Methane Formation under Charcoal Interaction with Atomic Hydrogen and Deuterium at 77 K

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Abstract. Charcoal is a working material for the sorption cryopumps in the ITER project. An interaction of thermal hydrogen (deuterium) atoms and molecules with the ITER-type charcoal has been analyzed by adsorption measurements at 77 K and TDS (77-300 K). A stream quartz tube of 100 cm length, 1 cm radius with an $H_2(D_2)$ RF discharge was used for the production of H(D) atoms. Under charcoal interaction with the $H(D)/H_2(D_2)$ mixtures (77 K) the methane or deuteromethane (CD_4) were recorded in mass spectrum at heating of a sample up to 300 K. The total number of methane molecules and hydrogen atoms absorbed by the charcoal was found to be comparable. This means that the sticking coefficient of atomic hydrogen for the charcoal surface is close to unity at 77 K. The charcoal absorbed the most part of atomic hydrogen entering the tube cross-section and transformed into methane. The production rate of methane was higher for the samples with lower mass. The methane yield increased with the exposure time. The CD_4 yield somewhat exceeded that of CH_4. The atomic deuterium did not interact with previously adsorbed methane. D atoms were captured by surface "active" centres regardless of the presence of considerable quantities of adsorbed methane in micropores. After increasing the temperature (up to 300 K) the samples exposed in the $H(D)/H_2(D_2)$ mixture remained hydrogenated. The decrease of hydrogen sorption capacity (T=77 K) observed in in- and ex-situ measurements made up several percent when carbon atoms (~0.1%) of charcoal transformed into methane.

1. Introduction

The hot plasma of ITER main chamber is a powerful source of deuterium and tritium atoms. It is supposed that the most part of D/T atoms recombines at the inlet of the reactor pump system. However, it is possible that some part of D/T atoms remains in exhausted $D/T/He/C_xQ_y$ mixture (C_xQ_y are hydrocarbons with different contents of hydrogen isotopes). C_xQ_y is the symbol used in ITER documentation. As is shown in [1], the active species (e.g., hydrocarbon radicals and atomic hydrogen) with a surface loss probability $<10^{-3}$ can reach the inner surface of cryopumps. Such events may occur if the surface of ITER pumping duct will be covered by hydrocarbon a-C:H films. Such films decrease the atomic hydrogen recombination coefficient down to values of 10^{-4}-10^{-3}. Moreover, the reactions between hydrocarbons and molecular hydrogen on tungsten "dome" surfaces may be an additional source of atomic hydrogen.

Charcoal is a working material for the sorption cryopumps in the ITER project [2]. For a proper design of these pumps two main questions have to be addressed. What products can be formed under charcoal interaction with atomic hydrogen? Will the absorbed atomic hydrogen and possible reaction products influence the charcoal ability to absorb hydrogen isotopes at low temperatures?

In the present work the interaction of thermal hydrogen (deuterium) molecules and atoms with the ITER-type charcoal (granular, coconut-shell based) has been analyzed by adsorption measurements at 77 K and Thermal Desorption Spectroscopy (TDS) at 77-300 K. Also the change of hydrogen sorption capacity at 77 K was investigated.

2. Experimental

A stream quartz tube of 100 cm length, 1 cm radius with an $H_2(D_2)$ RF inductive-coupled discharge (frequency 20 MHz, specific power 0.1 W/cm^3) under a pressure of 10-60 Pa was used for the production of H(D) atoms [3, 4]. A quadrupole mass-spectrometer QMS-511 (Balzers) with differential pumping was placed at the tube outlet. The reactor was pumped out by a rotary pump working in molecular regime [5]. For the majority of the experiments the mean flow velocity, **V**, was equal to 30-120 cm/s. The average residence time of gas particles in the tube varied between 0.3-1 s. The plasma region extended for about 15 cm in length and was limited by a thin (100 μm) stainless steel grid.

We have used three LN traps for deep purification of the inlet $H_2(D_2)$ gas from impurities [3]. Two traps (1) and (2) were placed on the tube inlet and outlet. The third trap was located directly before the container with charcoal. In this trap the water vapor formed as a result of atomic hydrogen interaction with the quartz was condensed. The container with charcoal was cooled by the forth LN trap. The charcoal mass was 10-60 mg. The weight of one charcoal granule was about 1 mg. Prior to exposure to the $H_2(D_2)$ RF discharge, the charcoal samples were regenerated in the tube (background pressure 4 Pa) for 0.5 hs at 620 K. A thermocouple was placed under the container with charcoal at an external tube side. In the calibration experiments the thermocouple was placed directly in the container with charcoal inside the tube.

