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Copper removal from effluents by various separation techniques

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Abstract

In this study, the recovery of copper ions from simulated and real wastewaters of a mine and minerals processing plant was investigated. The separation process employed was flotation, which was applied in three different mechanisms: (i) ion flotation using xanthates, (ii) precipitate flotation generating copper hydroxide and (iii) sorptive flotation using zeolites as sorbent material. Under the studied conditions, ion and sorptive flotation were found to be effective methods for copper removal with almost 100% Cu removal achieved, while the precipitation method failed. The copper removal was always higher in simulated mixture than in real effluents; it may be due to the presence of other minor constituents that they have not taken into account in simulated mixture (e.g. organic compounds). The bubble generation method was that of dispersed-air flotation. Reference is also given to economic aspects. An economic study of sorptive flotation showed that the capital investment for a 10 m³/h plant would be of the order of US\$1.15 million dollars. The operating costs are about US\$1.76 million per year. The total revenues from water recycling and reuse are US\$68,800 per annum, without calculating the benefits of copper recovery.

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Keywords: Copper removal; Ion flotation; Precipitate flotation; Sorptive flotation; Mine effluent

1. Introduction

The importance of froth flotation, as a separation process, to the economy of the whole industrial world is considered to be enormous (Fuerstenau, 1962). Without this process, many familiar metals and inorganic raw materials would be exceedingly scarce and costly (Matis and Zouboulis, 1995). Nevertheless, the process is beneficial to a large variety of chemical species too, such as the metal ions that can be concentrated from a solution or dispersion.

Several categories of the flotation process mechanism exist for removal of ions (Lemlich, 1972):

- *ion flotation* involves the removal of surface-inactive ions from aqueous solutions by adding ionic surfactants which act as collectors. The subsequent passage of gas bubbles through the solution transfers the surface-active ions to the top of the column, which permits the separation and concentration of the ionic species in a small volume of collapsed foam (Walkowiak and Grieves, 1976).
- *precipitate flotation* involves firstly the immobilization of ions as precipitates, e.g. by raising the respective concentrations may lead to precipitation of the ion as a surfactant floatable product, before

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air is passed. This means that it is not a solution anymore but rather dispersion. Different methods of *precipitate flotation* have been described based on the method of forming the precipitate, e.g. that of metal hydroxides by pH adjustment (Alexandrova and Grigorov, 1996; Zouboulis et al., 1992a).

- *sorptive flotation* (or adsorptive particulate flotation) involves the preliminary abstraction or scavenging of metal ions using bonding agents. Examples of tested sorbents are synthetic and natural zeolites (Rubio and Tessele, 1997; Matis et al., 2004) and different mineral fines (Zouboulis et al., 1992b; Matis et al., 1998). After sorption, follows the flotation stage where the metal-loaded sorbent particles are separated from the treated and cleaned solution. The technique can perhaps be envisaged as an “extension” of carrier flotation (Zouboulis and Matis, 1997).

According to the method used for the generation of bubbles, it is noted that two broad categories exist: (i) *dispersed-air flotation* and (ii) *dissolved-air flotation* (DAF) (Matis and Lazaridis, 2002). The application of flotation for metals removal could be either alone or may be in combination with other processes as membrane filtration, due mainly to the increasing environmental pressures (Lazaridis et al., 2004).

The discharge of organic and metal pollutants into the environment is a serious problem facing numerous industries. Wastewaters containing dissolved metal ions such as nickel, zinc and copper originate from a variety of sources such as photographic industries, refineries, abandoned metal mines, and metal plating operations. The concentrations of dissolved organics and metals in wastewaters are highly regulated due to their toxicity. Solvent extraction (SX) is widely utilized in metal recovery operations, including copper recovery, using soluble extractants. The solvent extraction is most suitable for removal of solutes that are present in high concentrations; for very dilute solutions the cost of power becomes high (Fillipi et al., 1998). It has been estimated that to economically recycle a copper concentrate requires up to 2 g Cu/L, presupposing that it is going to feed to SX. The aim of this work was copper recovery from a wastewater and (optionally) the treated effluent to obey the environmental standards. The set limit in Europe for indirect discharge of chemical industry effluents is 0.5 mg/L copper.

