

# Copper leaching from a sandy soil: Mechanism and parameters affecting EDTA extraction

L. Di Palma\*, P. Ferrantelli

*Dipartimento di Ingegneria Chimica, dei Materiali, delle Materie Prime, Metallurgia, Università di Roma "La Sapienza",  
via Eudossiana 18, 00184 Roma, Italy*

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## Abstract

A series of 24 h batch tests of copper extraction from a sandy soil were performed by washing the soil with aqueous solution of ethylenediaminetetraacetic acid, EDTA. EDTA versus copper molar ratio were in the range between 1 (equimolar tests) and 13.3. The tests were performed at three selected liquid/solid ratio, 5, 12.5 and 25. Results show that decreasing the pH of the washing solution an higher copper extraction yield was achieved: an almost complete copper extraction was achieved after 23 h of mixing at a L/S = 5, and after 5 h of mixing at an L/S = 12.5. The mechanism of copper extraction was found to involve two sequential processes: the former dissolution of metal salts, that lead to an initial high concentration of both copper and some competitive cations (essentially  $\text{Ca}^{2+}$ ), and the following EDTA exchange reaction between calcium and copper complexes, which corresponded an increase of pH in the washing solution. A negligible extraction of  $\text{Fe}^{3+}$  was also observed at the investigated operative conditions.

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## 1. Introduction

In this paper, an experimentation devoted to copper (Cu) extraction from a contaminated soil is presented. An artificially contaminated sandy soil was used. The extraction was performed by washing the soil with an aqueous solution of ethylenediaminetetraacetic acid (EDTA,  $\text{EDTA-H}_2$ ) [1].

The objective of the work was to investigate the mechanism of copper extraction and to evaluate the influence of the main parameters affecting the washing process, such as the EDTA/metal molar ratio, and the pH and EDTA concentration in the extraction solution. A special attention was devoted to the competitive effect on copper chelation of the other exchangeable cations present in the soil. For the tested soil the final goal was to remove enough copper to achieve a residual copper level in the soil suitable to a civil (120 mg Cu/kg of

soil) or at least an industrial (600 mg Cu/kg of soil) reuse of the soil, according to Italian Environmental Regulation [2].

In the ex situ soil washing [3,4] technology undesirable contaminants in soils are removed by dissolving or suspending them in a washing solution. In the case of heavy metal contaminated soil, the washing solution is generally an aqueous solution of a chelating agent. In the remediation of copper contaminated soil, the effectiveness of EDTA has been widely demonstrated as a chelating agent in washing treatment [5–8].

In comparison with other chelating agents, EDTA presents the following advantages: a low degree of biodegradability in groundwater [4] and soil [1,9,10] and, moreover, a high level of complexing capacity with respect to heavy metals [5,9,11]. Conversely, the low selectivity of EDTA causes a great consumption of this reagent due to the potential chelation of all the exchangeable cations present in soil, such as  $\text{Ca}^{2+}$ ,  $\text{Fe}^{3+}$  [12].

A substantial excess of EDTA is so generally adopted, thus increasing the cost of the whole remediation treatment.

\* Corresponding author. Tel.: +39 06 44585571; fax: +39 06 44585622.  
E-mail address: luca.di.palma@ingchim.ing.uniroma1.it (L. Di Palma).

Table 1  
Composition of the soil used in the experiment (ASTM classification)

Component	Gravel	Coarse sand	Medium and fine sand	Silt and clay
Particle size (mm)	>2	0.425–2	0.075–0.425	<0.002
vol.%	–	9	75	16

Several papers deal with the extraction of heavy metals, and copper in particular, by soil washing but the aim of most of them was to compare the effectiveness of different chelating agents (EDTA, citric acid) towards selected metal extraction or to optimise the solid/liquid ratio to achieve a stated metal extraction yield [9,10,13,14].

Only few papers focus their attention to the mechanism of metal extraction, since a lot of chemical reactions and physical processes are involved [15].

In this paper, a simple model is presented to illustrate the mechanism of the leaching process from a sandy soil: the initial dissolution of copper precipitates was followed by the chelation by EDTA, that, due to its non-selective nature, binded progressively all the dissolved or exchangeable cations until the equilibrium conditions did not occur.