In experiments with $H(D)/H_2(D_2)$ mixtures the ratio of H(D) atom flow versus molecular hydrogen flow in the tube cross section with charcoal was found to vary in a range $(2\text{-}30) \times 10^{-4}$ and to depend on the relative position of atomic source and sample and hydrogen pressure [3, 4]. The diffusion component of H(D) atom flow towards the charcoal sample exceeded the viscous component of molecular hydrogen flow. In most of the experiments the molecular hydrogen flows were 1-7 sccm (standard cubic centimeter per minute). The H/H_2 or D/D_2 mixture had to pass through the tube section of 6 cm length at tube wall temperature of 77 K before entering the zone with charcoal. We assumed that the gas mixture was in thermal equilibrium with the charcoal sample and, therefore, the gas had also the temperature of 77 K.

3. $CH_4(CD_4)$ formation in reactions of charcoal with H(D) atoms at 77 K

In preliminary experiments an adsorption of molecular gases (H_2, D_2, CH_4) has been studied. It has been found that in the pressure range of 10-50 Pa the H_2 (D_2) adsorption capacity varied between 1 and 6 scc/g (standard cubic centimeter). In this pressure range the methane adsorption capacity was equal to 170-220 scc/g. During heating of the charcoal the most part of sorbed hydrogen or deuterium was released at 100-110 K (*FIG. 1*). In a thermodesorption spectrum the second peak appeared at 140-160 K and contained hydrogen, oxygen, and nitrogen.

After the charcoal exposure in $H/H_2(D/D_2)$ mixture the RF discharge was switched off but the $H_2(D_2)$ flow remained permanent during subsequent temperature increase from 77 up to 300 K. The time interval between the end of the discharge and the beginning of temperature increase did not exceed 10 min. During the heating a measurable increase of the gas pressure at the tube outlet was observed (*FIG. 1*) due to desorption of hydrogen and other gases from the charcoal. The changes of pressure and gas composition at the tube outlet were observed by Pirani gauge TR 901 and gas sampling in the QMS-511 chamber.

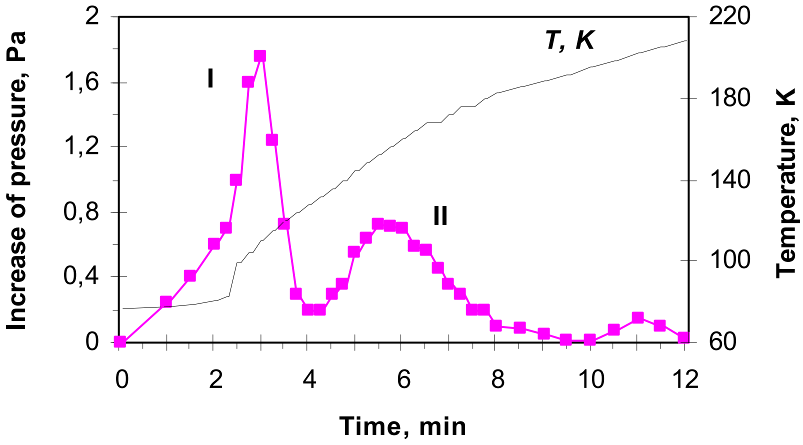

FIG. 1. Variation of pressure in the tube during deuterium desorption in D_2 flow ($F(D_2)=1$ sccm, $P(D_2)=46$ Pa). Charcoal sample weight was of 52 mg and consisted of 59 granules. Initially, the charcoal sample was exposed for 15 min in the D_2 gas at 46 Pa and 77 K. Deuterium was passed through palladium filter. Gas inleakage was below than 10^{-3} sccm.

Several calibration experiments were conducted and a noticeable methane formation was only observed for charcoal samples whose weight was less than 60 mg. For the heavier charcoal samples the effects of charcoal interaction with H atoms were shadowed by the effects of molecular hydrogen and impurities sorption because of the insufficiency of atomic hydrogen flow.

