

## Article

# The Effect of Polystyrene on the Carrier Flotation of Fine Smithsonite

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**Abstract:** Carrier flotation is a common technique used to improve flotation recovery of ultrafine ores. In this study, we used coarse polystyrene as the carrier material to enhance flotation recovery of fine smithsonite ( $\text{ZnCO}_3$ ) particles. Sodium oleate was used as the collector and played a role in the adhesion of fine smithsonite to polystyrene due to its amphipathic properties. The carrier feature of polystyrene was demonstrated using particle size analysis, total organic carbon, and scanning electron microscopy. The fine smithsonite particles coated the polystyrene particles through a reaction between the active zinc sites and the carboxyl head groups of the oleate adsorbed on smithsonite and through a hydrophobic interaction between polystyrene and the hydrocarbon chains of the oleate. Newly enlarged particle aggregates with smithsonite shells enhanced collision and attachment of the hydrophobized aggregates with bubbles, which accelerated smithsonite flotation recovery.

**Keywords:** carrier flotation; polystyrene; ultrafine particles; smithsonite

## 1. Introduction

The recovery of ultrafine particles is one of the most significant challenges faced during flotation due to the small mass and high surface areas of the particles [1–3]. For instance, the small mass of ultrafine particles leads to low particle inertia, which decreases the probability of collision between the particle and a bubble. In addition, the small mass makes it difficult for the ultrafine particles to overcome the energy barrier to form particle–particle or particle–bubble aggregates [4,5]. Further, high surface areas of the ultrafine solids directly lead to high water dissolution of the chemical species in the minerals, resulting in a rigid froth and high pulp viscosity [6–8].

A common strategy used in flotation separation of ultrafine particles is hydrophobic association, which include methods such as carrier flotation, shear flocculation, selective magnetic aggregation, and selective flocculation [9–13]. During a typical hydrophobic association process, such as carrier flotation, similar or matching hydrophobic materials with a relatively coarse size are added to the pulp. By controlling the pulp's chemical composition and hydrodynamic conditions, the added coarse materials act as carriers that adhere to the targeted ultrafine particles that have been modified to become hydrophobic by adsorbing the collector. Because of the enlarged size of particle aggregates formed from ultrafine particles coagulating with coarse carriers, the particles' contact frequency and attachment probability with air bubbles are enhanced, thus leading to a faster flotation recovery of ultrafine particles.

Polystyrene (PS) is a synthetic aromatic polymer made from styrene monomers and has a general chemical formula of  $(\text{C}_8\text{H}_8)_n$ . The long hydrocarbon chain with alternating carbon centers attached

to phenyl groups makes polystyrene hydrophobic [14,15], which makes it difficult to disperse polystyrene in water. However, this polymer can be uniformly distributed and floated in a sodium oleate solution. In general, polystyrene is not recycled or accepted by curbside collection recycling programs. Polypropylene, which has a similar structure to polystyrene, was used for carrier flotation of scheelite [16–18]. Therefore, polystyrene might be a promising carrier material for converting waste materials into useful products with both economic and environmental significance.

The floatability of smithsonite ( $\text{ZnCO}_3$ ) in sodium oleate solution has been reported by numerous investigators [19–21]. A high floatability of smithsonite has been observed with sodium oleate between pH 7 and pH 8 [22–25]. In the present study, sodium oleate was used as the collector and polystyrene as the carrier to capture very fine smithsonite particles. Different measurement methods, including particle size distribution, adsorption, and scanning electron microscopy (SEM), were applied to understand the underlying mechanisms of carrier flotation with polystyrene.

## 2. Materials and Methods

### 2.1. Materials and Reagents

Pure smithsonite samples were collected from Ruili, Yunnan province, China. The smithsonite samples were confirmed 98% pure by mineralogical and X-ray powder diffraction data. Pure polystyrene with diameter dimensions of 90 to 150  $\mu\text{m}$  was provided by Shanghai and Sheng Plastic Micropowder Technology Ltd., China. Hydrochloric acid (HCl) and sodium hydroxide (NaOH) were used to adjust the pH of work solutions. Sodium oleate (NaOL) was used as collector. Deionized water was used for all tests.

