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Selective removal of copper from heavy-metals-containing acidic solution by a mechanochemical reduction with zero-valent silicon

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ABSTRACT

It is always a challenge to deal with industrial wastewater containing heavy metals. Selective removal and recovery of valuable metals such as copper particularly from acidic solutions are very important from both stances of resource supplying and environmental purification. Among all the divalent heavy metals, copper has the potential of being reduced to monovalent state. A new approach was proposed to ball mill zero-valent silicon (ZVS) in $CuSO_4$ solution and the solutions containing multi-metal ions to serve the purpose. In this study, both quantitative and qualitative data were reported on the induced mechanochemical reduction reaction to convert Cu^{2+} into Cu_2O by ball milling with ZVS. Experimental parameters such as milling time and Si to Cu ratio were found to play important role in stimulating the reaction, and as a result, 97.32% Cu^{2+} was removed from the solution under Si/Cu molar ratio of 100. Even at a high concentration of sulfuric acid up to 4.6 mol/L, the copper removal percentage maintained a high value of 82.57%. Furthermore, in the sulfate solutions containing several other heavy metals of Zn, Mn, Ni, Cd, Co, Fe etc., the reduction reaction by zero-valent silicon occurred only on Cu^{2+} with other heavy metal ions remaining in the solutions. The feasibility of this technology has been verified by treating a leaching solution of NiS mineral, from which copper has been removed selectively from nickel, iron etc. This research may serve another purpose for applying waste silicon from the solar energy devices after lifetime in the future.

1. Introduction

With rapid growth of economy based on the over-exploitation of mines, the discharged wastewater contains a large number of harmful substances of high biocumulative toxicity and carcinogenicity, among which heavy metals are typical ones involved in various industries such as mining, metallurgy, printing, dyeing etc. in the discharged wastewater often with strong acidity [1,18,35]. Among various types of pollution, heavy metal pollution has become one of the major environmental problems in the world. Numerous studies have shown that exposure to high levels of heavy metal is a common cause of permanent intellectual and developmental impairment. Even traditional pollutants such as sulfur dioxide and nitrogen oxides have been controlled, heavy metal pollution poses still a greater risk to public health and sustainable development and requires stronger attention of policy makers [13,28,5]. Copper, an abundant element in mines and common industrial raw material, is often present in high concentrations in these effluents [25], causing potential health problems by harmful damages to the eyes and liver with unbalanced cellular processes [20,2]. Besides the traditional alkaline precipitation, many processes have been reported for the removal of copper including electrolysis method [32], hydrometallurgy method [24], electrodeposition method.

Copper plays an indispensable role in various fields due to its high melting point, good electrical conductivity and ductility. Copper production has increased year by year in recent years, exceeding 24 million tons in 2019. This also results in the e-waste washing fluid and copper mine wastewater containing a large amount of toxic copper substances, if not treated, will cause a great burden on the environment [8,22,30]. On the other hand, it is highly required to recover copper from these waste solutions to offer secondary resource to meet the increasing need. However, it remains as a great challenge to efficiently and selectively recover copper ion during environmental purification of waste liquid particularly at relatively high acidity [23], not to say the difficulty in obtaining high purity copper in cases of coexistence with other heavy

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metals.

In considering possible copper enrichment from other heavy metals, we noticed that copper may exist at both monovalent and divalent states, different from common divalent state of other heavy metals, and tried to reduce divalent copper ions into monovalent state to enlarge its difference from other heavy metal ions. Zero-valent silicon (ZVS) may serve as one choice from its wide range of sources and strong reducing power ($E^0_H = -0.807$ V). Silicon is the second most abundant element in the Earth's crust and generally does not produce secondary pollution. Since the rapid development of the world photovoltaic industry in 2000, the life of solar panels is only 20–30 years, leading to the retirement of a large number of used solar panels in 2030. Furthermore, the global solar panel installation scale has to be increased to reach about 100TWp in 2050 to give a real impact on the energy mix and carbon emissions [27]. Waste solar panels contain about 5% silicon, providing enough source in the near future.

