F-TriCDD/F was as follows.
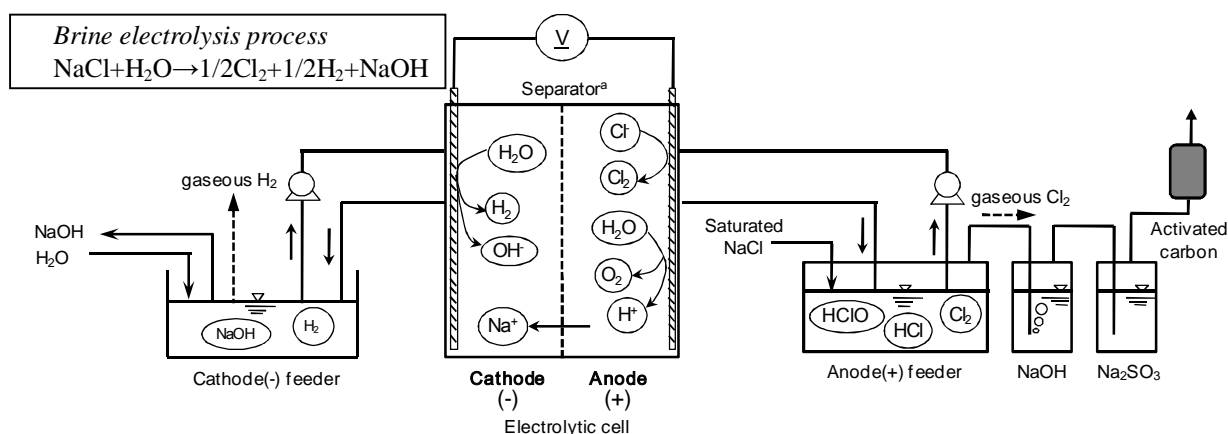

Fig. 1 **The laboratory unit of brine electrolysis by flow cell system consisted of electrolytic cell, anode/cathode feeder and circulating water system to supply solution**
[a]**ion-exchange membrane made by perfluorosulfonic acid-based film**

Table. 1 Experimental conditions and parameters in anode cell

Run	Anode	Anolyte	Pitch (mg/L)	Current density (kA/m^2)	Temperature (Ave.: °C)	pH		chlorine (ppm)[b]	period (h)
1	Graphite/Titanium	NaCl+Pitch		1.0	26.5	3.6	4.9	5,000	24
2	Titanium	NaCl+Pitch	12.5	1.0	58.4	2.7	5.3	2,000	24
3	Titanium	NaCl+Pitch		2.5	51.3	1.2	4.7	4,000	96
4	Graphite	NaCl+Pitch[a]		1.0	25.5	1.1	3.8	3,000	48

[a]Semi-liquid form pitch completely solved by heat at more than softening point
[b]Maximum values of available chlorine as Cl monitored in anode feeder

Temperature program used for congener specific separation of the MoCDD/F-TriCDD/F on SP-2331 column (60m x 0.25mm i.d. x 0.25μm film thickness): 120 °C, 1 min. isothermal; 30 °C /min. to 200 °C, 2 °C/min. to 260 °C. Quantification was carried out by isotope dilution mass spectrometry[19].

Mo, Di and TriCl-PAHs (21kinds of Cl-PAHs) were analyzed on a gas chromatograph (Agilent HP7890A) interfaced with a tandem quadrupole mass spectrometer (Waters Quattro micro GC). An DB-5ms capillary column (30 m x 0.25 mm i.d. x 0.25μm film thickness Agilent) was used. The GC column temperature was programmed from 100 (initial equilibrium time 1 min) to 200 °C via a ramp of 25 °C/min, 200–300 °C via a ramp of 5 °C/min and maintained at 300 °C for 5 min. The PAHs were analyzed on multi-component analysis method developed previously[20].