2. Experimental

2.1. Materials

In preliminary test runs, a simulated mixture was studied, composed of: Cu(II) 240, Mn(II) 40, Fe(III) 8, Pb(II) 0.2, SO_4^{2-} 4,200, Ca(II) 270 and Mg(II) 260 mg/L (as main constituents). Two separate samples of effluent were obtained from the Assarel–Medet open pit copper mine near Panagyurishte, Bulgaria (90 km southeast of Sofia). The first sample had Cu(II) 250, Mn(II) 82, Fe(III) 35, Ca(II) 312, Mg(II) 290, SO_4^{2-} 4,400 and Pb(II) 0.5 mg/L; the second sample had Cu(II) 315, Mn(II) 90, Fe(III) 40, Ca(II) 256, Mg(II) 304, SO_4^{2-} 4,000 and Pb(II) 0.1 mg/L. Both of them were clear solutions of the same colour and pH (~ 3.5).

A synthetic maximum aluminium p-type zeolite was tested as a sorptive (bonding) agent, hereafter denoted as BA. The material was of type 4A and with chemical structure $\text{Na}_2\text{O} \cdot 2\text{SiO}_2 \cdot \text{Al}_2\text{O}_3 \cdot n\text{H}_2\text{O}$ (designated as CA 150) has an ion exchange capacity of 6 meq/g and 65% of particles were 3–6 μm . The natural pH of zeolite in water was approximately 10–10.5. Zeta-potential measurements were also conducted and showed that the isoelectric point was around pH=8, which predicts the type of flotation surfactant which should be used, according to the solution pH value (Matis et al., 2004).

The following surface-active agents were also used as collectors in the flotation process: potassium *O*-ethyl dithiocarbonate, $\text{C}_2\text{H}_5\text{OCS}_2\text{K}$ (denoted as KETx), sodium oleate, $\text{C}_{18}\text{H}_{33}\text{NaO}_2$ (SO) and sodium dodecylsulphate, $\text{C}_{12}\text{H}_{25}\text{NaO}_4\text{S}$ (SDS).

Where flocculation was used, two flocculant reagents were used: a medium cationic, named Zetag 47 and a non-ionic, Magnafloc 351 (high molecular weight polyacrylamide) for the precipitates (Ciba, UK). Ethanol (0.1% v/v) was used as flotation frother. The pH value was adjusted by the addition of nitric acid or sodium hydroxide solutions when needed.

2.2. Methods

Experiments have been conducted in bench scale mode. The target metal ion solution was firstly treated in a mixing reactor, where all the needed reagents were added. After this stage, the content of the reactor

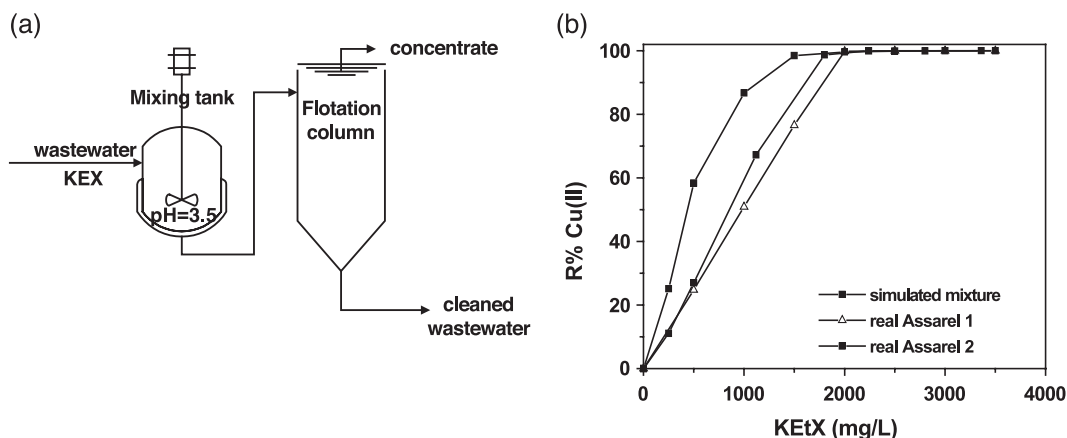


Fig. 1. (a) Flow diagram of copper ion flotation. (b) Influence of collector concentration on copper removal.

was transferred in the flotation reactor. Flotation was carried out in a typical laboratory cell made of plexiglass, with inside diameter of 4 cm and total height of 56.5 cm (Zouboulis and Matis, 1997). The gas diffuser was of Schott D4 type, situated at the bottom of the column, with an average porosity of 10–16 μm . The airflow rate was 100 cm^3/min and controlled by a rotameter. The following process time was applied to the various stages (unless otherwise stated): conditioning 20 min, flocculation 10 min (when applied), flotation 5 min.

