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An innovative procedure for gold recovery from Calcareous Sandstone Wadi Natash of Southeastern Desert, Egypt

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ABSTRACT

The calcareous sandstone of Wadi Natash of Southeastern Desert, Egypt has actually been subjected to several mineralization stages. These included several economic minerals of interesting metal values e.g. uranium, niobium, tantalum, zinc and copper besides gold. The present work takes advantage of the calcareous component of this ore material to form calcium sulfate by sulfuric acid treatment for gold recovery. Accordingly, while gold assay is as low as 1.7 ppm, it has been possible to be completely recovered by its surface adsorption upon calcium sulfate crystals that are in-situ formed at heat transfer surface at the top of the working slurry. It has thus been possible to recover gold from the working material to assay up to 0. 85% in the latter in a manner that a concentration factor of up to 5000 has been realized © 2014 Trade Science Inc. - INDIA

KEYWORDS

El Ghurfa;
Calcium sulfate;
Gold;
Wadi natash.

INTRODUCTION

Gold has actually been known and highly valued since prehistoric times and may even have been the first metal used by humans and was valued for ornamentation and rituals[1,2]. In nature, gold most often occurs in its native state though usually alloy with silver. Native gold usually contains 8-10% silver but often much more; alloys with a silver content over 20% are called electrum[2]. Gold abundance in the earth's crust is 0.002 per10^6 atoms of Si or else about 5ppb[3] while its economic abundance in the ore is today in the range of 0.1 to 0.2 oz /t i.e. 3.42 to 6.84 ppm, the latter thus represents a concentration factor of about 700-1400. However, deposits yielding grades to the fire assay which are as low as a 1/10th of those values are also exploited.

Approximately 60% of the gold mined today is held by governments and central banks and is actually considered as the most significant means of international payment[1]. Gold is the only metal that has a yellow color when massive and pure and such color is greatly modified by impurities e.g. silver lowering the tint while copper heightens it. Its electric conductivity is not as great as that of either copper or silver. If the electric conductivity of silver is rated at 100, gold is 76.7. Gold exceeds all other metals in malleability and ductility and can thus be beaten, when pure, into leaves one three hundred thousandth of an inch in thickness. The specific gravity of gold is 19.27 and in general liberated native gold can be recovered by gravity methods as long as the particle size is not too small. However, in the majority of cases, gold is in an extremely fine state and is even usually in the form of solid solution inclusion.

Gold can actually be recovered from its ores by one, or a combination of several methods that have been previously applied. According to[3], it has been indicated that although new processes are being proposed on a regular basis, there have in fact been no dramatic changes in the metallurgical techniques for gold extraction since the introduction of the cyanide process (cyanidation) by McArthur and Forrester in 1887[1,4,5] Previous techniques for gold recovery from its ores and which are classified in to the following major categories of commercially viable recovery processes can be summarized as follows:

1 Amalgamation (with mercury).
2. Gravity Concentration (using jogs, tables, spirals, Reichert cone, moving belt separator, etc.).
3. Flotation (as free particles or contained in base metal sulfide concentrates).
4. Pyrometallurgy (in the smelting and refining of base metal ores and concentrates).
5. Hydrometallurgy (direct cyanidation, cyanidation with carbon adsorption, heap-leach and chlorination-leach).
6. Refractory ore processing.
7. Alternative lixiviants.

By refractory ore processing, it is referred to the fact that such ores are those that do not allow the recovery of gold by standard gravity concentration or direct cyanide leaching. These ores include the very finely disseminated gold or else its presence in solid solution in sulfide matrix (mostly pyrite, pyrrhotite and arsenopyrite), the Au associated with tellurides ore contained in base in base metal sulfides of Pb, Cu, and Zn as well as those present in carbonaceous ores. In case of very finely disseminated Au or its presence in solid solution in sulfide matrix, the ore cannot practically be ground down fine enough to expose the Au particles. The objective of prior treatment for these ores (by roasting e.g.) is to remove enough of the sulfide so as expose at least a small portion of all Au particles is a manner to make them amenable to cyanidation. Concerning carbonaceous ores in which cyanidation will be followed by Au back adsorption onto the active carbon in the ore can be subjected to chlorination for carbon deactivation, roasting to burn a way carbon or else carbon-in-leach which introduces competing high activity carbon to preferentially adsorb Au that can be conveniently separated from the leach slurry.

