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Specific Cation Effect on the Flotation of Graphite

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Abstract: Inorganic electrolytes are assumed to significantly impact the flotation performance of graphite resources; however, the underlying mechanism is still unclear. In this work, the effect of three inorganic salts, including KCl, MgCl₂, and AlCl₃, was studied on the flotation of graphite. Floation results indicated significantly increased graphite recovery with the addition of KCl regardless of pulp pH. MgCl₂ improved the flotation performance under acidic and slightly alkaline conditions, while AlCl₃ had a better activation on graphite flotation under strong acidic and alkaline conditions. Contact angle and Zeta potential results confirmed that electrolytes substantially reduced the absolute value of surface charge and the hydration of graphite surface, thus improving the hydrophobicity. Froth stability studies indicated that multivalent Al³⁺ and Mg²⁺ ions exhibit superior foaming performance than K⁺ ions and contribute to more stable and abundant foam. Additionally, these salt ions increased the surface tension and prevented bubble coalescence, contributing to nanobubble formation. Therefore, adding MgCl₂ and KCl is of great significance for improved graphite flotation under neutral conditions.

Keywords: graphite; flotation; specific ion effect; kerosene; foam stability

1. Introduction

Froth flotation is one of the most commonly used methods for the beneficiation of natural graphite resources [1–4]. In graphite flotation, hydrophobic particles are selectively captured and transported by rising air bubbles, leaving hydrophilic gangue minerals in the suspension and discharging as tailings [5]. Therefore, bubble plays an indiscernible role in mineral flotation. However, the foam is typically in a meta-stable state in water [6,7], and many factors affect its stability, such as the surface charge of the liquid film, viscosity, and surface tension of the solution [8–10]. Surface-active reagents, such as collectors and frothers, are usually added to the slurry to enhance the hydrophobicity of graphite particles and modify the properties of the air-water interface [11,12]. Unlike surface-active surfactants, inorganic salt ions have no surface activity, but some can also effectively inhibit the coalescence of the bubble and significantly impact the flotation performance [13–16].

Although fresh water is usually used in the flotation process, it is inevitable to accumulate complex dissolved solutes from continuous solid feeding, which can seriously shape the flotation outcome [17]. In addition, many mining operations are often located near oceans and salt lakes, with limited access to fresh water [18–20]. The demand and shortage of water for factories in these areas make salt flotation the only sustainable solution. Therefore, it is of practical importance to investigate the role of dissolved electrolytes in mineral flotation.

Studies on flotation in seawater [15,19–21] and concentrated solutions [18,22] have been reported for decades. Table 1 summarizes recent studies on the flotation of naturally hydrophobic minerals, including coal, chalcopyrite, molybdenite, and pyrite, in the presence of dissolved salt ions. It was suggested that some inorganic salts can inhibit
bubble coalescence and retard the drainage between liquid films [23]. G.Bournival et al. [24] reported that NaCl in a higher concentration range (0.1 mol/L ~0.5 mol/L) had a pronounced inhibition effect on bubble coalescence in flotation. Moreover, fine-grained mineral particles are thermodynamically unstable and have a large specific surface area. Increasing the concentration of these cations would compress the electrical double layer around the particles [21,25]. Agglomeration easily occurs in aqueous solutions for some natural hydrophobic minerals, such as coal [26,27] and graphite [28]. In coal flotation, the saline water would increase the amount of froth and accelerate the settling of particles that detached from the froth [29]. Paulson O. et al. [30] studied graphite flotation in different electrolyte solutions. The results showed that adding electrolytes could compress the electric double layer on the particle surface and effectively reduce the electrostatic repulsion between particles, thus promoting flocculation formation and improving the flotation. It should be noted that the activation and inhibition of these ions are strongly pH-dependent, especially for the multivalent ions [31]. Under alkaline conditions, divalent cations (Ca2+ and Mg2+) could significantly decrease mineral surfaces’ hydrophobicity and reduce the probability of bubble-particle attachment (leading to reduced recovery). While the impact of salt ions on mineral flotation has been confirmed universal, few studies could be found in the flotation of graphite.