The analytical determination of metal (copper, iron, manganese) concentrations was conducted by atomic absorption (AAS) spectroscopy. The results are generally expressed as recovery ($R\%$), calculated from the

initial and final concentrations of the remaining metal ions. The solid content was analysed gravimetrically, collecting the concentrate from the surface of aqueous solution by suction.

3. Results and discussion

3.1. Ion flotation

O-alkyl dithiocarbonates, called usually xanthates in minerals engineering, and other thio reagents are known flotation collectors for mineral sulphides. The xanthates exhibit a high level of chemical reactivity for heavy metals (Stalidis et al., 1989). The reaction of

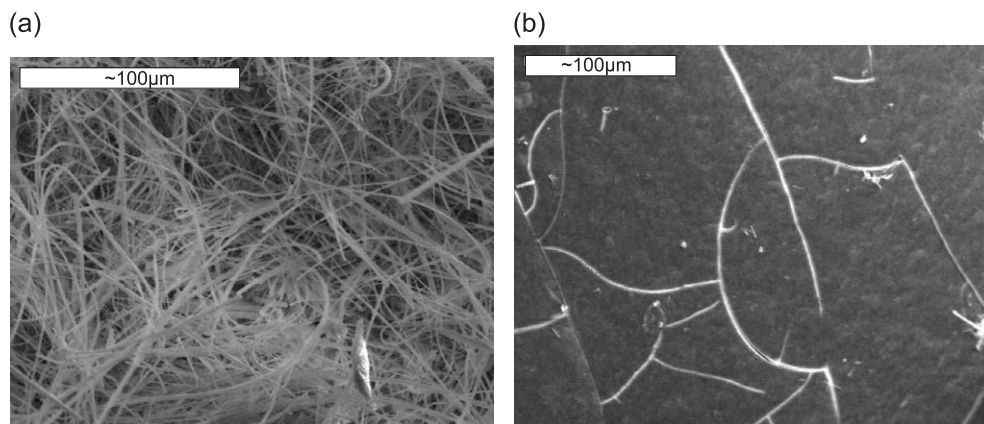


Fig. 2. SEM micrographs of the two phases precipitated at pH 4.5 from the real 1st sample, a white fibrous phase (a) and a brownish gelatinous phase (b).

Table 1

Composition of the two precipitates obtained from the first effluent sample, at pH 4.5

	Elemental analysis (wt.%)											
	Mg	Al	Si	S	K	Ca	Fe	Ni	Cu	Zn	Ba	Mn
Fibre	1.13	11.13	56.94	3.62	3.46	2.83	0.87	0.38	1.85	10.18	8.53	
Gel	0.57	54.77	2.44	32.58	0.18	–	5.1	–	4.03	–		0.28

certain dissolved metal ions, such as Cu^{2+} , with xanthate anions gives an unstable complex that decomposes to produce dioxanthogen, $(\text{EtX})_2$ and cuprous xanthate, CuEtX (Sparrow et al., 1977). Both precipitate out of solution as an agglomerate, its size being suitable for flotation separation. The pH from about 2.5 to 5.5 did not affect the removal. A 10% excess of xanthate was found to be best, in what was can be classified as precipitate flotation of third kind.

Fig. 1a shows the flow diagram applied for the ion flotation of copper, while Fig 1b presents the experimental results for the two plant effluents and the simulated effluent. Almost complete copper removal was obvious for all cases, however, the requisite xanthate dose was doubled in the case of the real effluents. In all cases, the residual copper concentration was lower than 0.11 mg/L.

3.2. Precipitate flotation

Precipitate flotation of metal ions from aqueous solutions is usually realized by the addition of sodium

hydroxide resulting in metal immobilisation as hydroxide precipitates followed by their flotation.