Among the alternative lixiviants, thiourea leaching was developed as a potential substitution to cyanide leaching due to lower toxicity and greats rate of Au and Ag dissolution[6,7]. Other lixiviants have also been advantage include bromides (acid and alkaline), chlorides and thiosulfate. From solutions, Au recovery techniques include carbon adsorption Merrill-Crowe process using Zn dust to precipitate Au from cyanide solution, Electrowinning beside Ion exchange/Solvent Extraction

In Egypt a low grade Au mineralization has lately been discovered at Gabel El Ghurfa area which is situated at the eastern part of Natash volcanics, south eastern Desert, . Gabel El Ghurfa forms indeed a ring dyke (2km^2) with a diameter of 1.2 km and is mainly composed of normal and alkaline trachyte at the outer zone with high relief (49 Ma, by ^{40}Ar/ ^{39}Ar method). On the other hand, the inner zone of the ring (600 m in diameter) is mainly represented by Cretaceous Lower Nubia Sandstones (LNSS) that are extruded by minor trachyte plug. The LNSS are mainly composed of quartz arenite (at the base), greywacke, calcareous sandstone and conglomerate (at the top). Wadi Natash LNSS are actually of great economic value as they have been subjected to the several mineralization phases that are manifested in the presence of important metal values specially U, REEs, Zr, Y, Cr, Ba, Sr and Nb in the form of several economic minerals.

Accordingly, the Lower Cretaceous sandstones of Wadi Natash (Figure 1) are bearing several radioactive minerals (metaheinrichite, autunite, uranophane and uranothorite), niobate- tantalite (yttrocolumbite and yttrotantalite), base metals (gold, brass alloy and zinc), sulfides (argentite, pyrite, galena and hauerits), and accessories (zircon, monazite, fluorite, taenite, rutile and allanite). Interest of wadi Natash LNSS has been intensified due to the presence of several uranium minerals (75-195ppm U) beside the occurrence of native gold (1.5-8 g/ton) ; a matter which is considered a first record in Egypt[8].

Due to the extremely low grade of Au mineralization, an innovative procedure has actually been applied in the present work for its recovery. This procedure depends on the up on and pushing of Au particles when it would meet some in- situ calcium sulfate scales. The suggested procedure depend indeed on the fact that the solubility of all calcium sulfate forms decreases with increasing the temperature and this is the reason of scale

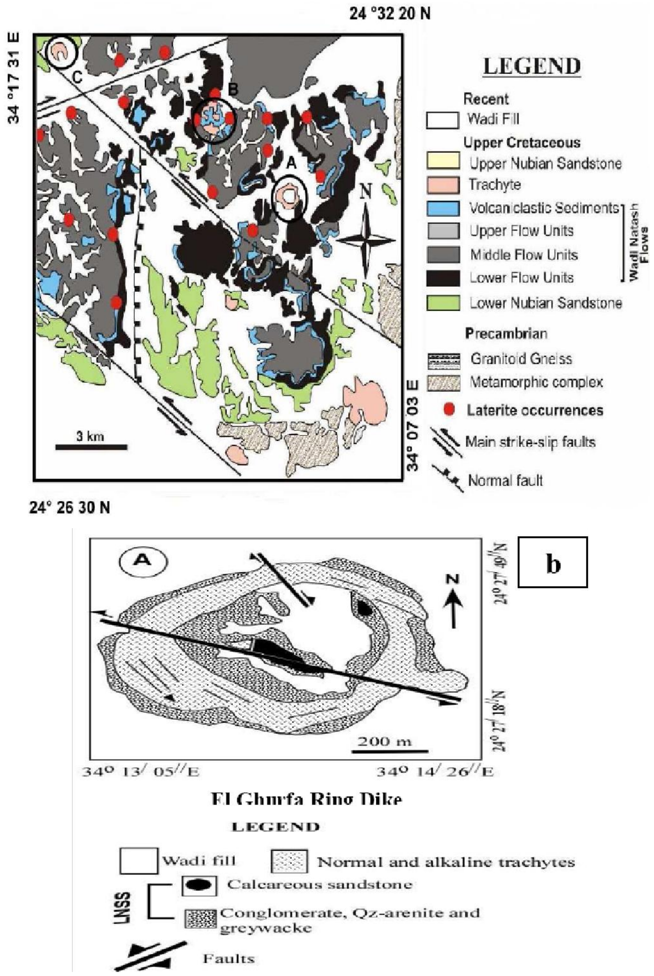


Figure 1 : Geologic map of Wadi Natash and Gabal El Ghurfa, Southeastern Desert, Egypt, (modified after Crawford et al, 1984 and Ibrahim, 2010).

formation at heat transfer surface.[9].