### 2.2. SEM Analysis

SEM was used to determine the morphology of floated materials in flotation concentrates. After flotation, a concentrate sample was air-dried. The SEM images were acquired using a Quanta 250 scanning electron microscope (Thermo Fisher Scientific Inc., Waltham, MA, USA). The detailed operating parameters for the SEM analyses were as follows: the accelerating voltage was 30.00 kV, the working distance was 20.2 mm, the pressure was  $-1.21 \times 10^{-4}$  Pa, and the spot size was 2.5 nm.

### 2.3. Microflotation Tests

The smithsonite samples were ground and sieved to collect a  $-38 \mu\text{m}$  fraction for microflotation tests. Single mineral flotation tests were carried out in a 40 mL hitch groove flotation cell with a spindle speed of 2000 r/min [26–28]. The polystyrene powder was added to a 10 mL sodium oleate solution and stirred in a beaker to form a uniform collector solution. The mineral suspension was prepared by adding 2.0 g of the minerals into a 30 mL solution inside a flotation cell. The 10 mL sodium oleate solution was poured into the flotation cell and stirred. The system was mixed and equilibrated for 5 min without air. The flotation experiment was carried out for 3 min under air. The obtained concentrate and tailing samples were filtered, dried, and weighed. Each experiment was performed in triplicate, and the average was reported as the final value. Standard deviations, which are presented as error bars, were calculated from the triplicate measurements using Origin 8.5 (OriginLab, Hampton, VA, USA).

### 2.4. Particle Size Analysis

The size of smithsonite and polystyrene particles were measured using a laser-based particle size analyzer (Mastersizer 2000, Malvern Instruments Ltd., Malvern, UK), which utilizes Fraunhofer diffraction of light formed by particles with diameters larger than the wavelength of the incident laser beam. An optical filter, lens, and photo detector were coupled with a computer loaded with the Mastersizer 2000 software (Malvern Instruments Ltd., Malvern, UK) to compute the particle size

distribution from the diffraction data. The data were analyzed as the volume percentage against the particle size.

### 2.5. Adsorption Tests

Sodium oleate solutions (40 mL each) of various concentrations were prepared. Polystyrene (0.14 g) was added to each sodium oleate solution in a centrifuge tube. The suspensions were magnetically stirred for 3 min and centrifuged for 10 min at 9000 rpm. The concentration of the sodium oleate in each supernatant was determined with a Total Organic Carbon (TOC) analyzer (Thermo Fisher Scientific Inc., Waltham, MA, USA). The adsorption density for each sample was calculated as follows [29]:

$$\Gamma = V(C_0 - C)/m.$$

In the above equation,  $\Gamma$  is the adsorption density,  $V$  is the volume of the solution,  $C_0$  is the initial concentration of sodium oleate,  $C$  is the concentration of sodium oleate in the centrifugal supernatant, and  $m$  is the mass of polystyrene.

## 3. Results and Discussion

### 3.1. SEM Results

SEM images of the raw ore and carrier flotation concentrate are shown in Figure 1. Notable differences were observed before and after carrier flotation. The feed contained individual solid particles (Figure 1A). SEM images of the concentrate with polystyrene (Figure 1B) revealed that fine smithsonite particles floated around polystyrene, forming a shell. Because all smithsonite particles adhered to the surface of polystyrene, forming a shell and generating larger polystyrene–smithsonite aggregates, individual fine smithsonite particles were virtually absent in the concentrate. As expected, the recovery of smithsonite increased with the increasing size of aggregates due to increased probability of collision and adhesion between enlarged particle aggregates and bubbles.