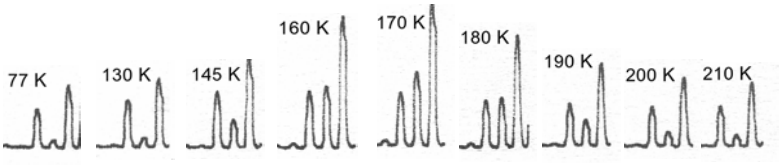

FIG. 2. The mass spectra of 14-16 amu recorded during the sample heating phase where the temperature increased from 77 to 210 K, after exposing the charcoal sample to an H/H_2 mixture for 1 h ($F(H_2)=7$ sccm, $P(H_2)=15$ Pa, H fluence was about 0.3 scc). The heating rate was 18 K/min. The charcoal sample consisted of 10 granules and weighted 10 mg. The signals 15 and 16 amu show methane desorption.

After H/H_2 exposure and following thermal annealing we observed methane desorption in a temperature range of 140-190 K (*FIG. 2*). Calibration experiments done (i) with H_2 RF discharge and without charcoal and (ii) with charcoal exposure but without discharge showed that the formation of methane was connected with the interaction of charcoal and H/H_2 mixture. The maximum of the methane desorption peak (T=165-180 K) coincided with a high-temperature shoulder of pressure change. Assuming that the pressure increase in the tube is connected mainly with the methane release, it is possible to compare the methane thermodesorption spectra in experiments with different masses and time exposures (Table I). In these experimental series the flow of atomic hydrogen flow was set to 2×10^{-3} sccm or 0.12 scc/h (T=77 K, $P(H_2)=35$ Pa, $F(H_2)=7$ sccm). The quantity of desorbed methane practically did not change for charcoal mass growing from 10 to 20 mg but it increased with time exposure in the H/H_2 mixture. In the experiments with the same condition for charcoal weight of 10 mg and exposure time 1 h, but with different numbers of granules (7, 9 and 12), the methane yield increased with the number of granules (0.017, 0.024 and 0.072 scc accordingly). In contrast to [6], ethane in our experiments was not revealed.

In experiments with deuterium the gas passed through a palladium filter and arrived at the RF discharge. The experimental conditions for D/D_2 mixtures were similar to those for H/H_2 mixture. We observed the formation of deuteromethane (CD_4) in the desorption spectra. QMS signals of 19 and 20 amu are shown in *FIG. 3*. The increase of the 20 amu signal at temperatures of 165-175 K is well seen. At the same time the signal of 19 amu remained practically unchanged and this fact can be attributed to the very small input of CD_3H into synthesized heavy methane. The pressure spectrum consisted of two desorption peaks (*FIG. 4*). The first desorption peak at 100 K contained deuterium (D_2), but the second one - deuteromethane (CD_4) and deuterium (D_2). The QMS signal (20 amu) calibrated and transformed into pressure is shown in the TDS spectrum (*FIG. 4)*. The total amount of synthesized CD_4 was up to 0.02 scc (0.38 scc/g) and 0.06 scc (1.14 scc/g) at fluences of deuterium atoms of 0.8 and 0.15 scc, respectively.

TABLE I: QUANTITY OF METHANE FORMED IN REACTION OF THE CHARCOAL WITH THE H/H_2 MIXTURE.

Weight, mg	CH_4 yield (scc) at exposure time, hs		
	1	2	2.5
10	0.024	---	0.08
20	0.02	0.038	---

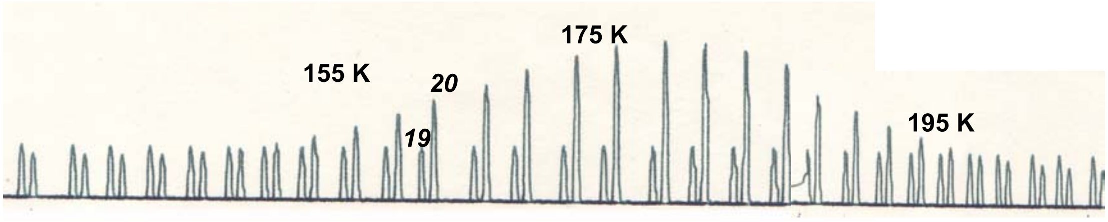

FIG. 3. The mass spectra of 19-20 amu during temperature increasing from 77 to 210 K after charcoal exposure in D/D_2 mixture during 1 h (F(D_2)=1 sccm, P(D_2)=46 Pa, D fluence was about 0.2 scc). The heating rate was 16 K/min. Charcoal weight was 52 mg, 59 granules. The signal of 20 amu demonstrates deuteromethane desorption.