### Table 1. The effects of cations on the flotation process of typical hydrophobic minerals [29,31–36].

| References          | Cations | Minerals                  | Conclusions                                                                 |
|---------------------|---------|---------------------------|-----------------------------------------------------------------------------|
| Kurniawan et al.    | Na+, Mg2+ | Coal                     | Mg2+ showed a greater flotation improvement compared to Na+. Increasing the Mg2+ concentration decreased the bubble size, which, in turn, increased the coal flotation kinetics and recovery. |
| Ozdemir et al.      | Na+, K+, Mg2+, Ca2+, La3+ | Coal and graphite          | The highest recoveries were obtained with Mg2+ and the lowest with Na+. Divalent ions were more effective than monovalent ions in the flotation of heat-treated coals in salt solutions. Only divalent ions of Ca2+ and Mg2+ significantly compressed the double electrical layer and enhanced the attachment between bubbles and coal particles. |
| Zheng et al.        | Na+, Mg2+, Ca2+ | Lignite                | At pH 11, both the molybdenite and chalcopyrite surfaces became hydrophilic due to the presence of Mg(OH)2 on the mineral surfaces. The kerosene-Mg(OH)2 aggregate prevented the adsorption of kerosene on the mineral surfaces. |
| Suyantara et al.    | Mg2+    | Molybdenite and chalcopyrite | Both Mg2+ and Ca2+ significantly reduce the floatability of chalcopyrite and molybdenite. Mg2+ exerts a more substantial effect than Ca2+ owing to the adsorption of Mg(OH)2; precipitates on the mineral surfaces. |
| Hirajima et al.     | Mg2+, Ca2+ | Molybdenite and chalcopyrite | Compared to Na+ and Mg2+, Al3+ could significantly change both minerals’ surface properties, relatively improved pyrite’s floatability, and decreased chalcopyrite recovery. Adsorption of Al(OH)3 on the minerals surface and the collector-Al(OH)3 aggregate could explain these variations. |
| Yang et al.         | Na+, Mg2+, Al3+ | Chalcopyrite and pyrite   |                                                                                     |

This paper aims to better understand the flotation of graphite in the presence of inorganic salts, including potassium chloride (KCl), magnesium chloride (MgCl2), and aluminum chloride (AlCl3). Surface tension and foam stability analysis were employed to study the effect of electrolytes on the properties of air bubbles. Contact angle and zeta potential were measured to investigate the surface properties of graphite particles as a function of different salt ions. Our results provided valuable insights into the development of salt-concentrated graphite flotation toward reduced reagent consumption.

### 2. Materials and Methods

#### 2.1. Materials and Reagents

The graphite sample, with a particle size fraction of ~45 μm ~ +38 μm, was obtained from Furunda Co., Ltd (Qingdao, China). It was purified with 1 mol/L HCl solution and repeatedly washed with deionized water to remove chemical reagents. X-ray diffraction (XRD) (D/MAX-RB, Rigaku, Japan) and X-ray fluorescence (XRF) (Zetium, Panalytical, Netherlands) analyses were used to determine the mineralogical and chemical compositions of the
sample, and the results are shown in Figure 1 and Table 2, respectively. All diffraction peaks are attributed to the graphite carbon, indicating a highly purified graphite sample. The main impurities are SiO$_2$, Al$_2$O$_3$, and MgO, with the contents of 0.21%, 0.18%, and 0.16%, respectively. The fixed carbon (FC) content of 99.37% was analyzed using the Chinese Standard GB/T3521-2008, as also reported in our previous studies [37,38].

The inorganic salts KCl, MgCl$_2$, AlCl$_3$, and pH regulators NaOH and HCl were all analytical grade, purchased from Sinopharm Chemical Reagent Co., Ltd, China. The collector kerosene and frother terpenic oil were obtained from Kermel Chemical Reagent Co., Ltd, Tianjin, China. All chemicals were directly used without further purification, and deionized water with a resistivity of 18.25 MΩ·cm was used in this work.