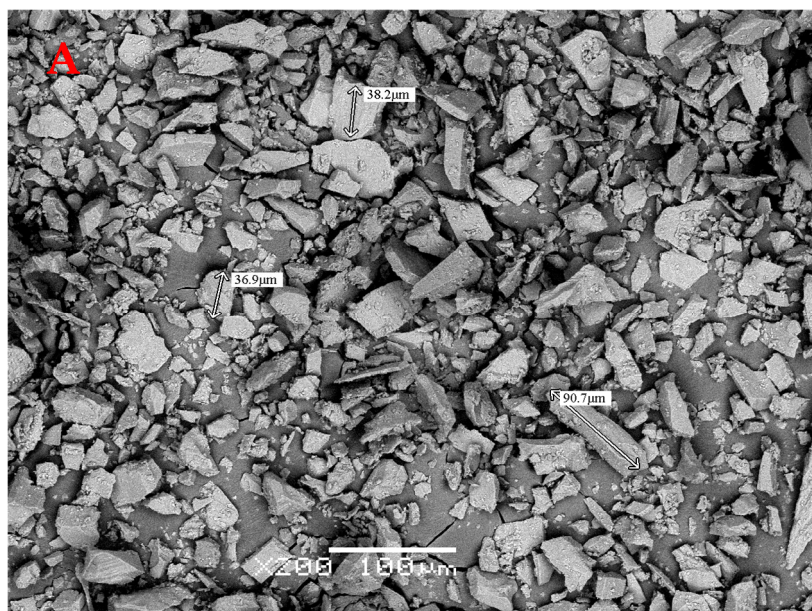
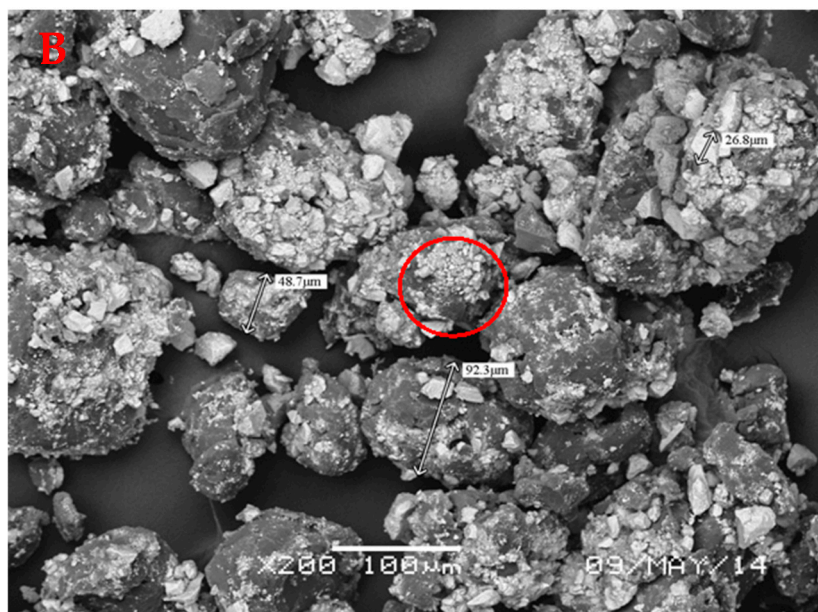


Figure 1. Cont.



**Figure 1.** Scanning electron microscopy (SEM) images. (A) Raw ore. (B) Smithsonite concentrate collected using 70 kg/t PS and  $8 \times 10^{-4}$  mol/L NaOL.