The pH of the mine effluent was around 3.5. Therefore, a pH adjustment to a value of 4.5 will separate out mainly iron. When applying such a precipitation, the product from the first plant effluent sample, after filtration and drying, consisted of two distinct phases; a white, fibrous, non-crystalline phase and an amorphous, brownish, gelatinous phase. Both of these were analysed using a scanning electron microscope (SEM) equipped with an energy dispersive system (EDS); micrographs are presented in Fig. 2 and elemental analyses are shown in Table 1.

With the real effluents, however, there was difficulty in the flotation of the precipitate, due to other constituents and the nature of the obtained precipitates. Therefore, the first stage of iron removal at pH 4.5 was by flotation for the simulated mixture, but by filtration for the real effluents. Copper hydroxide has a positive surface charge over the pH range examined, which explains the application

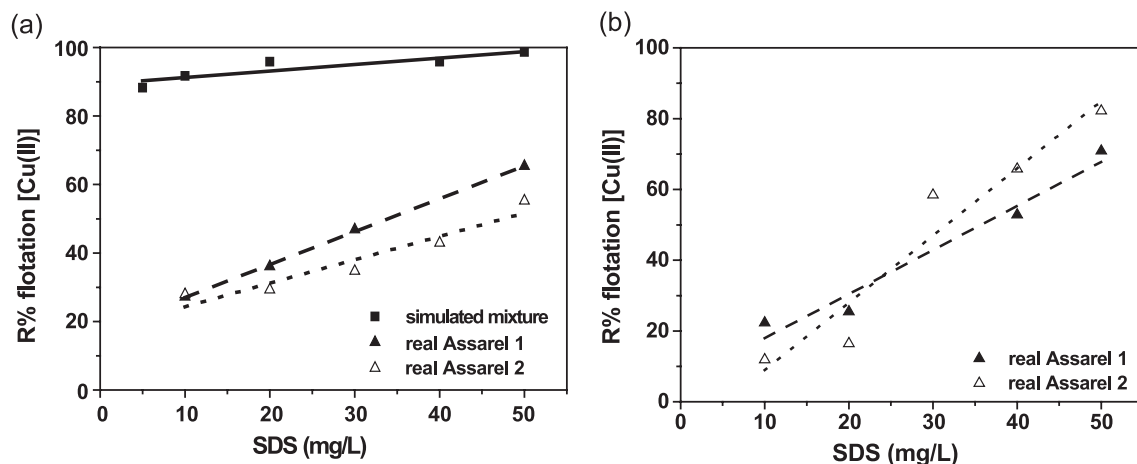


Fig. 3. Influence of collector concentration on copper removal in the (a) absence and (b) presence of flocculant, [Magnaflow 351] = 4 mg/L.

Table 2
Removal % of solids and metals in the sorptive flotation process

Type of effluent	R% zeolite	R% Cu(II)	R% Fe(III)	R% Mn(II)
Simulated mixture	98.12	99.83	99.24	79.33
Assarel 1	92.4	99.47	99.65	87.24
Assarel 2	81.6	99.73	99.65	88.96

For the simulated Assarel mixture 50 mg/L SO and 0.5 mg/L Zetag 47 were used.

of an anionic surfactant (such as sodium dodecyl sulphate) to collect the solid particles during flotation. After filtration, the clear solution was increased to pH 6.5 and SDS added prior to flotation. The influence of collector dose (SDS) is presented in Fig. 3a,b in the absence and presence of flocculant, respectively.

It is clear that copper recover was almost complete for the simulated wastewater, while under optimum conditions was about 80% for the real effluent. The latter can be interpreted by the fact that portion of the collector could bind to the other solids or ions present in the solution, thus eliminating the active concentration. The idea of using higher collector concentration was rejected because foam control problems were caused. The remaining copper concentration was in the range 50–150 mg/L for the real effluents, while for the simulated solution was only 2.5 mg/L.