![Figure 1. XRD pattern of the graphite sample.](image)

| Composition | SiO$_2$ | Al$_2$O$_3$ | MgO | CaO | Fe$_2$O$_3$ | SO$_3$ | Cl | FC |
|-------------|---------|-------------|-----|-----|-------------|-------|----|----|
| Content / wt% | 0.21 | 0.18 | 0.16 | 0.04 | 0.02 | 0.01 | 0.01 | 99.37 |

2.2. Froth Flotation Tests

The single graphite mineral flotation test was carried out in a 1 L RK/FD flotation cell (Wuhan Rock Crush & Grand Equipment Manufacture Co., Ltd, China). For each test, 60 g of graphite sample was added into deionized water for 1 min at an agitation speed of 2060 rpm at room temperature. NaOH solution (0.1 M) or HCl solution (0.1 M) were added for pH adjustment when necessary. The inorganic salt solution, collector kerosene, and frother terpenic oil were added into the slurry in sequence with 3 min condition time, respectively. After that, the aeration (with a constant airflow rate of 80 cm$^3$/min) and flotation were performed for 4 min. The flotation recovery was determined by calculating the mass fractions of both floated and un-floated products. Each test was triplicated, and the mean value was recorded for plotting.

2.3. Contact Angle Measurement

The sessile drop method was applied to measure the contact angle of graphite particles. In detail, a certain amount of graphite powder was mechanically compressed to a pellet (Φ = 12 mm × 2 mm). Then a droplet was introduced using a microsyringe and approached the pellet surface. The contact angle of the graphite surface was captured with a CCD camera and measured using the ImageJ software. Each sample was repeated three times, and the average value was selected for comparison.

2.4. Zeta Potential Measurement

The zeta potential of the graphite surface was measured using a 90Plus Zeta Size Analyzer. Specifically, 6 mg of graphite sample (particle size fraction of ~3 μm) was processed with 100 mL water and conditioned with desired electrolytes before adjusting to
different pH conditions. After ultrasonic treatment for 20 min, a small amount of upper suspension was subjected to electrophoretic measurement under ambient temperature. Each sample was measured five times to yield the average values.

2.5. Surface Tension Measurement and Foam Property Tests

The surface tension of the aqueous solution was measured using a K100 surface tensiometer (KRÜSS GmbH, Germany). Briefly, desired electrolytes were added into the solution and fully dispersed with the help of ultrasonic treatment. Then the surface tension was measured by a platinum ring method. The foam properties were analyzed using a self-made glass tube, as demonstrated in Figure 2. A fine frit (Φ = 10 μm–15 μm) is incorporated on the downside of the tube (45 mm in diameter). 20 mL of the desired solution was added into the tube first. After that, aeration was provided to generate multiple bubbles with a constant airflow rate of 180 L/min for 2 min. The foam height, h, was recorded to indicate the foaming ability immediately after closing the gas inlet valve, and the half-life time of the foam, t (the time required for the foam height to decrease to h/2), was calculated to characterize the foam stability.

![Figure 2. The illustration of the glass tube for foam properties analysis.](image)

3. Results

3.1. Effect of Salt Ion Concentration on Graphite Flotation

The flotation of graphite in the presence of KCl, MgCl₂, and AlCl₃ was conducted at pH = 6, pH = 6, and pH = 3, respectively, to investigate the effect of inorganic salt ion concentration on graphite flotation recovery. Note that the selection of pH 3 for AlCl₃ is mainly to avoid the hydrolysis of Al³⁺. Other factors, such as the dosages of the collector (280 g/t) and frother (133 g/t), were kept constant. Figure 3a shows the flotation recovery of graphite with different salt addition.

It is generally observed that all three salt ions significantly improve graphite flotation recovery, with the enhancing ability following the order of AlCl₃ > MgCl₂ > KCl. The flotation recovery of graphite is 60.44% in the absence of electrolyte. As the cation concentration increases to 0.07 mol/L, the maximum recovery of graphite with the addition of KCl, MgCl₂, or AlCl₃ reaches 84.54%, 94.82%, or 95.89%, respectively. Further increasing the electrolyte concentration shows an indiscernible change in the flotation performance.