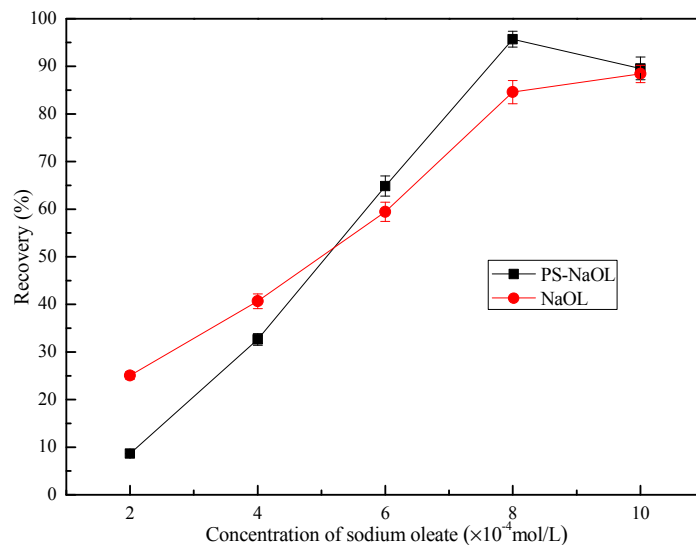
### 3.2. Flotation Behavior

The adhesion of smithsonite to polystyrene was found to depend on the adsorption of collectors on mineral surfaces. Figure 2 shows smithsonite recovery as a function of sodium oleate concentration, with and without polystyrene. When using 70 kg/t polystyrene (dry ore), the smithsonite recovery increased as sodium oleate concentration increased. A maximum recovery (95.69%) was obtained with  $8 \times 10^{-4}$  mol/L sodium oleate. Without polystyrene, the smithsonite recovery increased as sodium oleate concentration increased up to  $10 \times 10^{-4}$  mol/L. The difference in flotation behavior, with and without polystyrene, might have been caused by the different adsorption densities of the sodium oleate on polystyrene and smithsonite. At a low oleate concentration ( $<5 \times 10^{-4}$  mol/L), the adsorption density on smithsonite particles would be higher without polystyrene than that with polystyrene. Because some oleate could have been adsorbed on the polystyrene, the oleate concentration available in the pulp for smithsonite adsorption would decrease. At such a low concentration of sodium oleate, the hydrophobicity of smithsonite can be relatively low, resulting in a low smithsonite aggregation and recovery. The low hydrophobicity of smithsonite would also limit hydrophobic coagulation between smithsonite and polystyrene. As a result, a lower smithsonite recovery was observed with a polystyrene addition compared to that observed without such an addition.

Further, the orientation of the adsorbed oleate on the smithsonite particles could be different from that of the oleate adsorbed on polystyrene. For the adsorption of the oleate on smithsonite, the driving force is mainly the surface reaction between the head group of the oleate and the zinc sites of the smithsonite. Hence, the orientation of the oleate on smithsonite would be in such a way that the oleate polar groups face smithsonite and the hydrocarbon chains face water, thus increasing hydrophobicity of smithsonite as oleate concentration increases and thereby as smithsonite recovery increases [30,31].

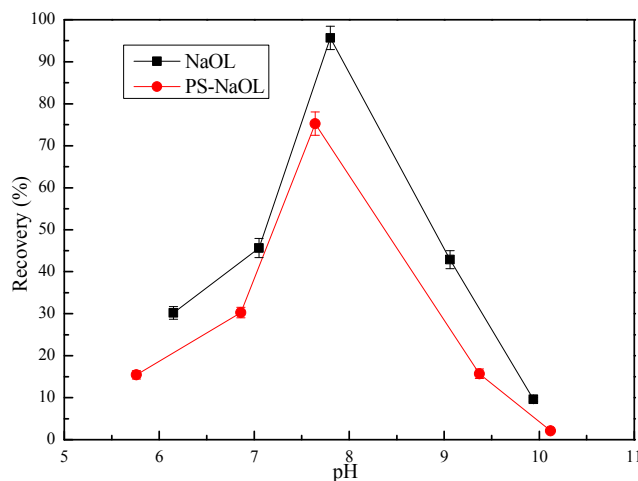
Because polystyrene is highly hydrophobic, the adsorption of the oleate on polystyrene mainly occur via hydrophobic interaction; hence, the hydrocarbon chains of oleate face polystyrene, and the head groups face water. Accordingly, the hydrophobicity of polystyrene is progressively reduced as oleate concentration increases, which results in a decrease in smithsonite recovery, as observed when the oleate concentration was greater than  $8 \times 10^{-4}$  mol/L.