Results and Discussion

Comparison of total concentrations and relative compositions of PCDFs during brine electrolysis with pitch are shown in Fig. 2. Concentration of PCDDs was detected below the detection limit (200pg/L>). Total concentrations of PCDFs formed in brine electrolysis at Run1 were from 130,000-220,000pg/L (620-2,400pg-TEQ/L). The experiment at high current density and/or high temperature (Run2, Run3) had slight increase in concentration of PCDFs. While drastic increase of PCDFs was observed in case with semi-liquid form pitch (Run4). The level of PCDFs was up to 1,800,000pg/L (28,000pg-TEQ/L) at 2days run. This elevated value corresponds approximately to 150μg/g (4.4μg-TEQ/g). Slight shift from lower to higher homologues of PCDF were apparently observed according to passing of electrolysis and/or its condition.
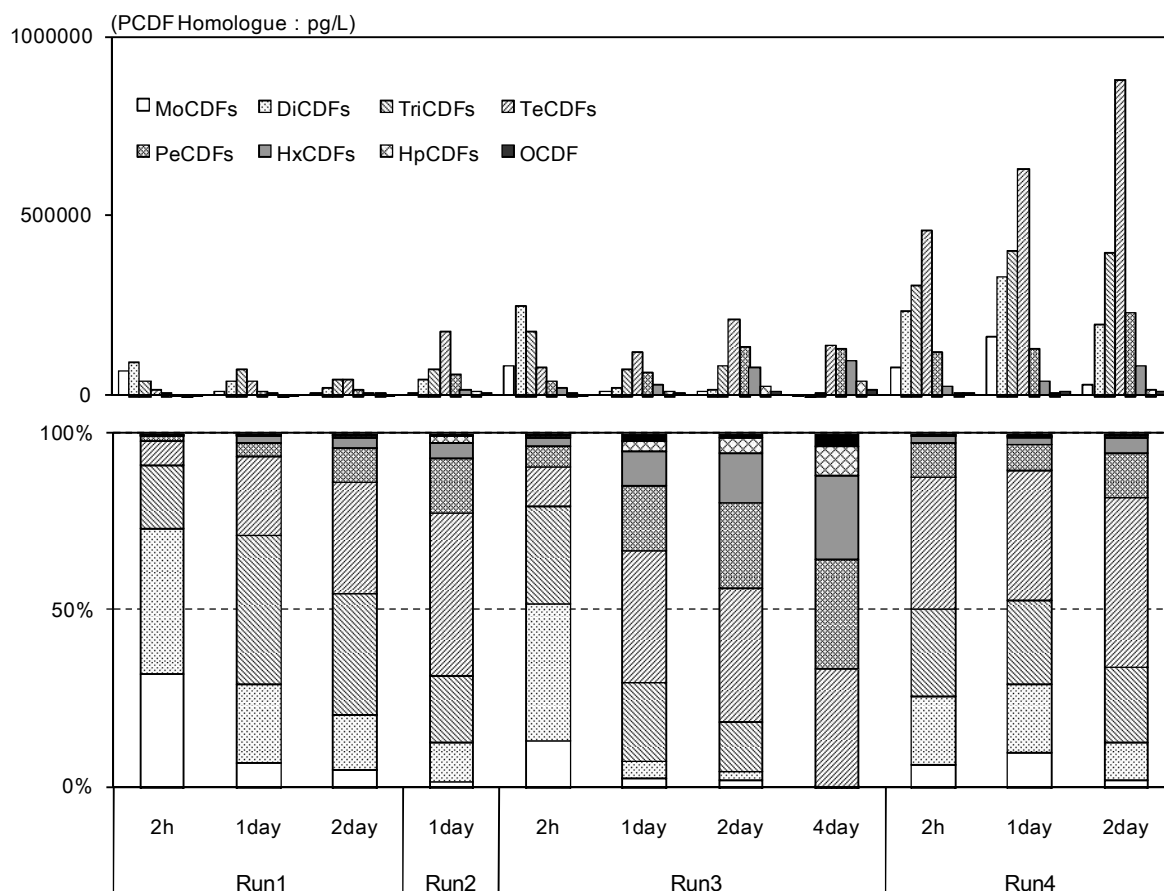