Calcium sulfate is indeed commercially used as the major component for plaster formation Hamdona and Al-Hadad (2007)[10] have indicated in this regard that in order to ensure adequate increase during the crystal growth of calcium sulfate dihydrate and its precipitation in turn, the crystal surfaces should be devoid of any metal ions which would hinder the required growth. Accordingly, this phenomenon has indeed been made use of in the recovery in native gold from its calcareous sandstone mineralization of Wadi Natash, To realize the objective, a representative sample of the latter assaying 1.7 ppm Au has been collected and was subjected to a chemical treatment that would result in the formation of calcium sulfate. This has successfully been achieved by reacting the working calcareous ore sample with sulfuric acid and heating the reaction medium at 100 °C whereby boiling and the resultant carbon dioxide would upwardly carry the extremely minute Au particles that have been liberated from the calcareous component of the working sample. In the meantime, the ascending Au particles would be adsorbed upon the formed calcium sulfate scales that are in-situ formed at heat transfer surfaces.

EXPERIMENTAL

Material characterization

A technological ore sample of Wadi Natash mineralized sandstone has been collected and properly ground to -60 mesh size. Quartering of the latter was performed to obtain a representative sample for the required analyses of the working ore material. This sample was then subjected to complete chemical analysis for its major oxides. Analysis of Au and several trace elements beside U, Th, Zr, Y, Cu and Zn has also been performed.

Experimental procedures

Sulfuric acid was used as a leaching reagent which in addition to its ability for dissolution of several metal values in the ore material would react with the calcium carbonate to form calcium sulfate. Some of the latter would be crystallized at heat transfer surfaces on the top of the slurry where the upwardly liberated minute Au particles would be adsorbed in a manner to hinder further crystallization. The formed crystals carrying the Au particle and which are floated would be helped through boiling and CO_2 evolution as previously mentioned. However, due to the exceedingly low assay of Au in the working ore material, it was found convenient to study the relevant factors after being enriched with a commercial sample of 21-kirat Au in a manner to become as high as 1%. After optimization of these factors (acid concentration, temperature, time and S/L ratio) two actual test was then performed using the optimum values upon a non-enriched ore sample wt of 1 kg(1.7mg Au)

Analytical procedures

Ore analysis

The complete chemical analysis of the major oxides was achieved using conventional analytical methods of Shapiro and Brannock (1962)[11]. In the latter, SiO_2, Al_2O_3, TiO_2 and P_2O_5 have been spectrophotometically analyzed while Na and K were determined by a flame photometry. Titration methods were used for Fe, Mg and Ca where as the loss on ignition (L.O.I) was gravimetrically determined. On the other hand, all the analyzed trace elements have been assayed using XRF. Concerning Au analysis it has been determined in the working technological sample by fire assay. The estimated error for major constituents is not more than ±1 %.

Control analysis

To follow up the efficiency of Au separation during optimization of Au experiments, it was found practical to filter the collected Au/$CaSO_4$ float samples followed by extensive washing of $CaSO_4$ through the paper. The remaining Au sample left behind was then weighed. In this regard, it is interesting to mention that the weight ratio of the floated $CaSO_4$ to its total formed amount has been about 3.5 % in the Au enriched ore material while it has been only 0.02 % in the natural ore material. Accordingly, the Au assay in the former attained about 30% while in the natural ore the Au assay in the floated $CaSO_4$ attained about 0.85%. Thus, the concentration factor of up to 5000 times has been realized in the natural ore.

Product analysis

Finally, the obtained gold products have qualitatively been analyzed using ESEM-EDX analysis and Microscopic Image 400µm.