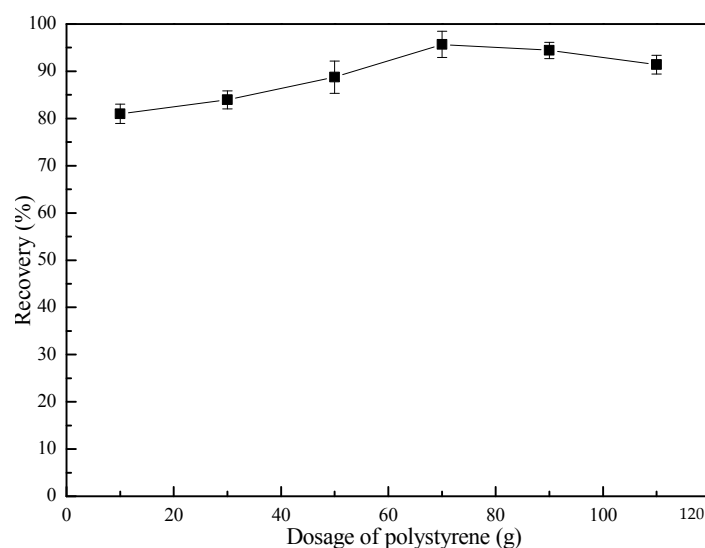
**Figure 2.** Effect of the NaOL concentration on smithsonite recovery at pH 7.5.

For a given flotation system, an optimal pH value exists for maximizing flotation recovery [32]. The pH could affect particle–bubble interaction [33], slurry characteristics, and charge of the species present in the pulp (ionization, dissociation, and dissolution). These effects influenced the hydration of the mineral surface and the reagent properties, which consequently interfered with the adsorption and success of mineral collection. The relationship between smithsonite recovery and pulp pH is plotted in Figure 3. The sodium oleate concentration was fixed to  $8 \times 10^{-4}$  mol/L, and polystyrene was added at 70 kg/t ore. Maximum smithsonite recovery occurred at a pH range of 7.5 to 8.5, which corresponds to the highest adsorption of the oleate—this finding will be further discussed in the adsorption results section.



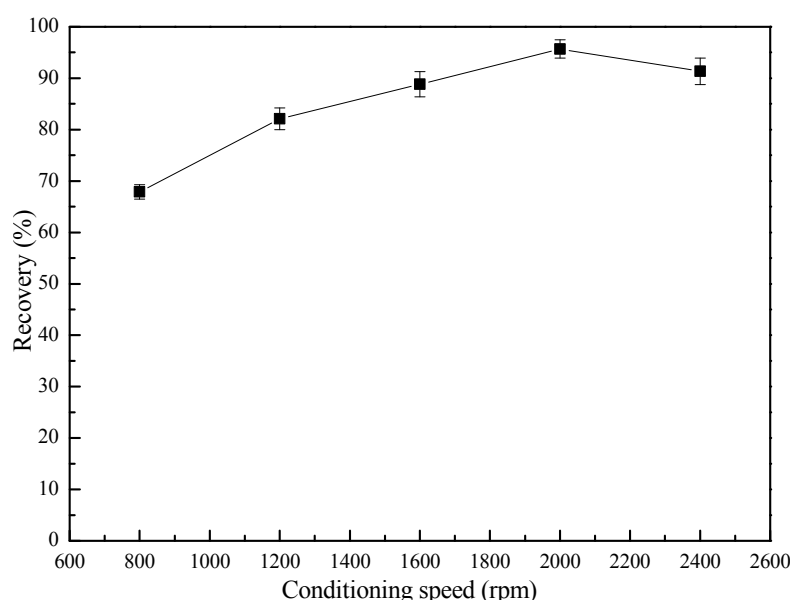
**Figure 3.** Recovery of smithsonite as a function of pH ( $8 \times 10^{-4}$  mol/L NaOL; 70 kg/t PS).