Fig. 2 Concentrations and homologue profiles of PCDFs during brine electrolysis with pitch.
   ***Homologues concentrations of PCDD/Fs in pitch before starting sample were beside the level of detection limit.**
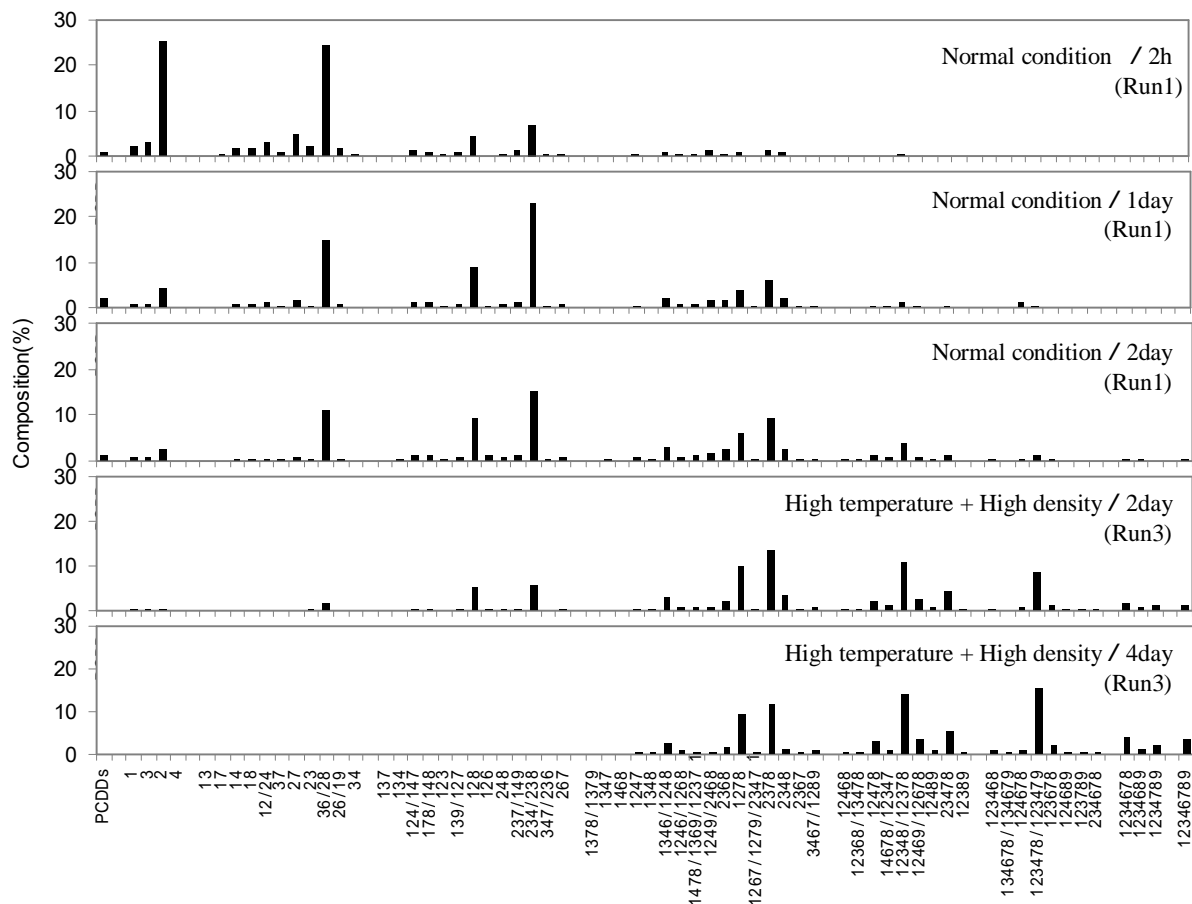
Fig. 3 Relative compositions (%) of total PCDDs[a] and each PCDF congeners during brine electrolysis with additional pitch (Run1, Run3)
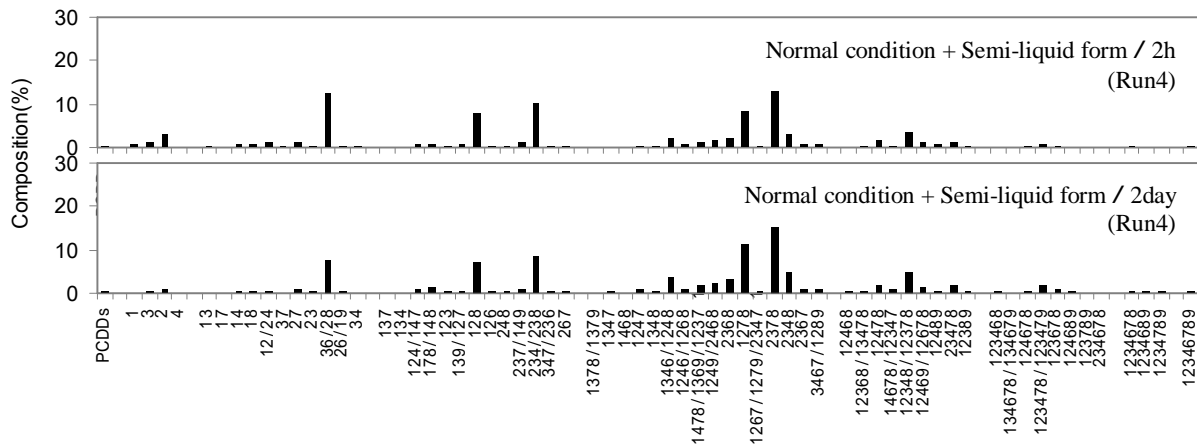[a]Total concentrations of Mono- to Octa- chloinated PCDD congeners.