3.3. Sorption flotation

Sorption flotation is a general term describing the attachment of charged species from a solution to a coexisting solid surface. Three types of processes are mainly identified for the sorption phenomena: (i) surface adsorption, which is limited to the accumulation of sorbate on the external surface of a solid,

Table 3
Equipment costs for the process system examined

Equipment (quantity)	Description	Cost (US\$)
Blending tank (1)	Volume = 11.2 m ³	22,000
Blending tank (1)	Volume = 5.6 m ³	17,000
Blower (1)	Pressure change = 3 bar, Power = 0.22 kW	3000
Flotation column (1)	Height = 10.4 m, Diameter = 1.1 m	44,000
Microfilter (2)	Membrane area = 54.51 m ²	112,000

Table 4
Fixed capital estimate for this process system

Fixed capital estimate summary (2003 prices)	Cost (US\$)
(A) Total plant direct cost (equipment purchase cost, installation, process piping, instrumentation, insulation, electrical, buildings, yard improvement, auxiliary facilities)	679,000
(B) Total plant indirect cost (engineering, construction)	122,000
(C) Other costs (contractor's fee, contingency)	120,000

including several mechanisms such as ion exchange and surface complexation; (ii) adsorption or diffusion into the solid; and (iii) precipitation or coprecipitation (Matis et al., 1998).

This route was examined by applying zeolite as the sorbent material, at the natural pH 6.5, for solubility reasons. Zeolites were practically insoluble in water at pH above 5 approximately, value where less than 0.5% of solid was dissolved; while at pH 4, ~ 30% was dissolving. The used flow sheet was the same as in Fig. 1a, 4 g/L zeolite was added with the wastewater along with 200 mg/L SO and 4 mg/L Zetag 47. The mixing tank operated at pH 6.5.

Salient experimental results are presented in Table 2. Almost complete copper and ferric ion recovery was accompanied by high solids and manganese removal. Copper remaining in solution was always inside the accepted standards. Sodium oleate was chosen as the appropriate collector due to the positive surface charge of the zeolite that favours the attraction of anionic collectors.

Copper ion removal by natural zeolites was studied by Panayotova (2001) and can be described by the

Table 5
Annual operating cost for the process system

Cost item	Including depreciation		Excluding depreciation	
	US\$/Year	%	US\$/Year	%
Raw materials	655,700	37	655,700	39
Labor-dependent	306,600	17	306,600	18
Equipment-dependent	539,000	31	451,500	27
Laboratory/QC/QA	32,800	2	32,800	2
Consumables	215,900	12	215,900	13
Utilities	11,000	1	10,300	1
Total annual operating cost	1,761,000	100	1,672,800	100

Langmuir adsorption isotherm. From the thermodynamic calculations (of apparent activation energy, equilibrium constant, ΔG° and ΔH°), it was proven that sorption could be easily carried out with a satisfactory rate and a moderate affinity was found; a spontaneous and endothermic nature of the uptake process was concluded.

The conditions of desorption of cadmium from natural zeolite was elsewhere investigated and these results were used to characterize the ion exchange nature of the interaction of metal ions-zeolite (Vasy-lechko et al., 2003); potassium salts were found best, desorbing up to around 90%. The application of inorganic acids as eluants would dissolve the metal hydroxides, if partially created and below pH 5, also the zeolite itself. Hence, desorption is possibly not a readily reversible process as happens in other cases, i.e. sorption of ions in the bulk aqueous phase onto organic matter or certain minerals, as reported by Subramaniam et al. (2001). A more extensive study of such phenomena has been recently published (Mavrov et al., 2003).

3.4. Economic considerations

Tables 3–5 present briefly the techno-economic study, applying the software tool SuperPro Designer (Intelligen). A model for a flotation column had to be inserted in this programme as it offers only dissolved

air flotation which is the dominant flotation method in water treatment. Fig. 4 gives the flowsheet for sorptive flotation followed by microfiltration downstream; the latter was considered necessary, for the production of solid free effluent.

The heavy metal ions (mainly Cu, Mg, Fe) of the Assarel effluent were sorbed onto the zeolite bonding agent, as earlier obtained. An 80% flotation recovery was adopted. The scale-up for 10 m³/h wastewater was based on the experimental results in the laboratory. A cost comparison was also tried with a respective new hybrid unit, i.e. combining flotation and microfiltration in the same cell (data unpublished).