Figure 4 shows that smithsonite recovery with  $8 \times 10^{-4}$  mol/L sodium oleate at pH 7.5 is relative to the amount of polystyrene added. Smithsonite recovery increased as the addition of polystyrene increased, reaching a maximum recovery with 70 kg/t polystyrene. A further increase in polystyrene resulted in decreased smithsonite recovery. This result may be due to the increased proportion of the oleate adsorbed on polystyrene, which results in reduced oleate adsorbed on smithsonite and reduced smithsonite hydrophobicity. The above results indicate that an optimal amount and proportion of polystyrene and sodium oleate for achieving maximum flotation recovery exists.



**Figure 4.** Recovery of smithsonite as a function of polystyrene dosage ( $8 \times 10^{-4}$  mol/L NaOL; pH 7.5).

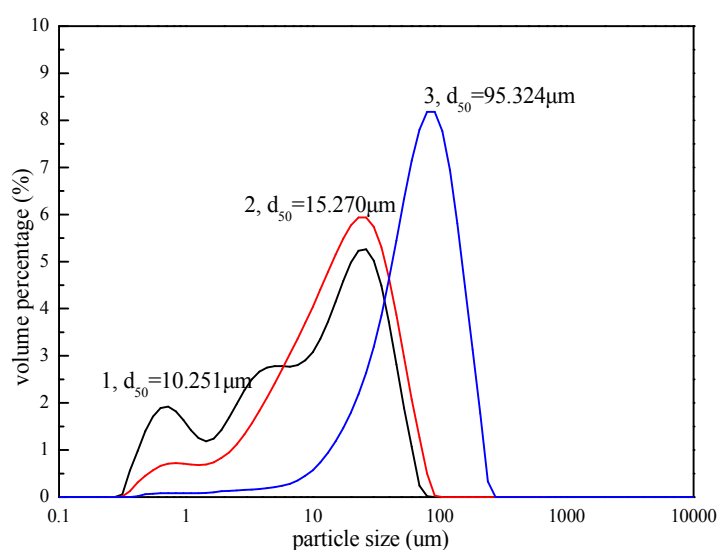
Analogous to bubble–particle interactions, the adhesion between smithsonite and polystyrene can be explained using the probabilities of attachment and detachment. Figure 5 shows smithsonite recovery as a function of stirring intensity. As agitation intensity increased, the system’s energy input was able to overcome the medium resistance raised from particle collision. This energy can also be used to overcome the energy barrier amid smithsonite–polystyrene–bubble interaction. As a result, the hydrophobized fine smithsonite particles interacted with and adhered to the surface of coarse polystyrene particles when the agitation was increased up to 2000 rpm, which led to a high recovery of smithsonite. A further increase in conditioning speed (>2000 rpm) would cause detachment of the adhered ultrafine particles or disrupt the formed smithsonite–polystyrene aggregates due to the high shear forces at the contact surface [34].



**Figure 5.** Recovery of smithsonite as a function of stirring intensity ( $8 \times 10^{-4}$  mol/L NaOL; 70 kg/t PS; pH 7.5).

### 3.3. Particle Size Analysis

Particle size distribution has a significant effect on the efficiency of flotation because different collision frequencies exist among the varyingly sized particles in turbulent flow. Therefore, the floatability is directly proportional to the apparent sizes of the fine smithsonite aggregates. As shown in Figure 6, the addition of sodium oleate increased the particle size of the concentrate to some degree (Curve 2) as compared with the solids in the feed (Curve 1). This increase in aggregate size is due to the hydrophobic coagulation of the fine smithsonite particles after a sodium oleate addition. Larger sizes of the concentrate solids were obtained by adding both polystyrene and the oleate (Curve 3). In general, the aggregate size increased from approximately  $10\ \mu\text{m}$  (without polystyrene; Curve 2) to approximately  $100\ \mu\text{m}$  (with polystyrene; Curve 3), indicating that the coarse carrier material polystyrene indeed captured the fine hydrophobized smithsonite particles. On the other hand, the amount of ultrafine particles ( $<10\ \mu\text{m}$ ) was significantly reduced, further confirming that the fine smithsonite particles adhered to coarse polystyrene.