Fig. 4 Relative compositions (%) of total PCDDs and each PCDF congeners during brine electrolysis with additional semi-liquid form pitch (Run4)

At first, MoCDFs, DiCDFs and TriCDFs were predominant components. TriCDFs and TeCDFs followed by were major component at Run1. TeCDFs, PeCDFs and even HxCDFs were detected as major components at Run2 and Run3, respectively. Though HpCDFs and OCDF were detected at these runs, relative low levels of them were observed. Effect of temperature to advance PCDFs profile has been already indicated in several previous studies[5, 21]. However these results were indicated that pitch form could be also severely influenced PCDFs formation of brine electrolysis. Nevertheless, low levels of PCDDs were formed in brine electrolysis with pitch, though dibenzo-*p*-dioxin was also more reactive in chlorination than dibenzofuran[6]. These results were indicated much higher levels of non-chlorinated dibenzofuran contained in pitch as a precursor of PCDF than non-chlorinated dibenzo-*p*-dioxin.

Comparison in relative compositions of sum of PCDD congeners and individual PCDF congeners in each sample at different conditions of brine electrolysis are shown in Fig. 3 and Fig. 4. At the beginning in electrolysis run, the dominant congeners in each PCDF homologue were 2-MoCDF (chlorine substitution in order: 2->>3- 1- 4-), 2,8-/3,6-DiCDF (2,8-/3,6->2,7->>others) and 1,2,8- TriCDF or 2,3,4-/2,3,8- (1,2,8- 2,3,4-/2,3,8->> others). The form of 1,2,7,8-TeCDF and 2,3,7,8- TeCDF were subsequently detected. These results support the assumption of typical PCDF pattern resulting in 1,2,7,8-TeCDF and 2,3,7,8-TeCDF as major congeners detected in the samples taken at a past factory site having chlor-alkali process and chlorine production process.

The graphite electrodes contain coal tar pitch so as to avoid corrosion in chlor-alkali process. Formation levels of PCDFs after brine electrolysis with pitch are shown in Fig. 5. Average levels of PCDFs per unit concentration of pitch were approximately 10,000 -100,000ng/g-pitch. Non-chlorinated dibenzofuran concentration contained in the pitch used the series of experiments back calculated from these values was corresponding about 0.1-1.2%. .