## 2. Materials and methods

### 2.1. Soil characterisation

The soil used in the experiments was a volcanic loamy sand collected in a cave near Bracciano, Rome, Italy. It was chosen as representative of a typical sandy soil in central southern Italy.

The soil was initially passed through a 2 mm sieve: the resulting soil composition is given in Table 1. The soil was mixed for 24 h in a Hobart-type mixer at 120 rpm.

After chemically and physically characterizing the soil, 1 kg samples were placed in plastic containers prior to artificial contamination.

Table 2 shows the characteristics of the soil used, determined according to Italian regulation [16]. pH was measured after mixing 10 g of soil samples with 25 ml of a 0.01 M solution of CaCl<sub>2</sub>.

The total porosity was determined using 100 g of air-dried soil [17]. The sample was weighed: then a known amount of water was added until saturation was obtained. The total porosity ( $f$ ) was determined from:

$$f = \frac{V}{V + V_s} \quad (1)$$

where  $V$  is the volume of water added and  $V_s$ , the volume of the dried soil particles [17], calculated as:

$$V_s = \frac{M}{\rho_s} \quad (2)$$

where  $M$  is the mass of the dry soil (g) and  $\rho_s$  (g/cm<sup>3</sup>) is soil particles density.

Table 2  
Characteristics of the soil used

Parameter	Value
pH	8.2
Organic carbon (%)	0.9
Water permeability (cm/s)	$3.18 \times 10^{-2}$
Total porosity (%)	46
Moisture content (g/kg)	24.5
Bulk density (g/cm <sup>3</sup> )	1.25
Soil particle density (g/cm <sup>3</sup> )	2.3
Pore volume (ml)	32
CaCO <sub>3</sub> (g/kg)	139
Conducibility (mS)	0.217
Metals (mg/kg)	
P	90
Fe	12.2
Mn	3.8
Cu	2.2
Zn	5.2
Ca	1550
Mg	230
K	260
Na	120
Cationic exchange capacity (meq/100 g)	
Total	10.85
Calcium	7.75
Magnesium	1.92
Potassium	0.66
Sodium	0.52

The pore volume of the soil (PV) was calculated using:

$$PV = \frac{f}{100} \times V_c \quad (3)$$

where  $V_c$  is the column volume.

The soil permeability was determined according to the ASTM D2434 standard test (Liu and Evett [18]).

### 2.2. Soil contamination

Soil contamination was carried out by mixing for 48 h at 120 rpm in a Hobart-type mixer 1 kg of soil and 0.51 of a saturated aqueous solution of dihydrate copper chloride, CuCl<sub>2</sub>·2H<sub>2</sub>O. After mixing, the samples were air dried by exposure to ambient air for 30 days and stored in plastic containers.

The contamination was carried out so as to obtain a Cu concentration of at least twice the Italian regulation limit for an industrial site.

Subsequent to preliminary acid digestion, a Philips PU 9200 atomic absorption spectrophotometer was used to determine the metal content of six 1 g samples of each contaminated soil. The average Cu concentration was 1230 mg Cu/kg with a standard deviation of  $\pm 98.5$  mg.

Samples (100 g) were prepared from the contaminated soil and stored in plastic containers.

Table 3  
Experimental conditions and results

Test	L/S ratio (ml sol/g soil)	EDTA:Cu	EDTA [M]	mol EDTA/kg soil	pH <sub>0</sub>	pH <sub>f</sub>	t <sub>50%</sub> (min)	η <sub>24h</sub> (%)
W1	5	1	0.0037	0.018	4.80	8.30	1140	51.49
W5	5	1	0.0037	0.018	5.33	8.54	>1440	47.50
	5	2	0.0074	0.037	4.90	8.54	<10	70.31
	5	4	0.0148	0.074	4.67	8.50	<10	89.94
	5	8	0.0296	0.148	4.52	8.55	<10	100
W0	5	–	0.0037	0.018	4.90	8.49	–	–
	5	–	–	–	4.90	8.18	–	–
W001	5	2.7	0.0100	0.050	4.94	8.39	<10	88.67
	12.5	6.75	0.0100	0.125	4.94	8.57	<10	100
	25	13.5	0.0100	0.250	4.94	8.62	<10	100
W125	12.5	1	0.00148	0.018	6.56	8.56	>1440	43.46
	12.5	2	0.00296	0.037	5.69	8.50	120	61.02
	12.5	4	0.00592	0.074	5.03	8.53	40	65.00
	12.5	8	0.01184	0.148	4.80	8.55	<10	100
	12.5	8	0.01184	0.148	4.80	8.55	<10	100

### 2.3. Experimental procedure

The washing solution was prepared by dissolving EDTA–Na<sub>2</sub> in distilled or tap water.