Figure 3b shows the flotation recovery of graphite as a function of different pH conditions in the absence and presence of electrolytes. Note that the concentrations of KCl, MgCl₂, and AlCl₃ were determined to be 0.01 mol/L, 0.02 mol/L, and 0.01 mol/L, respectively. The graphite flotation recovery without electrolytes shows a slight decrease from around 68% to 60% as the solution changes from pH 2 to 12. Despite a similar decreasing trend, an activated flotation of graphite by KCl was constantly observed in the
whole pH range. However, more complicated cation effects of MgCl₂ and AlCl₃ were observed under different pH conditions. Specifically, when MgCl₂ is added, the flotation recovery of graphite gradually increases from around 60% to nearly 85% as the solution pH increases from 2 to 8. Further increase in the pulp pH dramatically deteriorates the flotation. The flotation recovery plunges to almost 0 when the pH is higher than 11, indicating a complete inhibition effect of MgCl₂ on graphite flotation at higher pH conditions. When it comes to AlCl₃ solution, a substantial inhibition effect is obtained at the pH range of 4–6, with the lowest flotation recovery of just 20%. As a result, KCl enhances the graphite flotation regardless of the solution pH. MgCl₂ has an activation effect on graphite flotation when the pulp is acidic or weakly alkaline. AlCl₃ can promote graphite flotation under strong acidification and alkaline conditions.

Apart from enhancing flotation recovery, it was also observed that the addition of inorganic ions could improve the flotation kinetics. For example, Figure 3c compares the graphite flotation with different scarping times in the absence and presence of MgCl₂ under neutral pH conditions where good flotation performance was expected.

With the increase in foaming time, the flotation recoveries show an upward trend. Compared to the flotation without MgCl₂ addition, the flotation recoveries with MgCl₂ are constantly 10%–15% higher with the same scarping time. In addition, the flotation recoveries of scarping for 3 min account for 88.98% (without MgCl₂) and 96.52% (with MgCl₂) of those scraped for 4 min, respectively. Therefore, it is evident that the addition of MgCl₂ could not only improve the flotation recovery but also enhance the flotation kinetics of graphite.

![Figure 3](image)

**Figure 3.** (a) The effect of inorganic salt concentration on graphite flotation; (b) The effect of pH on the flotation of graphite in the presence of inorganic salt ions; (c) Comparison of the flotation performance of graphite under different scarping times with and without MgCl₂ addition.

### 3.2. Effect of Salt Ions on the Surface Properties of Graphite Particles

#### 3.2.1. Contact Angle

Although the above flotation results showed an enhanced flotation of graphite as a function of electrolytes, the underlying interactions are still unclear. There are two hypotheses: (1) the ions can modify the properties of the air-water interface and thus the
foam stability; (2) the salt ions can shape the properties of graphite surfaces, such as the hydrophobicity. Therefore, the contact angles of graphite surfaces under different inorganic salt concentrations were measured. Figure 4 shows the contact angle results of graphite surface as a function of different salt concentrations, and the representative contact angle snapshots are given in Figure 5. Note that the pH conditions were kept consistent with the flotation tests mentioned above; that is, the test in the presence of KCl, MgCl₂, and AlCl₃ was conducted at pH = 6, pH = 6, and pH = 3, respectively.

![Figure 4](image)

**Figure 4.** Contact angle of graphite as a function of inorganic salt concentration in the (a) absence and (b) presence of collectors.

It can be seen from Figure 4a that the contact angle of untreated graphite (without electrolyte addition) is 50.5°, confirming the natural hydrophobicity of graphite minerals. As the salt concentration increases to 0.2 mol/L, the contact angles of graphite in the three inorganic salt solutions increase to 53.5°, 55.0°, and 59.5°, respectively. The ability of the three inorganic salts to increase the hydrophobicity of the graphite surface follows the decreasing order of AlCl₃, MgCl₂, and KCl, which is consistent with the single flotation results in Figure 3b. As a non-polar mineral, the surface of graphite is mainly governed by Van der Waals force. There will be a difference in the force field between polar water molecules and non-polar graphite surface, resulting in the formation of hydrophobic bonds to weaken their attraction to each other. Adding inorganic salts increases the difference in the surface force field between water molecules and graphite, making the surface of graphite more hydrophobic.

The contact angles of graphite surfaces in the presence of collectors were also measured, as shown in Figure 4b, to determine the effect of salt ions on the collection behavior of kerosene. After being treated with kerosene, the contact angle of graphite increased from 50.5° to 69°, indicating that the addition of kerosene can significantly improve the surface hydrophobicity of graphite. Moreover, the contact angles were further improved to 74.0°, 77.0°, and 79.5°, respectively, in the presence of KCl, MgCl₂, and AlCl₃ at 0.2 mol/L. As a result, it is assumed that the salt ions can significantly enhance the hydrophobicity of graphite particles and promote the adsorption of kerosene on graphite particles, leading to higher flotation recoveries.
3.2.2 Zeta Potential

To further analyze the influence of three inorganic salt solutions on the graphite surface, the zeta potential of graphite particles with different electrolytes under different pH conditions was tested, as shown in Figure 6.