RESULTS AND DISCUSSION

Material characteristics

The chemical analysis of the major constituent of the working technological w. Natash lower Nubia sandstone sample was found to be highly enriched in carbonate consistent as shown in TABLE (1). From the latter, it is obviously evident that besides a loss on ignition of up to 33 % and CaO of up to 38% indicating high carbonate content, the working material assays 20 % silica, 2 and 6.5 of Al_2O_3 and Fe_2O_3 respectively. The principal possible mineralogical composition has been calculated in the light of the chemical composition and has shown the presence of about 68% of the carbonate mineral calcite.

TABLE 1 : The chemical composition of the working technological ore sample from Wadi Natash LNSS

Component	wt.%	Component	wt.%
SiO_2	20.0	CaO	38.0
TiO_2	0.3	K_2O	0.1
Al_2O_3	2.0	P_2O_5	0.2
Fe_2O_3	6.5	Na_2O	0.2
MnO	0.6	L.O.I .(1000^0C)*	33.0
MgO	1.5	Total	102.4

*L.O.I. = loss on ignition

Another part of the working representative sample was subjected to X-ray fluorescence analysis for several trace elements using a Philips X-ray unit. These analyses (TABLE 2). have revealed the presence of interesting values of Ba, Zr and Sr; namely 693, 118, 339 beside 182 uranium and 1.7 ppm of Au respectively.

Optimization of the relevant factors (1%Au)

As mentioned above the optimization of relevant factors for upgrading Au from the working sample (which is quite low in Au assay) a part of the latter was enriched with a commercial sample of 21 kt of Au to assay up to 1%.

TABLE 2 : XRF analytical results of trace elements of the working technological ore sample from Wadi Natash LNSS

Elements	ppm	Elements	ppm	Elements	ppm	Elements	ppm
Ba	693	Nb	7	Sn	0.3	Cd	0.4
Cu	11	Sr	339	Be	1	Sb	0.1
Pb	7	U*	182	Sc	2	Bi	0.1
Zn	22	Th*	47	Ta	0.3	Hf	1
Ni	17	Cr	29	Cs	0.1	Li	9
Zr	118	Ga	3	Mo	3	Au	1.7
Y	33	V	48	Co	6		
Rb	8	W	1	As	2		

* Chemically analyzed.

Effect of sulfuric acid concentration

The effect of H_2SO_4 concentration upon Au recovery through its adsorption upon upwardly in- situ formed calcium sulfate was studied between 60 and 180 g/l, while the other experimental conditions were fixed at 20 min. agitation time, 100°C temperature and using a S/L ratio of 1/10. The extraction efficiency of upwardly collected Au upon in-situ formed calcium sulfate scales are given in TABLE (3). The latter indicate that the best conc. is 120 g H_2SO_4 /l where the recovered Au has attained 99%. It has to be indicated herein that under the experimental condition of using 120 g/l acid in a S/l ratio of 1/10, the $CaCO_3$ content of the ore sample (about 68%) has almost been completely converted to $CaSO_4$. The latter would precipitate in the reaction medium after saturating the aqueous medium. Scales of the latter would then be in-situ formed near the top of the reaction medium at heat transfer surface and where the liberated Au particles (original and added) would move upwardly by boiling and CO_2 effervescence to be adsorbed upon these scales. It has also to be mentioned that the formed scales were found to be attain about 0.35 g from each treated 10 g ore sample. In the latter, the Au assay from the added 1% of each input ore sample would approach about 30%. On other wards, a concentration factors of about 30 has been realized.

TABLE 3 : Effect of H_2SO_4 acid concentration upon Au adsorption efficiency upon in-situ formed calcium sulfate scales (20 min. agitation time at 100°C, S/l ratio 1:10,-60 mesh size).

H_2SO_4 concentration, g/l	Au adsorption efficiency,%
60	76
120	99
180	99

Effect of temperature

Three Au adsorption experiments upon in-situ formed calcium sulfate scales have been performed to investigate the effect of the reaction temperature in the range from room (about 25 °C) up to 90 °C. In these experiments, the other adsorption conditions were fixed at a H_2SO_4 acid concentration of 120 g/l, 20 min. agitation time and using a S/L ratio of 1/10. From the obtained data given in TABLE (4), in comparison to that obtained at 100 °C, it is clearly revealed that the working temperature is quite important to obtain a high adsorption efficiency of Au metal. Working at room temperature under the mentioned conditions did not result in more than 28 % Au recovery while at 90 °C, Au recovery has attained only 82 %. Further temperature increase to 100°C, increased the Au adsorption efficiency to 99%. It can thus be mentioned that the optimum Au adsorption temperature under the above mentioned conditions would be the boiling point (100°C).