**Figure 6.** Particle size distribution curves. (1) Raw ore. (2) Concentrate of smithsonite collected with  $8 \times 10^{-4}$  mol/L NaOL. (3) Concentrate of smithsonite collected using 70 kg/t PS and  $8 \times 10^{-4}$  mol/L NaOL.

### 3.4. Adsorption Results

As shown in Figure 2, smithsonite recovery increased as oleate concentration increased (with and without polystyrene), indicating the importance of oleate adsorption on smithsonite. To verify that the improved smithsonite flotation recovery is due to oleate adsorption, the adsorption density of sodium oleate on polystyrene was measured. The results in Figure 7 show that the adsorption density of sodium oleate on the polystyrene surface increased as sodium oleate concentration increased, which reached  $8 \times 10^{-4}$  mol/L sodium oleate before dropping rapidly. The maximum adsorption density of the oleate on polystyrene correlated well with the maximum smithsonite recovery (Figure 2 vs. Figure 7). A further increase in the sodium oleate concentration to higher than  $8 \times 10^{-4}$  mol/L resulted in a drastic reduction in adsorption, which also correlated well with reduced smithsonite recovery at the same oleate concentration (with polystyrene addition). Based on the critical micelle concentration (CMC) of oleate  $1.0 \times 10^{-3}$  mol/L [35], we infer that the formation of micelles led to the sharp decrease in oleate adsorption on polystyrene when the oleate concentration was greater than  $8 \times 10^{-4}$  mol/L.

The results of the above experiments suggest a mechanism for the behavior of polystyrene as a carrier. A schematic representation of the flotation process with polystyrene as the carrier is

shown in Figure 8. Accordingly, after polystyrene was added to the sodium oleate solution, stirred, and uniformly dispersed, the oleate hydrocarbon tail adhered to the polystyrene surface through hydrophobic association; the polar heads faced water, thus generating a stabilized polystyrene suspension. Subsequently, the prepared solution was poured into a pulp with smithsonite, at which point the smithsonite particles interacted with polystyrene via two possible routes.

In the first possible route, when the smithsonite particles are mixed with the prepared polystyrene suspension, the zinc particles react with the carboxyl groups of the oleate adsorbed on polystyrene, thus coating the polystyrene particles. The remaining available surface area on the smithsonite adsorbs the residual oleate in the suspension, which makes the smithsonite particles hydrophobic. The formed hydrophobic aggregates then attach to air bubbles, accelerating smithsonite recovery. In the second route, smithsonite reacts with the oleate in the suspension first; thus, the oleate head groups interact with the smithsonite zinc sites and the hydrocarbon chains face water, thereby forming hydrophobized smithsonite. The hydrophobized smithsonite particles then coagulate with polystyrene by hydrophobic interaction, which increases the aggregates size, facilitates the interaction between aggregates and bubbles, and enhances smithsonite recovery. The strength of the smithsonite–polystyrene aggregates is further enhanced by the interaction of the smithsonite zinc sites with the head group of the oleate adsorbed on polystyrene.