Three L/S ratio were tested: in a previous study [13] a L/S ratio of 12.5 was found as optimum for lead and zinc extraction by washing. So, this value and L/S ratios of 25 and 5 were chosen to perform the experimental tests. This last value is often assumed as a lower limit in metal extraction from soil, to ensure a good mixing of the soil slurry.

As regard the EDTA/Cu molar ratio, the tests were performed at equimolar concentration (using distilled water) and at different excesses of EDTA (2, 4 and 8—using tap water). An excess of EDTA is in fact generally adopted in metal extraction from soil, because of the non-selective nature of EDTA. A further series of tests were carried out by washing the soil with a 0.01 M EDTA solution, the typical EDTA concentration generally adopted in other soil remediation lab-scale experiences.

The excess of EDTA at a fixed L/S ratio was realized by increasing the EDTA concentration in the washing solution and, so, as a consequence, by using more acid washing solutions.

The experimental conditions of the tests performed are summarized in Table 3: in particular, the initial pH of the different washing solutions (pH<sub>0</sub>) is reported.

Tests W0 were performed on not contaminated soil samples after acidifying the washing solutions up to pH 4.9 by adding chloridric acid.

All the tests were performed by mixing at 175 rpm in a magnetic stirrer 100g of soil and the corresponding volume of washing solution according to the L/S ratio adopted. At selected times (every 10 min within the first reaction hour, every 30 min between the first and the third hour, and after 4, 5, 7, 10, 15, 20, 23, and 24 h), the contact solution was sampled (5 ml) and the metal content was determined using a Philips 7200 atomic adsorption spectrophotometer. A sedimentation time of 2 min

was always allowed to the soil slurry, prior to any sampling.

## 3. Results and discussion

### 3.1. Extraction mechanism

Prior to the soil washing experiments, a permeability test using a 0.05 M EDTA solution was performed according to [18], to verify the possibility of a flushing treatment of the soil. Though the soil water permeability was in the typical range for soil flushing technique ( $K < 10^{-3}$  cm/s [3]) this process was not realizable for the investigated soil, since the percolation of the 0.05 M solution of EDTA was not easy: the soil packing was in fact observed and the measured permeability was about  $10^{-5}$  cm/s. This confirms that a soil washing technology is required to successfully achieve soil remediation.

Fig. 1 shows the molar concentration of Ca, Cu, Fe along time during the washing test W1, performed using an equimolar ratio between the EDTA added in the washing solution and copper content in soil. The trend of metals concentration along the reaction time is the same observed in all

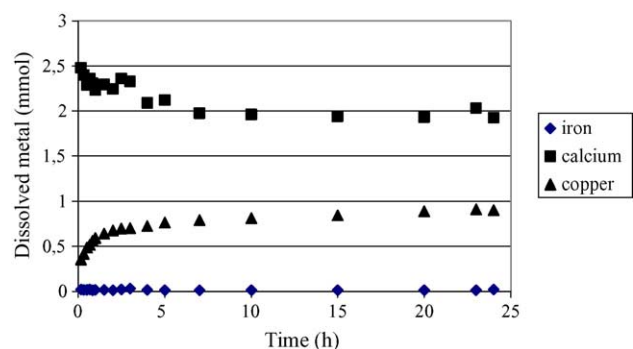


Fig. 1. Experimental results: test W1, equimolar conditions.

the tests performed and can be interpreted through a simple dissolution–chelation mechanism.

An initial great availability of  $\text{Ca}^{2+}$  in solution was in fact observed: since the tests were performed by dissolving EDTA– $\text{Na}_2$  in distilled water, the  $\text{Ca}^{2+}$  in solution was only due both to the exchangeable calcium ions ( $\text{Ca}_{\text{ads}}^{2+}$ ):



and, mostly, to the dissolution of calcium carbonate that in acid conditions quickly occurs, according to the:



Simultaneously a lower immediate availability of  $\text{Cu}^{2+}$  in solution was observed.