The number of formed CH_4(CD_4) molecules and H(D) atoms in the tube containing the samples was similar. This means that the sticking coefficient of atomic hydrogen to the charcoal surface at 77 K is close to unity (see also [7]). The charcoal absorbs the majority of atomic hydrogen entering the tube cross section and methane is produced. The methane yield was found to increase with the exposure time. The charcoal interaction with D/D_2 mixture led to formation of deuteromethane (CD_4). The increase of the CD_4 yield exceeded that of CH_4 under similar experimental conditions. The rate of CH_4(CD_4) molecules accumulation was higher for the samples with lower mass. Based on these observations, we believe that the formation of CH_4 occurs via a reaction with sequential steps of H atom adding to "active" centres of the charcoal. It is possible that also some absorbed molecular hydrogen takes part in the reaction on the “active” centres. The higher charcoal mass is the higher number of the reaction “centres”. This in turn increases the probability of subsequentially adding hydrogen atoms to the reaction “centre” and, hence, reduces the probability of forming methane. The most probable “active” centre of H(D) atomic chemisorption is the edge atom of carbon net or surface of amorphous inclusions which are the charcoal structure elements [8]. The concentration of such chemisorption centres can reach 10 at.% of all carbon atoms. It is rather difficult to imagine the course of a consecutive chemical reaction on a certain active centre with formation finally of methane molecule (CH_4) without facilitated surface diffusion of adsorbed hydrogen atom. An obvious question arises – can the other hydrocarbons of type C_2Q_y be formed at charcoal interaction with H/H_2 mixtures?

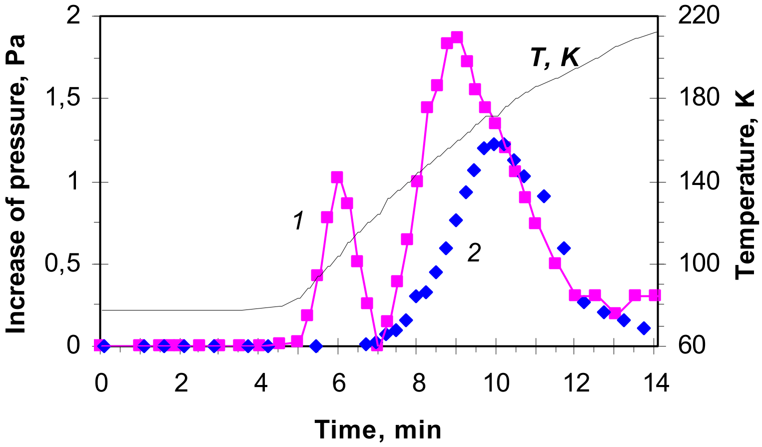

FIG. 4. Change of pressure (curve 1) in the tube after charcoal exposure in D/D_2 mixture during 1 h, ($F(D_2)=1$ sccm, $P(D_2)=46$ Pa, $T=77$ K). The deuteromethane QMS signal was transformed in CD_4 partial pressure (curve 2).

It should be noted that one molecule of formed methane fitted at 5000-10000 carbon atoms. In such conditions the probability of reaction between atomic hydrogen and methane is evidently quite low. To study the reactions between adsorbed methane and atomic deuterium we performed a series of experiments in which methane was preliminary introduced in the charcoal sample at 77 K and partial pressure of 25-30 Pa. Then, methane atmosphere was replaced by deuterium one. After that the charcoal sample was exposed in D/D_2 mixture for 0.5 h.

To our surprise at subsequent TDS analysis we did not find any other hydrocarbon besides CH_4 and CD_4 *(FIG. 5)*. The CD_4 yield was about 2-3 times higher than that in the analogous experiments but without preliminary CH_4 adsorption. The signal of 19 amu (CD_3H) was an order of magnitude less than that of 20 amu. We infer from results of this experiment that atomic deuterium forms CD_4 in consecutive reaction with matrix carbon atoms. Reaction of D atoms with adsorbed CH_4 proceeds with significantly lower probability than the D atoms reaction with the matrix. Adsorbed methane does not interact also with possible CD_y complexes, intermediate products in formation of CD_4.