The study showed that the capital investment of the plant would be of the order of US\$0.92M. The operating costs are about US\$1.76M per year. The processing rate is 68.83×10^6 kg/year of influent and the unit processing cost 0.0256 \$/MT of influent. The total revenues from water recycling and reuse are US\$68,800 per annum. It is noted that this only accounted for the environmental costs and did not consider any credit due to copper recovery.

It is perhaps surprising that in an Environmental Protection Agency (2001) report there is a table given (as number 3) on the applicability of treatment technologies to contaminated groundwater; however, flotation is described as “not applicable” for heavy metal contaminants, while applicable to PCBs, diox-

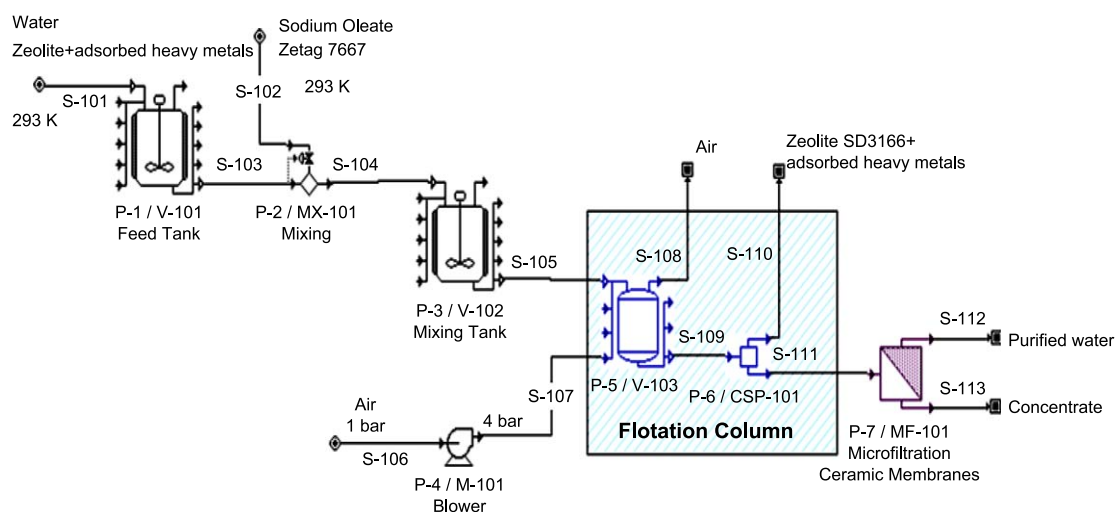


Fig. 4. Flowsheet used in the technico-economical study: sorptive flotation followed by microfiltration.

ins, oil and grease/floating materials and potentially applicable to semi-volatile organics and pesticides. Perhaps, an explanation for this statement is that the term “flotation” was there applied may be in the strict meaning of this operation, as it is known from mineral processing. An innovative treatment technology (as the EPA terms) is one that has been tested, selected or used for treatment of hazardous waste or contaminated materials but lack well-documented cost and performance data under a variety of operating conditions.

It has been reported that there is a gap between froth (i.e. dispersed-air) flotation and dissolved-air flotation; maybe even for historical reasons and this was the sub-theme of the Flotation conference by United Engineering Foundation held in Tahoe City, CA on May 2001. The feeling is that the “gap” mainly originates from the separate areas of flotation application, i.e. the separate traditions and the seldom interaction among them. But also the different aims (selective separation or not), difference in particles concentration, use or not of collectors and other chemical reagents (modifiers, frothers) for environmental reasons, etc. From an economic point of view, the things are completely different, too; as mineral processing is obviously economically attractive, while no one really wants to pay (at least too much) to treat the effluents (Matis et al., 2003).

4. Conclusions

It is believed that quite promising results were obtained in the present paper on the flotation recovery of copper ions from synthetic and real wastewaters. Three flotation techniques were applied: ion, precipitate and sorptive flotation by dispersed-air under appropriate conditions. The following copper recovery sequence was established for real effluents: ion flotation>sorptive flotation>precipitate flotation with the residual mean copper concentration was 0.10, 0.25, 60 mg/L, respectively.

These flotation techniques deserve wider attention for their successful industrial application; combining both the need for effluent treatment due to environmental reasons and, mainly, recovery of metal values that otherwise perhaps will be lost.

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