TABLE 4 : Effect of the medium temperature on Au adsorption efficiency upon in- situ formed calcium sulfate scales (20 min. agitation time, acid concentration 120 g/l, S/l ratio 1:10,-60 mesh size).

Temp, °C	Au adsorption efficiency,%
25	28
70	43
90	82
100	99

Effect of agitation time

In a trial to study the effect of lowering the agitation time upon Au adsorption efficiency upon in- situ formed calcium sulfate scales from the working technological ore sample from Wadi Natash LNSS, an adsorption experiment was performed using only 10 minutes. The other adsorption conditions were fixed at 120 g /l H_2SO_4 acid concentration, a medium temperature of 100 ^{0}C and using a solid liquid ratio of 1/10. The obtained efficiency has revealed that Au recovery has been decreased to 90% while the adsorption efficiency of 99% occurs at an agitation time of 20 min. The formed in-situ calcium sulfate scales were also found to amount to about 0.35 g from each treated 100 g ore sample.

Effect of the solid/liquid ratio

It was interesting to explore the effect of the solid/liquid ratio upon Au adsorption efficiencies upon in-situ formed calcium sulfate from the working technological sample from Wadi Natash LNSS between S/L ratios of 1/5 and 1/30. In these experiments, the fixed adsorption conditions involved a H_2SO_4 acid concentration of 120g/l, an adsorption temperature of 100 ^{0}C for 20 min. agitation time. From the obtained adsorption efficiencies, it was found that almost complete Au adsorption efficiency has been achieved in the studied range of S/L ratios (1/5 to1/30). In the meantime it has also been found that the in-situ formed calcium sulfate scales has amounted to about 0.35 g from each treated 10g ore sample in all the tested S/L ratios.

From the above studied Au adsorption efficiencies from the working technological ore sample from W. Natash LNSS under different experimental conditions, it can be concluded that the optimum adsorption conditions would be summarized as follows:

H_2SO_4 acid concentration : 120g/l
Adsorption time : 20 minutes
Adsorption temperature : 100 °C.
Solid/liquid ratio : 10/50

Under these conditions, an amount of about 0.35 g Au bearing calcium sulfate scales has been obtained in a manner that Au assay has approached about 30%.

Application of Au adsorption from the non –enriched working ore sample

Using the above- studied optimum working conditions of Au adsorption from the enriched working technological ore sample (1% Au) ; namely H_2SO_4 acid concentration of 120 g /l, an ore ground to -60 mesh size a solid / liquid of 1/5 and boiled for 20 min., an adsorption experiment was made using 1Kg of the ore sample, however non-enriched with any commercial Au. From the obtained result, it was revealed that 0.2g in-situ formed calcium sulfate scales assaying 0.85 % Au has been obtained. Accordingly, a concentration factor of 5000 has actually been realized. The obtained relatively low calcium sulfate weight 0.2 might be due to the lesser S/L ratio used in this experiment. In the meantime, the ascending gold particles were found to be surface adsorbed the in-situ formed $CaSO_4$ (Figure 2). In the latter, native Au particles (1.7mg) from the working sample have been collected.