At the pH of the soil (pH 8.2), copper added to simulate contamination was mostly present as copper hydroxide [19]: the solubility of this compound is very low in a quite wide range of pH (from 7 to 14 [20]) but dramatically increases in an acid medium (pH < 5), when the reaction



occurs.

The first step of the extraction mechanism was, therefore, dependant upon the pH of the extractant solution. The same trend was in fact observed in all the other washing tests, when a lower or higher initial dissolution of both calcium and copper occurred, since in those tests a different alkaline washing solution was used with respect to the one used in the equimolar test W1.

The possibility to extract other metal than  $\text{Cu}^{2+}$  or  $\text{Ca}^{2+}$  from the soil was also investigated.

On the basis of the CEC data reported in Table 2, also magnesium dissolution would be expected, but a negligible  $\text{Mg}^{2+}$  amount was measured in solution in all the tests performed, due to the little amount of exchangeable  $\text{Mg}^{2+}$  in the soil, as reported in Table 2. Due to the high stability of the Fe–EDTA complex also  $\text{Fe}^{3+}$  content was measured: this was always very low with respect to the other two metals concentration.

Once in solution,  $\text{Ca}^{2+}$  and  $\text{Cu}^{2+}$  ions could react with EDTA, according to the reactions:



Reaction (7) was initially favored with respect to reaction (8), because of the larger calcium immediate availability in solution with respect to copper (about 2.5 mmol against 0.3 mmol, as shown in Fig. 1).

After the initial dissolution of metal precipitates, a progressive decrease in calcium content in solution was observed, together with a corresponding increase in copper content. After 24 h of mixing, the 1.85 mmol of EDTA were approximately equally distributed among copper and calcium complexes, while a calcium exceeding amount of about 1 mmol was observed, caused by the dissolution of the calcareous constituent of the soil.

Table 4  
 $\text{Ca}^{2+}$ ,  $\text{Cu}^{2+}$ , and  $\text{Fe}^{3+}$  concentration and their variation along time (test W1)

Parameter	Mixing time				
	10 min	1 h	4 h	7 h	24 h
mmol Fe	0.020591	0.01551	0.017038	0.015228	0.021188
$\Delta$ mmol Fe	0	–0.00508	–0.00355	–0.00536	0.000597
mmol Ca	2.47625	2.228119	2.08925	1.971945	1.923548
$\Delta$ mmol Ca	0	–0.24813	–0.387	–0.50431	–0.5527
mmol Cu	0.353265	0.593922	0.727201	0.791901	0.902537
$\Delta$ mmol Cu	0	0.240657	0.373935	0.438636	0.549272
rim %Cu	20.15	33.88	41.48	45.18	51.49
pH	4.80	7.61	8.01	8.16	8.3
IC (mmol C)	3.352	3.162	3.109	2.935	2.877

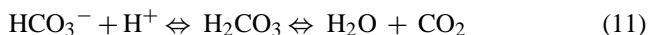
Table 4 shows the variation of  $\text{Ca}^{2+}$ ,  $\text{Cu}^{2+}$  and  $\text{Fe}^{3+}$  concentration in the contact solution along time for the test W1, performed at equimolar conditions between EDTA and copper, and so without any EDTA excess in the extraction solution. It can be noted that while  $\text{Fe}^{3+}$  concentration was always negligible, the strong reduction of  $\text{Ca}^{2+}$  molar concentration corresponded to an almost equal increase in  $\text{Cu}^{2+}$  molar concentration.

Due to the higher EDTA affinity of  $\text{Cu}^{2+}$  ( $\log K_{\text{Cu-EDTA}} = 18.79$ ;  $\log K_{\text{Ca-EDTA}} = 10.59$  [21]), an exchange reaction in fact occurred between Ca–EDTA and Cu–EDTA, according to the:



that show how an equimolar exchange between  $\text{Ca}^{2+}$  and  $\text{Cu}^{2+}$  occurred, as confirmed by the data reported in Table 4.