It can be seen from Figure 6 that the zeta potential of graphite surface in deionized water changes from 22.8 mV to -54.07 mV with the increase of pH from 2 to 12. The zero point is around pH = 3.2. Adding KCl or MgCl₂ could slightly increase the zeta potential values of graphite surfaces but has not altered the sign yet. By contrast, AlCl₃ has a more significant impact on the zeta potential of graphite, changing its sign to positive at pH lower than 9, probably due to some specific adsorption of Al species on the graphite surface. The reduced absolute value of zeta potential indicates the reduction in the long-range repulsive force between the graphite particle and bubbles, thus improving the hydrophobicity of graphite surfaces.

3.3. Effect of Salt Ions on the Properties of Foam

3.3.1. Solution Chemistry Analysis

Compared to KCl, MgCl₂ and AlCl₃ will undergo a series of hydrolysis reactions in water to produce various products. The phase diagrams of Mg²⁺ and Al³⁺ in the solution at different pH are shown in Figure 7.
The Mg\(^{2+}\) remains free as pH gradually increases to 9, while MgOH\(^+\) appears at pH around 5.2 and reaches the maximum value at pH around 9.3. The content of Mg\(^{2+}\) and MgOH\(^+\) decreased rapidly in alkaline conditions and disappeared when the pH was greater than 12. In contrast, Mg(OH)\(_2\) appears at a pH of 9.3 and rapidly dominates at higher pH conditions. When comparing with the flotation result in Error! Reference source not found. b, it is unreasonable to assume that the enhanced flotation at lower pH should be related to the presence of Mg\(^{2+}\). In contrast, the inhibition of flotation at higher pH conditions is likely attributed to the precipitation of Mg(OH)\(_2\), which adhered to the graphite surface and changed the surface properties. Similar observations have been reported by Kurniawan et al [32] in coal flotation and Suyantara et al [35,36] in the flotation of molybdenite and chalcopyrite.

The hydrolysis of Al\(^{3+}\) in water is much more complicated, yielding multiple components throughout the wide pH range. Specifically, Al\(^{3+}\) dominates at acidic pH conditions, with AlOH\(^+\) and Al(OH)\(^+\) formed at a pH higher than 3. As the pH increases to around 6, both Al\(^{3+}\), AlOH\(^+\), and Al(OH)\(^+\) dramatically lose their existence, and Al(OH)\(_3\)^\(\text{sol}\) rapidly dominates. Al(OH)\(^+\) gradually takes charge when the solution increases to alkaline conditions. As seen from the flotation results in Figure 3b, it is speculated that the precipitation of Al(OH)\(_3\)^\(\text{sol}\) at pH around 6–7 has a detrimental effect on graphite flotation, which is consistent with the reduced flotation of chalcopyrite due to the adsorption of Al(OH)\(_3\)^\(\text{sol}\) on the minerals surface [31]. By contrast, the presence of Al\(^{3+}\) at lower pH conditions and the presence of Al(OH)\(^+\) at higher pH conditions both contribute to graphite flotation. However, further investigation is required to confirm such a hypothesis.

3.3.2. Froth Stability Analysis

Figure 8 shows the effect of KCl, MgCl\(_2\), and AlCl\(_3\) salt ions on the foaming ability and stability during flotation. As shown in Figure 8a, no foam was generated when no salt was added to the solution. As the increase in salt concentration in the solution, the foam height gradually increases, indicating that inorganic salt ions could significantly enhance the foaming ability of a solution. When the salt concentration gradually increases from 0 to 0.20 mol/L, the foam heights gradually increase to 21 mm, 36 mm, and 41 mm for KCl, MgCl\(_2\), and AlCl\(_3\), respectively. Moreover, Figure 8b shows the half-time of foaming. With the increase in KCl, MgCl\(_2\), and AlCl\(_3\) concentration, the foam stability increases, as evident by the increased half-life of the foam. When the salt concentration increases to 0.20 mol/L, the three inorganic salts (KCl, MgCl\(_2\), AlCl\(_3\)), the foam half-lives are 3 s, 6 s, and 8 s, respectively, for KCl, MgCl\(_2\), and AlCl\(_3\).
Figure 8. The effect of inorganic salt concentration on (a) foam height and (b) foam half-life.