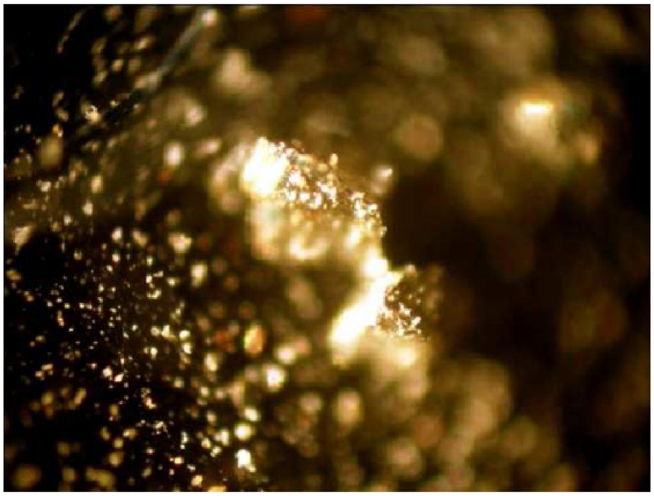
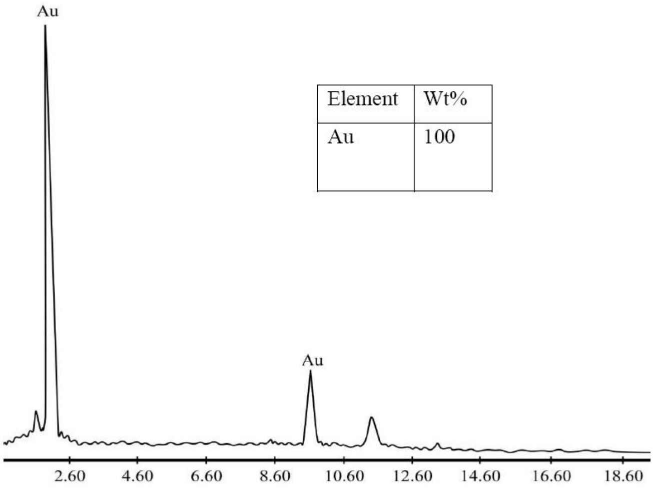


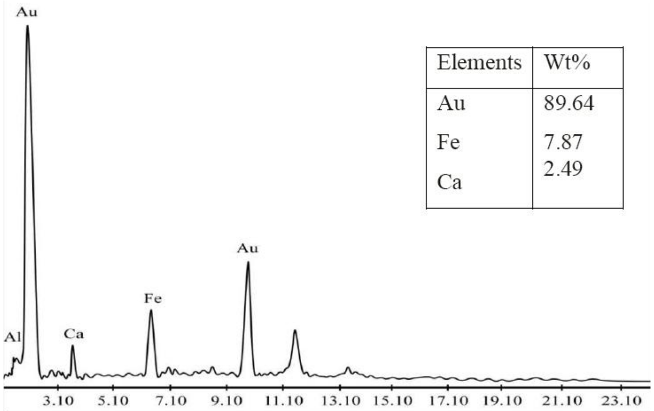
Figure 2 : photo of the native gold adsorbed upon surface of gypsum (400µm)

To recover the adsorbed Au from the calcium sulfate scales, two possible ways can be applied; the first one is to wash the calcium sulfate with a large amount of water up to 2 liters through the filter paper to leave behind the Au particles. To apply the second way of Au recovery, another application experiment was performed. However in the latter the obtained calcium sulfate scales were dissolved in aqua regia (3/1of conc. HCl /HNO_3) followed by iron cementation at a pH value of about 5.5 through water dilution. The two obtained Au products have then been analyzed by ESEM-EDX analysis where in the first way of Au recovery, Au of 100% purity was revealed Figure (3). In the second way using iron cementation, Au particles of less purity attained 89.6 % were obtained Figure (4). In the latter the excess iron beside some dissolved Ca has been found contaminating Au product. As a matter of fact, it



Element	Wt%
Au	100

Figure 3 : ESEM- EDX analysis of the native gold product after water washing of the calcium sulfate Au-carrier



Elements	Wt%
Au	89.64
Fe	7.87
Ca	2.49

Figure 4 : ESEM- EDX analysis of the gold product after iron cementation from aqua regia solution.

would be greatly advantageous if $CaSO_4$ scales carrying the gold particles and dissolved in dilute HCl instead of Au dissolution and cementation.

CONCLUSIONS

A successful innovative procedure for Au recovery has been applied upon calcareous sandstone of Wadi Natash of Southeastern Desert, Egypt. The new procedure involved Au adsorption upon a carrier of in-situ formed calcium sulfate scales. The studied optimum conditions involved ore ground to -60 mesh size treatment with 120 g H_2SO_4/l concentration in a solid / liquid ratio of 1/5 at 100°C for 20 min. The in-situ formed calcium sulfate scales have been formed on the top of the slurry at heat transfer surface. Under these conditions the adsorption efficiency of gold was found to attain 99% and pure gold products have been prepared by different ways.

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