While this exchange occurred, the great availability of  $\text{CO}_3^{2-}$  in the contact solution due to the initial calcium carbonate dissolution lead to a dramatic pH increase, caused by the reactions:



The pH increase was mainly observed during the first hour of treatment, and determined a progressive reduction in the efficiencies of the dissolution reactions (5) and (6). In the tests W1, after 1 h of treatment, a pH of 7.61 was observed, as shown in Table 4: at this pH value, precipitation of  $\text{CaCO}_3$  strongly occurred, as a result of reaction (5) reverse development. This is confirmed by the inorganic carbon content data, reported in Fig. 2 for selected tests, that in all the performed tests showed a progressive decreasing trend, mainly within the first five hours of mixing.

Fig. 2 shows that this behaviour was also observed in the tests performed on not contaminated soil samples (tests W0) both using acidified water (at pH 4.90) and the 0.0037 M EDTA solution as leaching solution. By comparing results of these two last tests, it can be assessed that in the tests performed in the presence of EDTA a greater amount of inorganic carbon in solution was observed, as a consequence of

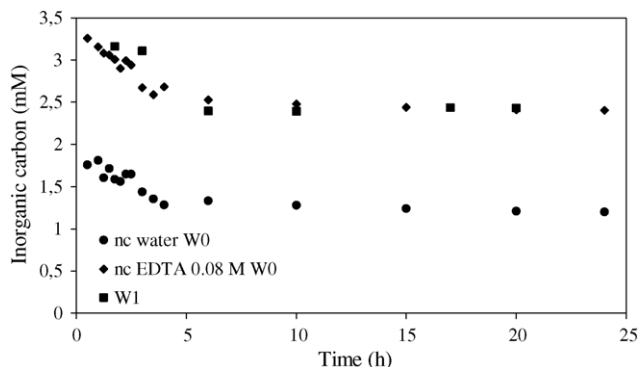


Fig. 2. Inorganic carbon content along time (tests W0 and W1).

the effect of EDTA on the dissolution of calcium carbonate (about 40% of increase after 30 min).

In addition, results show that in the equimolar test, the copper level for an industrial reuse of the contaminated soil (600 mg Cu/Kg of soil, corresponding to an extraction yield of 50%) was achieved after about 23 h of mixing.

### 3.2. Process optimization

Results obtained in all the different tests performed are presented in Table 3. To a better comparison of experimental results, Table 3 also reports the copper extraction yield achieved after 24 h of mixing ( $\eta_{24h}$ ) in all the tests performed, together with the half-life time for copper concentration ( $t_{50\%}$ ). The final pH values measured in the solution ( $pH_f$ ) are also shown.

Fig. 3 shows the results of tests W001. In those tests, the investigated parameter was the liquid versus solid ratio: the tests were in fact performed using a 0.01 M EDTA solution, that, in each test ensured a large excess of EDTA with respect to the copper content in soil. In a previous study [13], performed at the same experimental conditions, a L/S ratio of 12.5 was found optimum for lead and zinc extraction from a contaminated soil: an increase in L/S ratio did not provided any further metal extraction. The results obtained in the present experimentation, show that, since an increase in the L/S ratio did not correspond to an higher EDTA amount

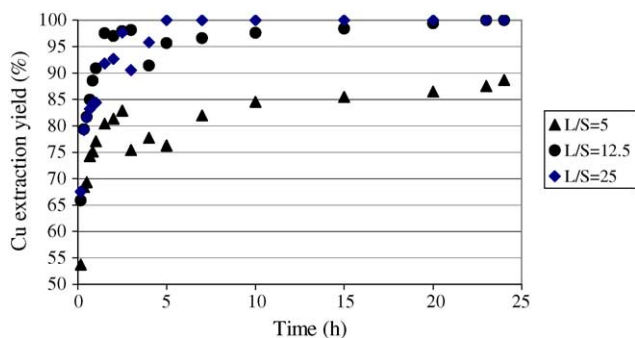


Fig. 3. Experimental results (tests W001): influence of L/S ratio on copper leaching ([EDTA] = 0.01 M).

