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# Flotation Mechanisms of Boron Minerals

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## ABSTRACT

The development of reagent strategies for the flotation of boron minerals requires an understanding of flotation chemistry of reagent/mineral interactions. The floatability of a typical boron mineral, colemanite, was investigated in a microflotation cell by using anionic and cationic surfactants as collectors and tannic acid as a depressant. The results obtained with zeta potential measurements together with flotation tests reveal that colemanite is floatable with both anionic and cationic surfactants at its natural pH of 9.3. While the floatability of colemanite with anionic surfactants decreases with increasing pH, that with a cationic surfactant exhibits a maximum at pH 10.2, indicating the major role of electrostatic interactions in the system.

## INTRODUCTION

Borates and their products have become essential ingredients used in various industries with an annual world consumption of over one million tons of equivalent $B_2O_3$. Although more than 150 boron minerals have been identified, only about a dozen of them are found in commercial deposits and less than half of these are considered ore (1). The most important boron minerals of commercial importance are borax ($Na_2B_4O_7 \cdot 10H_2O$), colemanite ($Ca_2B_6O_{11} \cdot 5H_2O$), ulexite ($NaCaB_5O_9 \cdot 8H_2O$), and kernite ($Na_2B_4O_7 \cdot 4H_2O$).

The concentration of boron minerals in a deposit requires evaporation of a boron-rich solution to a point of borate precipitation. Diagenesis plays an important role whether a deposit is commercially viable because it is a major parameter dictating the water content of the mineral and, in turn, the mineralogical composition of the deposit. Borax and colemanite constitute a set of two extrema exemplifying highly soluble and sparingly soluble boron minerals, respectively.

Turkey has the largest borate deposits in the world, with reserves of over one billion tons. Development activities in the last 30 years have also made Turkey the second largest borate producer and the premier exporter. The Turkish borate deposits occur in lenticular beds of moderately deformed sedimentary rocks which were laid down during a late Tertiary tectonic-volcanic episode (2). The boron deposits in Turkey are located in the western part of the country and consist of mainly colemanite, borax, and ulexite.

Beneficiation of these minerals usually involves a preconcentration step to separate the undesirable clay minerals in some form of scrubbing operation. However, since boron minerals are rather friable, they tend to be found in the finer fractions and consequently may be lost in the tailings. The fines, mostly below 0.2 mm in size, are often discarded as waste from commercial operations even though they often contain large amounts of valuable boron minerals.

Recovery of these fines requires an advanced beneficiation method such as flotation. Although flotation is applied in the United States, very little information exists on its technology and "know-how." Borax is reportedly floated from sylvite with oleic and naphthenic acids plus xylene, turpentine, and kerosene (3). Colemanite decomposed to boric acid by sulfuric acid has been shown to become naturally hydrophobic and floatable with a frother alone (4). Yarar investigated the floatability of colemanite in the presence of commercial alkyl sulfonates, naphthenic acid, and kerosene in different combinations (5). The same author later discussed the mechanisms of calcite–colemanite separation by anionic surfactants (6). Ayok and Tolun (7) studied the role of various complexing agents, e.g., polyols used in the solvent extraction of boric acid, in colemanite flotation. Polyols alone and particularly in the presence of alkyl sulfonates were found to improve flotation recoveries.

The flotation chemistry of boron minerals has been very sparingly reported in the literature. The difficulty arises from the fact that boron minerals exhibit a range of solubilities, and the presence of different ions, e.g., Na, Ca, and Mg in the lattice structure of boron minerals, impart different characteristics to these minerals. A successful separation of boron minerals from the gangue, or from each other, necessitates development of suitable reagent strategies. This emphasizes the need for fundamental knowledge on the flotation chemistry of boron minerals.

It is the aim of this study to understand the flotation properties of a typical boron mineral, colemanite, in the presence of anionic and cationic reagents. Microflotation tests and zeta potential measurements on pure minerals have been conducted to elucidate the interfacial mechanisms governing the flotation of this boron mineral.

## EXPERIMENTAL

### Materials

Colemanite crystals were handpicked from the Bigadic Deposit of Turkey. The samples were first crushed with a hammer and then by an agate mortar and pestle to obtain a sample of $150 \times 210$ μm ($65 \times 100$ mesh) in size for flotation tests. The finer fractions (−150 μm) were used for zeta potential measurements. The assay of both samples showed purity of greater than 98% (36.10% $B_2O_3$).