Figure 9 compares the foaming ability of KCl, MgCl$_2$, and AlCl$_3$ solutions at a concentration of 0.1 mol/L. It is clear that the foaming ability of AlCl$_3$ is significantly more robust than that of the KCl solution. More intuitively, Figure 10 presents the top-view photos of the flotation foam in the absence and presence of MgCl$_2$. Specifically, the foam size is substantially reduced after the addition of MgCl$_2$ salt, and the froth layer becomes more thickened and denser, indicating more stable bubbles and stronger foam stability in the pulp. Similar phenomena were reported by Kurniawan et al. in coal flotation with Mg$^{2+}$ ions [32]. Inorganic salts can promote the formation of a hydration film on the surface of the bubbles, inhibiting their coalescence. The size of the formed foam is small and stable. As a result, the collision probability between the graphite particles and finer bubbles increases, resulting in enhanced flotation efficiency of graphite.

Figure 9. The foam structure of the solution in the presence of (a) KCl, (b) MgCl$_2$, and (c) AlCl$_3$ at 0.10 mol/L.

Figure 10. The top-view of the flotation foam in the (a) absence and (b) presence of MgCl$_2$ at 0.2 mol/L.
3.3.3. Surface Tension

To further study the foaming mechanism of inorganic salts, the surface tension of KCl, MgCl₂, and AlCl₃ inorganic salt solutions with different concentrations was measured, and the results are shown in Figure 11.

![Figure 11. Surface tension of the solution as a function of inorganic salt concentration.](image)

Figure 11 with the increase in K⁺, Mg²⁺, or Al³⁺ concentration, the surface tension of the solution increases slightly. When the concentration of inorganic salt increased to 0.20 mol/L, the surface tension of the three inorganic salt solutions was 74.89 mN/m, 75.07 mN/m, and 75.28 mN/m, respectively.

It is reported that inorganic ions will migrate from the air-liquid interface toward the bulk solution, and a well-ordered polarized water shell would form as induced by the charged bulk electrolytes, giving rise to increased surface tension. According to the Collin’s law of matching water affinity, the multivalent Al³⁺ ion shows the most substantial hydration ability, followed by Mg²⁺, and K⁺ shows the weakest hydration. As a result, the foaming ability of Al³⁺ is higher than Mg²⁺ and K⁺.

Due to the different migration speeds of electrolytes at the liquid-gas interface, a cumulative charge excess of certain ions is generated, leading to a net charge at the air-water interface. The increased net charge at the bubble surface would enhance the electrical repulsion between bubbles, thus preventing the bubble coalescence. The huge gap in migration speed of the positive and negative ions contributes to more significant repulsion and, thereby, more stable bubbles. It is suggested that the migration rate of different ions in solution follows the order of Cl⁻ > K⁺ > Mg²⁺ > Al³⁺; therefore, the largest migration discrepancy between Al³⁺ and Cl⁻ renders AlCl₃ more efficient in enhancing the foam stability, compared to the less diversified KCl.

4. Conclusions

The effect of three different inorganic salts: KCl, MgCl₂, and AlCl₃, on the flotation of graphite was investigated in this study. Contact angle, zeta potential, and surface tension were measured to understand the specific cation effects on the properties of both solid graphite surface and the flotation foam. Some conclusions can be drawn as follows:

The activation of KCl on graphite flotation is less sensitive to the pulp pH, while the flotation of graphite in the presence of MgCl₂ and AlCl₃ is strongly pH-dependent. While MgCl₂ promotes graphite flotation at acidic and weak alkaline conditions, it completely depresses the flotation at a pH higher than 12. In contrast, AlCl₃ severely inhibits graphite flotation at pH around 5–6.

The addition of KCl and MgCl₂ at neutral pH conditions can significantly improve the hydrophobicity of graphite surface and enhance the foaming ability and stability; therefore, it is of great significance for enhanced graphite flotation.
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