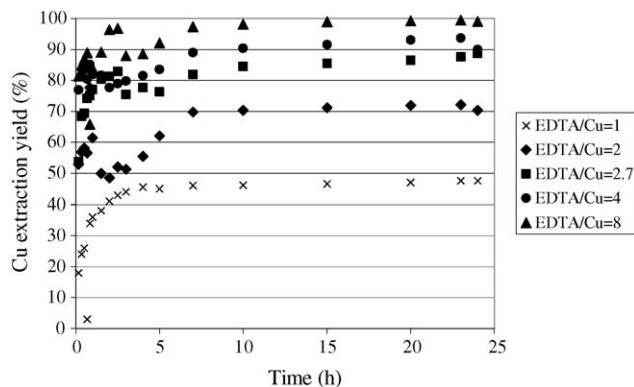


Fig. 4. Experimental results: leaching at L/S = 5.

for kg of soil (as shown in Table 3), a lower copper extraction yield was observed at any selected time of sampling. The two results are not in contrast, because while in the above cited experimentation increasing the L/S ratio the total amount of EDTA also increased, in the present experimentation the solutions used to perform the tests at the L/S ratio of 12.5 were only diluted with respect to the ones used for the tests at the L/S ratio of 12.5.

Fig. 3 shows that increasing the L/S ratio, and so consequently, increasing the EDTA:Cu ratio, a faster copper chelation was observed: 24 h hours of mixing were enough to remove completely copper from the soil in the tests at L/S = 12.5 and 25. An about 100% extraction yield was in fact observed after 23 h of mixing at a L/S = 12.5, and after only 5 h of mixing at an L/S = 12.5. It can be assessed that the remaining fraction of EDTA was mainly bonded to the  $Ca^{2+}$  ions of both soil and tap water (hardness = 20.3 °F).

Fig. 4 show the results obtained in the tests performed at a L/S ratio of 5 (experimental series W5).

Fig. 5 show the results obtained in the tests performed at L/S ratio of 12.5 (experimental series W125).

After a rapid extraction of copper generally observed within the first 5 h, copper extraction yield achieved a plateau value corresponding to equilibrium conditions. This plateau value was higher increasing the EDTA:Cu ratio. Equilibrium conditions were also achieved first when EDTA:Cu ratio was higher.

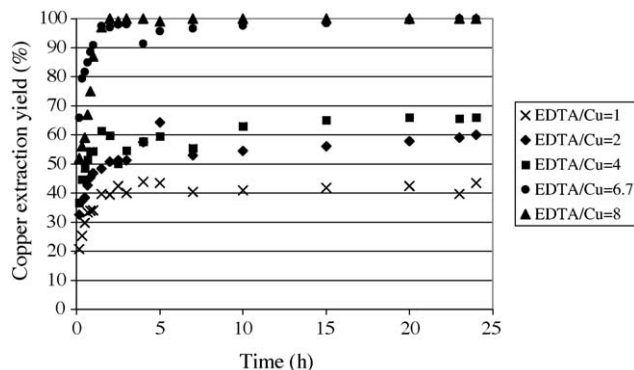


Fig. 5. Experimental results: leaching at L/S = 12.5.

Results confirm that at a fixed EDTA/Cu ratio, lowering the pH of the extractant solution resulted in an increase of Cu extraction yield, because of the higher initial copper salt dissolution due to the higher copper availability in the liquid phase. Increasing the EDTA/Cu ratio, the higher EDTA amount provided an higher Cu<sup>2+</sup> chelation.

#### 4. Conclusions

A sandy soil contaminated with copper was subjected to 24 h batch extraction with EDTA aqueous solution at different EDTA concentrations and L/S ratio to assess the optimal conditions for soil remediation.

Leaching mechanisms of copper and the main competitive cations (Ca<sup>2+</sup> and Fe<sup>3+</sup>) were also investigated.

Results show that:

- the leaching process was a two step dissolution–chelation process where, after metal salts dissolution due to the strong acidity of the extractant solution, EDTA chelation occurred, displacing competitive ions (in particular Ca<sup>2+</sup>) and so favouring the formation of Ca<sup>2+</sup>–EDTA complexes;
- Cu<sup>2+</sup> extraction yield strongly depend on both L/S ratio and EDTA:Cu ratio;
- the greater amount of copper (from 80% to 90% of the total extracted amount depending on the experimental conditions) was extracted within the first 5 h of the treatment;
- according to Italian Environmental Regulation, complete soil remediation was successfully achieved for EDTA:Cu = 4 at L/S = 5 and EDTA:Cu = 8 at L/S = 12.5.

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