The anionic surfactants, petroleum sulfonate (Dodiflood V3622; MW, 385), α-olefin sulfonate (Hostapur OS; MW, 330), and a cationic surfactant (Flotigam T) were supplied by Hoechst Chemical Company. The depressant, tannic acid, was of Merck quality. All solutions were prepared using distilled water.

### Methods

Flotability of colemanite was determined using a 150-mL column cell (25 × 220 mm) with a fine frit and magnetic stirrer. One gram of sample was used in each microflotation test. The samples were conditioned in 150 mL of a solution containing the desired reagent, i.e., sulfonates, Flotigam T, and tannic acid, for 30, 10, and 10 minutes, respectively. Colemanite samples were floated for 1 minute using nitrogen at a flow rate of 50 $cm^3$/min. The flotation tests were carried out by an electronically controlled microflotation apparatus designed and constructed in our laboratories. A schematic diagram of the circuitry together with the experimental design is shown in Fig. 1.

The zeta potential of colemanite was measured by means of a Zeta Meter 3.0 equipped with a microprocessor unit. The procedure for zeta potential measurements is described elsewhere (8). Since colemanite is a slightly soluble mineral, the solid-to-liquid ratio was found to exert a major influence on zeta potential measurements. While samples containing less than 0.5 g/100 mL produced negative zeta potentials, positive zeta potentials were measured above this solids concentrations. The zeta potentials became constant above approximately 1 g/100 mL, which was used in all subsequent measurements. All measurements were carried out at ambient temperature (22 ± 1°C).

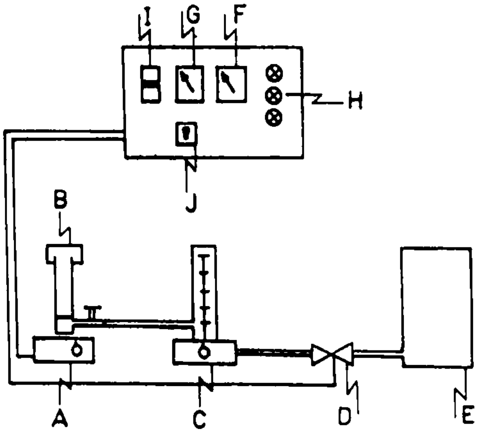

FIG. 1 Electronically controlled experimental set-up used in microflotation tests: (A) magnetic stirrer, (B) flotation cell, (C) flowmeter, (D) flow control valve, (E) nitrogen cylinder, (F) time relay 1, (G) time relay 2, (H) signal lamps, (I) fuse, (J) start button.

## RESULTS AND DISCUSSION

### Equilibrium Kinetics

Colemanite is composed of $[B_3O_4(OH)_3]_n^{2n-}$ polyanions or equivalent form $[B_4O_7{\cdot}2H_2O]^{2-}$ groups (9). The polymeric structure of colemanite is formed by B—O—B bridges which are joined laterally to form sheets by calcium anion bonding. The sheets are then held together by weak hydrogen bonds involving both water molecules and hydroxyl groups (10). A simplified schematic structure of colemanite is presented in Fig. 2 (11).

Figure 3 illustrates the effect of mixing time as a function of pH on dissolution of colemanite. The mixing tests were performed with a mag-

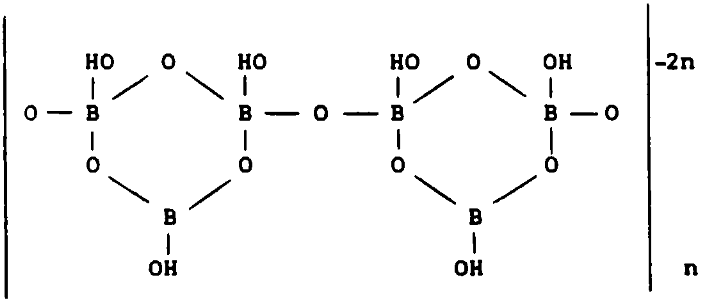

FIG. 2 Schematic structure of colemanite.