Thus, the experiments with preliminary adsorption of methane have shown that the atomic hydrogen or deuterium introduced in charcoal interacts mainly with carbon matrix. D atoms are captured by surface “active” centres regardless of presence of considerable quantities of adsorbed methane.

It is quite reasonable to suppose that the surface complexes of type CD, CD_2 and CD_3 were the precursors of deuteromethane. Signals of 19 and 20 amu (CD_3H/DHO and CD_4/D_2O, respectively) were also observed during charcoal heating in the temperature range 300-800 K in ex-situ desorption experiments (I.I. Arkhipov in [9]). After H(D)/$H_2(D_2)$ exposure at 77 K the hydrogenated charcoal appeared. Thus, irreversible hydrogen sorption took place during charcoal exposure in the H(D)/$H_2(D_2)$ gas mixture at 77 K.

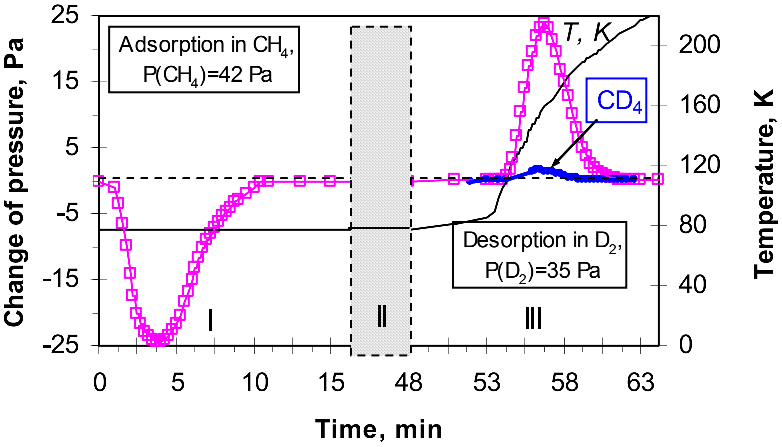

FIG. 5. Change of methane pressure during adsorption/desorption processes for charcoal: Stage I. Adsorption during exposure in CH_4 gas (T=77 K, P(CH_4)=26 Pa, F=3.5 sccm). Stage II. Methane flow was switched off at 18th minute and charcoal was exposed to a D/D_2 mixture for 0.5 hs, (T=77 K, P(D_2)=35 Pa, F=2 sccm, D atom fluence ~0.2 scc). Stage III. The atomic D flow was switched off and the charcoal sample was exposed to molecular deuterium with simultaneous temperature rising. CH_4 and CD_4 desorption occurred during the heating of the sample at permanent deuterium flow (P(D_2)=35 Pa, F=1 sccm). The charcoal sample weight was 51.8 mg, 59 granules.

4. Change of hydrogen sorption capacity of charcoal (T=77 K) under interaction with H/H_2 and D/D_2 mixtures

The measurements of the hydrogen adsorption capacity (V, scc) were performed in two ways: (i) in-situ in adsorption experiments in the tube and (ii) ex-situ by a static compensation technique [9]. In the in-situ experiments (hydrogen pressure range 30-60 Pa) we measured the change of pressure (ΔP, Pa) in the tube and tracked the signals of 2 or 4 amu by keeping constant hydrogen (deuterium) inlet flow (F, sccm) and by cooling the sample to 77 K. The area under the pressure curve normalized to coefficient $Z=\Delta P/\Delta F$ [Pa/sccm] corresponded to the adsorbed amount of hydrogen. The coefficient Z was determined in special experiments where the functional relationship between inlet gas flow F and the pressure in the tube P was established. Measuring the area before and after sample exposure in H/H_2 or D/D_2 mixtures and by knowing the sample weight it was possible to define the change of sorption capacity. The sorption capacities, V, are shown in Table II for the case of charcoal exposure in H/H_2 mixtures. The H atom fluence, charcoal mass, exposure time, and methane yield were 0.3 scc, 28.6 mg, 2 hs, and 0.02-0.03 scc, respectively. As it can be seen, the decrease of sorption capacity is quite small. However, it can be noted that the quantity, ΔV, is of the same order as the methane production yield, Y(CH_4):