PCDFs and Cl-PAHs concentrations and their ratios in the brine electrolysis samples with pitch are shown in Fig. 6. Cl-PAHs are known to be similar in toxicity and characteristic to dioxin[22, 23]. Concentrations of
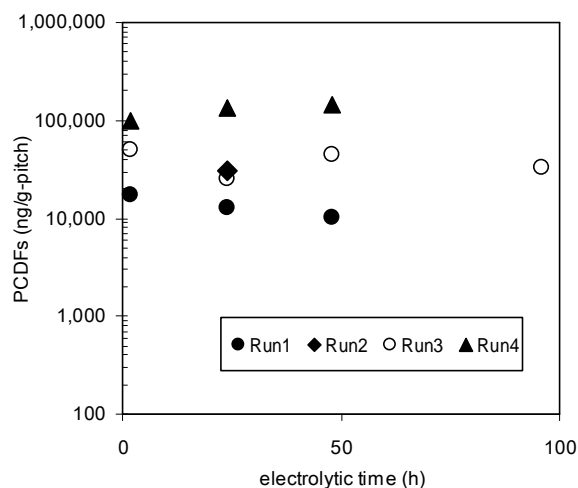

Fig. 5   Average levels of PCDFs formation during brine electrolysis with pitch
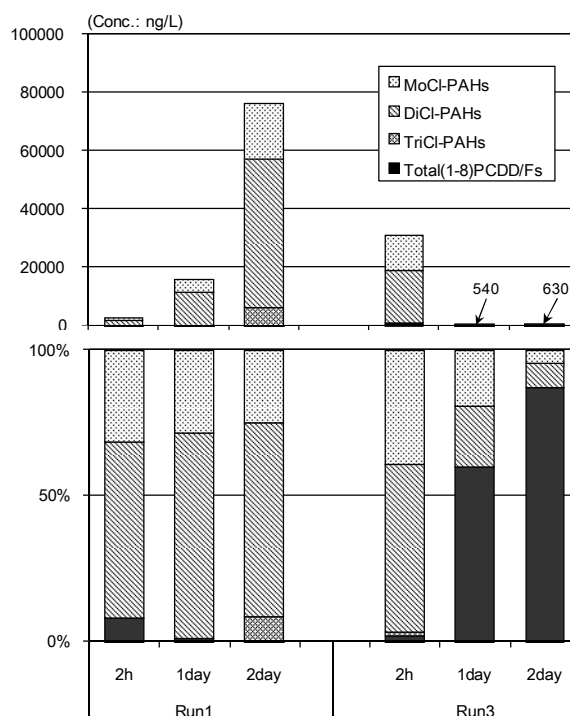
Fig. 6   PCDFs and Cl-PAHs concentrations and their ratios in brine electrolysis samples with pitch

Cl-PAHs were significantly increased in Mo-, Di- and TriCl-PAHs according to passing of electrolysis at Run1. The ratios of PCDFs were 0.2-7.8% of total concentrations of PCDFs and Cl-PAHs. In the Run3 case (under high temperature and high current density condition), the amounts of Mo-, Di- and TriCl-PAHs increased more than at Run1 at 2h. However, all the homologue concentrations of Cl-PAHs were observed to decrease after 1day reaction. The ratio of PCDFs was up to 87% of total concentrations of PCDFs and Cl-PAHs at 2day. Since limited PAHs (Mo- to TriCl-PAHs) were analyzed, it seemed that higher substituted Cl-PAHs were generated

according to electrolysis process. These results may indicate that similar shift of congeners in even Cl-PAHs were advanced. And much more abundant amounts of Cl-PAHs were formed during brine electrolysis compared to those of PCDFs.

Since coal tar pitch contains many kinds of PAHs as precursor, it suggested that the pitch was important supply source of Cl-PAHs as dioxin-like compounds. Until 1980s, the chlor-alkali plants in the world had adopted graphite electrode contained pitch. Therefore, high levels of PCDFs and many dioxin-like compounds such as Cl-PAHs were particularly detected in experimental electrolysis samples as well as soil in the past factory sites of chlor-alkali processes[11,15].

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