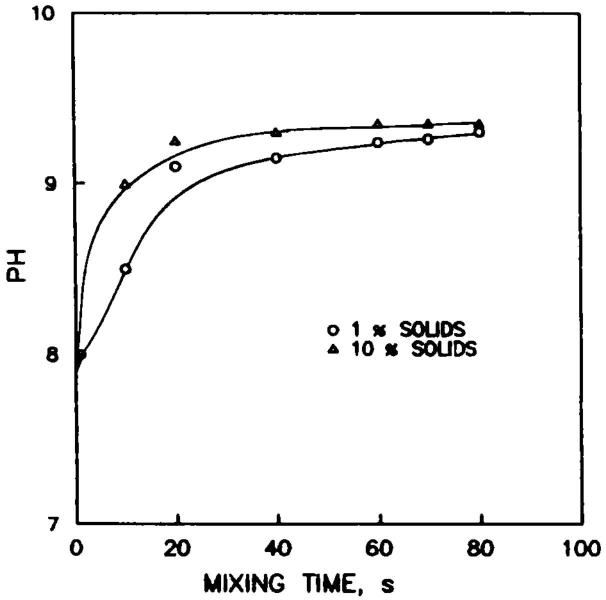

FIG. 3 Effect of mixing time as a function of pH on dissolution of colemanite.

netic stirrer using a 1-inch long spin bar. The stirring speed was selected such that all colemanite particles were suspended in the solution. The results reveal that colemanite suspensions of up to solid-to-liquid ratios of 0.1 approach a final pH of 9.3 in less than a minute. This is attributed to the amphoteric nature of colemanite in undergoing acid–base reactions in the vicinity of minimum solubility. All solutions having initial pH values between 3 and 10 resulted in final pH values of approximately 9.3.

As colemanite is a boron mineral containing $Ca^{2+}$ in its lattice structure, it reacts with $CO_2$ in the atmosphere as follows (12, 13):

$$CO_2 + H_2O \rightleftharpoons H_2CO_3 \quad (1)$$

$$H_2CO_3 + H_2O \rightleftharpoons H_3O^+ + HCO_3^- \quad (2)$$

$$2CaO \cdot 3B_2O_3 \cdot 5H_2O + 4H_3O^+ \rightleftharpoons 2Ca^{2+} + 6H_3BO_3 + 2H_2O \quad (3)$$

and the overall reaction is

$$2CaO \cdot 3B_2O_3 \cdot 5H_2O + 4CO_2 + 6H_2O \rightleftharpoons 2Ca^{2+} + 6H_3BO_3 + 4HCO_3^- \quad (4)$$

and in the absence of $CO_2$:

$$Ca_2B_6O_{11} + 11H_2O \rightleftharpoons 2Ca^{2+} + 4B(OH)_4^- + 2B(OH)_3 \qquad (5)$$

Based on Reaction (5), the colemanite supernatants should contain approximately 1 g/L borate and boric acid, which is close to its reported solubility of 0.8 g/L (6).

## Electrokinetic Measurements

Sparingly soluble minerals such as colemanite will release a number of ions into solution. These ions will be either produced at the solid/liquid interface or may form in solution and subsequently adsorb on the solid in amounts proportional to their concentrations. The variation of zeta potentials of colemanite with pH is presented in Fig. 4. The isoelectric point (iep) of colemanite in the presence of $2 \times 10^{-3}$ M NaCl was determined to be approximately 10.5, in agreement with the reported value of 10.7 by Yarar (6). The potential-determining ions for colemanite are the lattice components of colemanite, $Ca^{2+}$, and borate $B_4O_7^{2-}$ (6). In addition, similar to calcite, $H^+$ and $OH^-$ ions also play a major role in estab-