$$\Delta V(H_2) \sim Y(CH_4) \text{ or } \sim Y(CD_4).$$

Deuterium and hydrogen sorption capacities are shown in Table III for the case of charcoal exposure in D/D_2 mixtures. The D atom fluence, charcoal mass, exposure time, and deuteromethane yield were 0.15 scc, 52 mg, 1 h, and 0.04-0.06 scc, respectively. The initial hydrogen sorption capacity of charcoal turned to be approximately equal to that with deuterium one. In experiments with D/D_2 mixtures the decrease of sorption capacity was 5-10% from initial value.

TABLE II. HYDROGEN ADSORPTION CAPACITY OF THE CHARCOAL (IN SCC) BEFORE AND AFTER EXPOSURE IN H/H_2 MIXTURE AT 77 K.

	In-situ		Ex-situ			
	$P(H_2)$=34 Pa		$P(H_2)$=2000 Pa		$P(H_2)$=3418 Pa	
	Initial	Final	Initial	Final	Initial	Final
Adsorp-tion	0.18±0.02	0.13±0.02	--	--	--	--
Desorp-tion	0.15±0.02	0.13±0.02	1.35	1.28	1.67	1.56

TABLE III. DEUTERIUM AND HYDROGEN ADSORPTION CAPACITY OF THE CHARCOAL (IN SCC) BEFORE AND AFTER EXPOSURE IN D/D_2 MIXTURE AT T=77 K.

	In-situ		Ex-situ			
	$P(D_2)$=37 Pa		$P(H_2)$=2450 Pa		$P(H_2)$=4000 Pa	
	Initial	Final	Initial	Final	Initial	Final
Adsorp-tion	0.22±0.02	0.23±0.02	--	--	--	--
Desorp-tion		0.20±0.02	2.53	2.40	3.10	2.95

The measured decrease of sorption capacity is close to the experimental error of measurements. However, from the data a tendency of reduction of sorption capacity could be recognised as a result of charcoal reaction with H atoms and notably with D atoms. This decrease of hydrogen sorption capacity (T=77 K) could be as high as few percent when carbon atoms (~0.1%) of charcoal transformed into methane.

5. Conclusions

By exposing charcoal to the $H(D)/H_2(D_2)$ mixtures (at 77 K) methane or deuteromethane (CD_4) was observed in the thermodesorption spectra. The methane desorption peak appeared at 160-170 K. The amounts of $CH_4(CD_4)$ molecules and H(D) atoms absorbed by the charcoal were comparable. The sticking coefficient of H(D) atoms to the charcoal surface at 77 K was close to unity. The charcoal absorbs the majority part of H atoms entering the tube cross section and a reaction occurs leading to the formation of methane. The methane yield, $Y(CH_4)$, was found to increase with the exposure time in H/H_2 mixture. The rate of methane production was higher for the samples with lower mass.

Based on these observations, we believe that the formation of CH_4 occurs via a reaction with sequential steps of H atom adding to “active” centres of the charcoal. It is possible that some absorbed molecular hydrogen also takes part in the reaction with the “active” centres.

The experiments with preliminary adsorption of methane and following exposure in D/D_2 mixture have shown that the atomic deuterium introduced in charcoal interacts mainly with the carbon matrix. H and D atoms are captured by surface “active” centres irrespective of the presence of considerable quantities of adsorbed methane in micropores.

After H/H_2 or D/D_2 exposure (77 K) the hydrogen sorption capacity decreases because of charcoal hydrogenation and $CH_4(CD_4)$ formation. This effect will be investigated in more detail under ITER relevant temperature (4.5 K) and including the sorption capacities for helium, which is the design driving requirement for the size of the ITER cryopumps.

Future experiments are planned to study the combined joint adsorption of unsaturated hydrocarbons (ethylene or acetylene type) and atomic hydrogen on the charcoal. This may represent a typical situation which may occur in ITER because of the reaction with gaseous water as it is the case under high temperature regeneration of the ITER cryopumps. In this case the number of possible reaction products will increase and we believe that the change of hydrogen sorption capacity may turn out to be more significant.

Acknowledgements

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