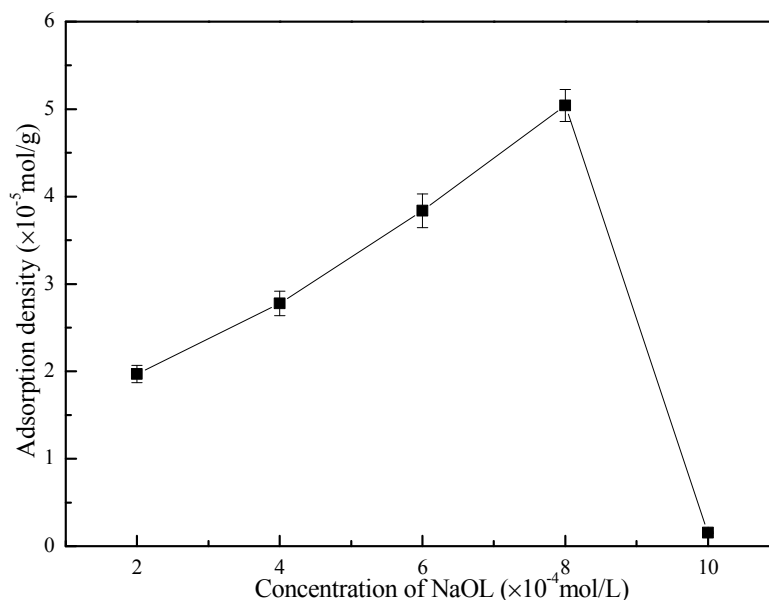


Figure 7. Adsorption density as a function of sodium oleate concentration.

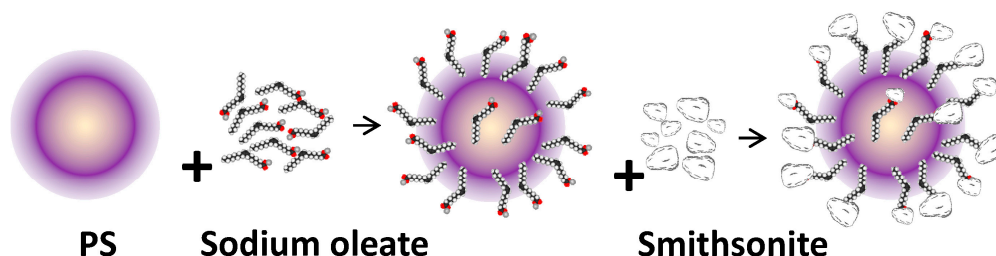


Figure 8. Schematic representation of flotation with polystyrene as the carrier.

#### 4. Conclusions

Tests of ultrafine smithsonite flotation have been conducted. In this study, the flotation performance was improved by adding coarse polystyrene as the carrier, as compared to that of conventional flotation



methods. Sodium oleate was used as the collector to hydrophobize fine smithsonite. A maximum flotation recovery of 95.69% was achieved at a neutral pH with  $8 \times 10^{-4}$  mol/L sodium oleate and 70 kg/t polystyrene at 2000 rpm.

An optimal sodium oleate concentration was observed when the amount of polystyrene remained constant. This optimal value changed with the size of the added polystyrene. The effect of varying the amount of polystyrene on the optimal oleate concentration will be studied in future work.

During flotation, the oleate tail may adhere to the surface of polystyrene. Alternatively, the oleate can adsorb on smithsonite, while the hydrocarbon chains face water and the head groups face smithsonite. These hydrophobized fine smithsonite particles can coat the polystyrene particles through the association of the zinc sites of smithsonite with carboxyl groups of the oleate and through the hydrophobic interaction between polystyrene and the hydrocarbon chains of the oleate adsorbed on smithsonite. The newly enlarged particle aggregates with the hydrophobized smithsonite shells enhanced collision with and attachment to bubbles, thus accelerating the flotation recovery of ultrafine smithsonite.

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**Author Contributions:** Yuehua Hu, Wei Sun, and Longhua Xu conceived and designed the experiments; Xiangfeng Zhang performed the experiments and analyzed the data; Yuehua Hu and Wei Sun contributed reagents and materials; Xiangfeng Zhang and Longhua Xu wrote the paper.

**Conflicts of Interest:** The authors declare no conflict of interest.

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