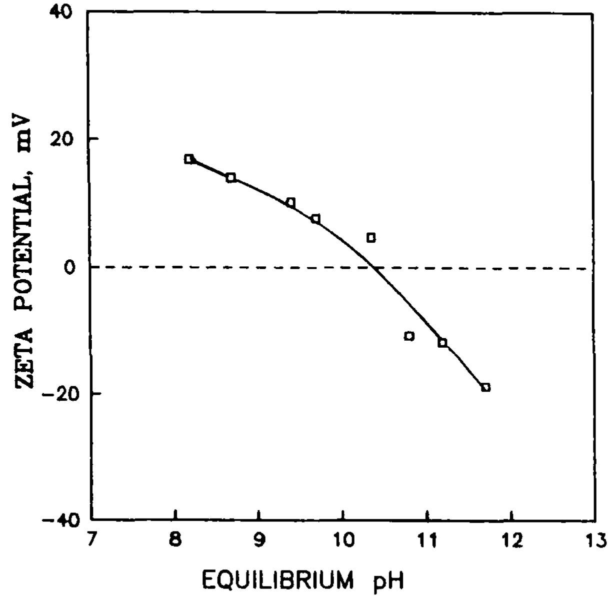

FIG. 4 Variation of zeta potential of colemanite versus pH.

lishing the solution equilibrium because they are in equilibrium with $CO_3^{2-}$ and $HCO_3^-$.

## Flotation of Colemanite

The floatability of colemanite with two different anionic surfactants, petroleum sulfonate and α-olefin sulfonate, is presented in Fig. 5 as a function of their concentrations. Both surfactants float colemanite similarly at concentrations above 0.002 g/L and yield plateau values at about 0.009 and 0.02 g/L, respectively. The better floatability of colemanite with petroleum sulfonate can be ascribed to its higher molecular weight and the corresponding hydrocarbon chain length. Considering the plateau values, colemanite floats at concentrations five times lower than calcite, a similar salt-type mineral (14).

The data presented in Fig. 6 exhibit flotation recoveries of colemanite versus equilibrium pH. The data clearly show that the extent of flotation recoveries with petroleum sulfonate is dependent upon the pH. Flotation gradually decreases with increasing pH and is very low at the iep, indicating that the interaction of anionic sulfonate with the positively charged colemanite surface is mainly governed by electrostatic interactions. Flota-

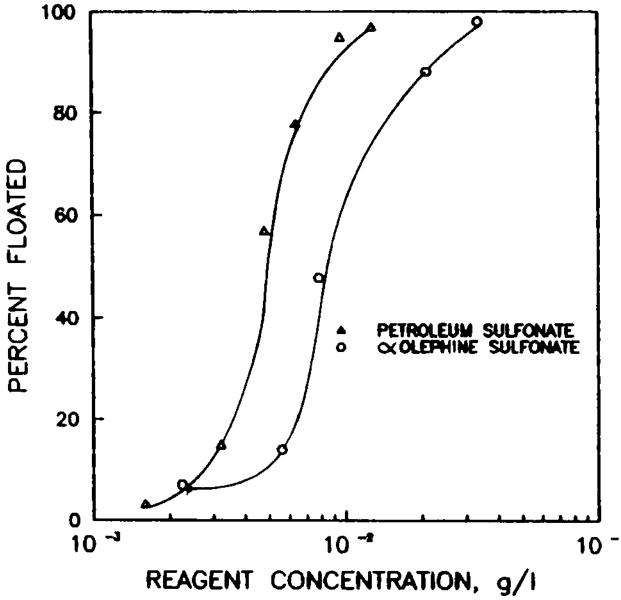

FIG. 5 Floatability of colemanite in the presence of anionic surfactants.

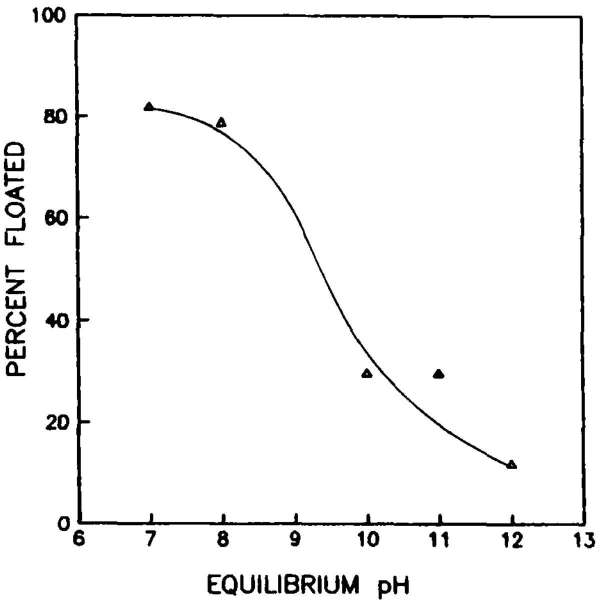

FIG. 6 Flotation recoveries of colemanite as a function of pH using 0.005 g/L petroleum sulfonate.

tion continues to occur until the positive charges cease to exist. A salt-type mineral such as colemanite is very much more sensitive to dissolution below its natural pH. Dissolution of colemanite starts below pH 9 and continues rather drastically below pH 7. Since it is difficult to maintain the pH below 7, flotation reagent strategies should be considered at or above its natural pH for practical applications.

Flotation of colemanite with a cationic surfactant (aliphatic primary amine acetate) is shown in Fig. 7. This particular amine has a hydrocarbon chain averaging 17 $CH_2$ groups as opposed to petroleum sulfonate which has, on average, 13 $CH_2$ groups plus a benzene ring. Thus, the flotation recoveries with amine at pH 9.3 occur at concentrations lower than that with sulfonate. Figure 8 presents the effect of pH on the flotation recoveries of colemanite in the presence of amine. Flotation exhibits a maximum at pH 10, which corresponds to the formation of ion molecular complexes $(RNH_2{\cdot}RNH_3)^+$ (15). The pH of maximum flotation is also close to the iep. Flotation, however, decreases both above and below the iep. Below the iep, the colemanite surface becomes increasingly positive and consequently is not conducive to amine adsorption. Above the iep, although the surface becomes negatively charged with increasing pH, the decrease

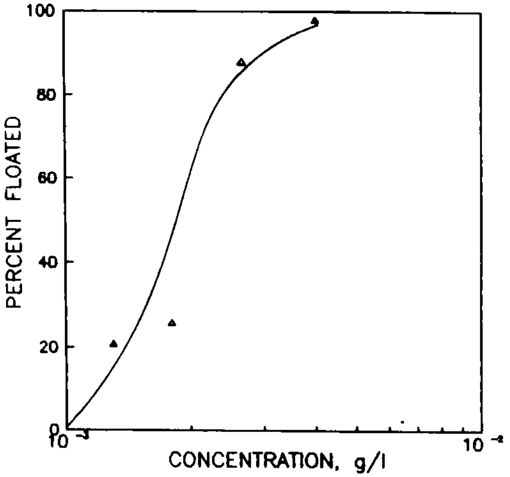

FIG. 7 Floatability of colemanite with a cationic surfactant (Flotigam T).

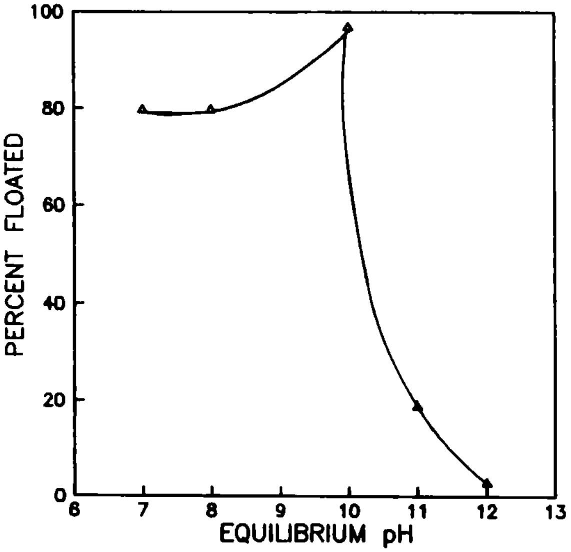

FIG. 8 Effect of pH on flotation recoveries of colemanite using 0.004 g/L cationic surfactant.

in the amount of ion molecular complexes and precipitation of the neutral amine form contribute to the decrease observed in flotation recoveries. The net effect appears to favor the latter two mechanisms. The p$K_b$ value of amine is 10.63 (15). At pH 10.2, the point of maximum flotation recovery obtained in Fig. 8, the amine molecule ionizes as

$$RNH_3^+ + OH^- \rightleftharpoons RNH_2 + H_2O \qquad (6)$$

At this pH, $RNH_3^+$ (62%) and $RNH_2$ (38%) are present, and the former decreases rapidly with increasing pH (16, 17). The adsorption mechanism of amine onto colemanite, based on the formation of ion molecular complexes, is illustrated in Fig. 9.

Selective flotation of colemanite from its associated gangue minerals, e.g., clays, may in some cases necessitate depression of colemanite. Such a depression can be achieved through the use of depressant agents such as tannic acid. Figure 10 shows the effect of tannic acid on the depression of colemanite. Evidently, colemanite is fully depressed at tannic acid concentrations above 0.01 g/L. The proposed depression mechanisms of tannin on calcite are direct Ca—O bonding, $Ca^{2+}$ activation, hydrogen bond-

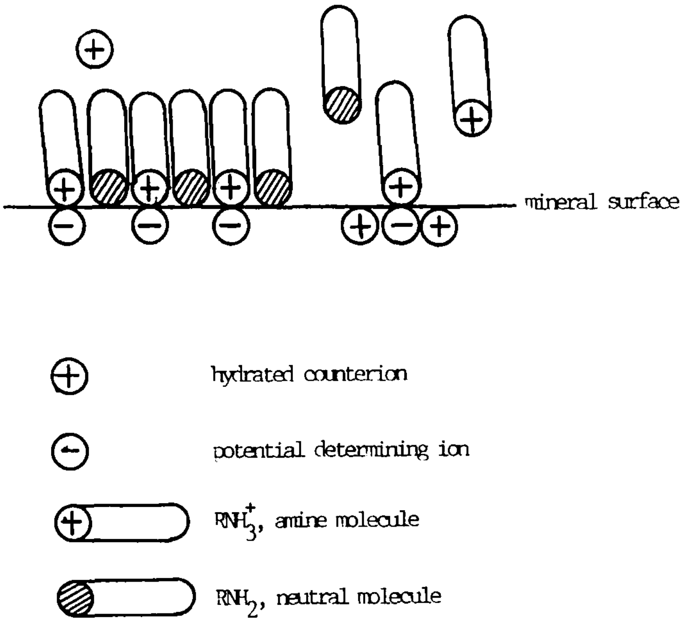

FIG. 9 A schematic illustration of the adsorption mechanism of amine onto colemanite.

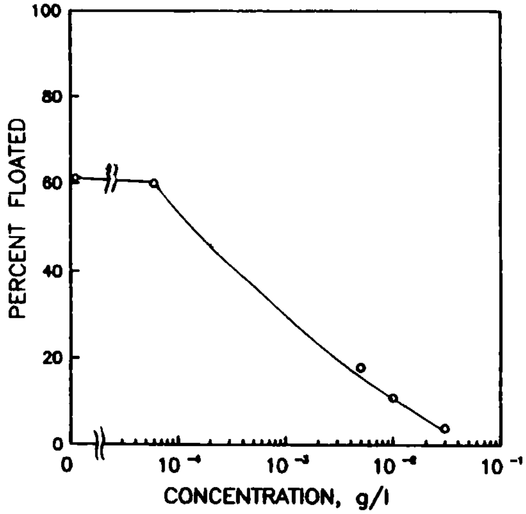

FIG. 10 Flotation recoveries of colemanite in the presence of a depressant, tannic acid, at natural pH.

ing, and electrostatic attraction (18). Since colemanite is a salt-type mineral like calcite, it may experience all the mechanisms proposed above.

Adsorption of sulfonate and amine on colemanite is being studied in order to further identify the interfacial reactions involved in the flotation of boron minerals.

## CONCLUSIONS

1. Colemanite undergoes acid–base reactions in the vicinity of pH 9.3. The isoelectric point of colemanite, as measured by the electrophoresis technique, is 10.5. The potential-determining ions for colemanite are $Ca^{2+}$, $B_4O_7^{2-}$, $H^+$, $OH^-$, $CO_3^{2-}$, $HCO_3^-$.

2. The anionic surfactants (petroleum sulfonate and α-olefin sulfonate) and the cationic surfactant (Flotigam T) float colemanite similarly.

3. Flotation of colemanite with petroleum sulfonate shows a decrease with increasing pH, indicating the role of electrostatic interactions in the system.

4. Flotation of colemanite with amine exhibits a maximum at pH 10 where the maximum amounts of ion molecular complexes form. Flotation then decreases due to precipitation of amine above this pH.

5. Tannic acid is an effective depressant for colemanite. It depresses colemanite at concentrations as low as 1 g/L.

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