At present, the application of zero-valent silicon in the treatment of heavy metal ion pollution has not been reported. The high reducing activity may act as a barrier for potential application, due to easy oxidization of its surface to form less active silicon oxygen compounds that inhibit the direct contact between zero-valent silicon and heavy metal ions. Zero-valent silicon is oxidized in contact with air to form a core of zero-valent silicon with high activity, while the surface is silicon oxide, which is difficult to play the role of zero valence. Mechanochemistry is widely used in the preparation of composites that can be used as contaminant removers [29,12,33], because under the action of mechanochemistry, the surface activity of substances can be improved and chemical reactions between substances can be promoted. Our research demonstrated it is possible to coat the surface treatment of zero-valent iron or silicon for maintaining the active reducing ability by cogrinding some coating powders [26,14]. The treatment of zero-valent silicon particles by mechanochemical method can continuously update the surface of zero-valent silicon and expose the zero-valent silicon with high reducing activity in the core. However, cogrinding with other powders would not serve the purpose for copper reduction.

In this work, selective removal of copper ions is achieved by co-grinding zero-valent silicon directly in copper-containing solution to stimulate a mechanochemical reduction reaction for copper ion precipitation. The effects of several parameters such as silicon to copper molar ratio, ball milling speed, solid–liquid ratio and initial solution acidity on copper selective removal were investigated. The ball milling process not only improves the reactivity of the reactants, but also continuously removes surface layers to expose the fresh surface, so that the zero-valent silicon and copper ions can directly undergo electron transport. This research proposes an alternative to the large numbers of searches for recycling copper from waste solutions even at high acidity.

2. Materials and methods

2.1. Reagents and instruments

In this experiment, zero-valent silicon (ZVS) powder (99% purity) came from discarded solar panels, provided by Zhejiang Lichen Electric Power Company. All reagents ($CuSO_4{\cdot}5H_2O$, $MnSO_4{\cdot}H_2O$, $CdSO_4{\cdot}8/3H_2O$, $ZnSO_4{\cdot}7H_2O$, $NiSO_4{\cdot}6H_2O$, $Cr_2(SO_4)_3{\cdot}6H_2O$, $Al_2(SO_4)_3{\cdot}18H_2O$, $MgSO_4$, Na_2SO_4, K_2SO_4, $Li_2SO_4{\cdot}H_2O$, $FeSO_4{\cdot}7H_2O$, $CoSO_4{\cdot}7H_2O$) used in this investigation were analytical grade chemicals purchased from Sinopharm Chemical Reagent Co., Ltd, China and used as received without further treatment. The pH value of the solution was adjusted with analytical grade sulfuric acid (H_2SO_4, 98 wt%) and sodium hydroxide (NaOH). All experiments used ultra-pure water (18.25 M ω cm resistance) to prepare the working solution. Milling operation was performed in a lab-scale stirred ball milling equipment (Changsha Tian Chuang Powder Technology Corporation, YS7124-JM-1L, China). The cylindrical chamber (total volume 1000 mL) with diameter of 115 mm, height of 120 mm and the inner wall was lined with Al_2O_3 material of 10 mm thickness. The used balls were yttrium-stabilized zirconia milling beads of 3 mm in diameter.

Real mixed heavy metal ion wastewater came from a leaching solution of nickel sulfide ore by the Chinese Institute of Scientific Process Engineering, and the specific components are shown in Table 1. The main heavy metal ions contained in the actual wastewater are Ni^{2+}, $Fe^{2+/3+}$, Cu^{2+}, and Co^{2+}, with a pH value of 1.64. With the verifying test, 3 g of ZVS were added to 2 mL of this solution to subject to milling operation (4 h, 300 rpm) at the same operation conditions for next analyses.

2.2. Procedure

Firstly, copper sulfate reagent, a certain volume of grinding beads, zero-valent silicon, and an appropriate amount of deionized water were added to the grinding chamber for grinding operation, and the parameters included the grinding speed, grinding time, and the change of Si/Cu molar ratio. After the running, the ball-milled slurry was washed with deionized water into a beaker and stirred at 400 rpm for 2 h to obtain the supernatant for pH and remaining metal concentrations measurement, the remaining suspension was filtered to collect the precipitated phase, and the product was dried at room temperature for 24 h for further analysis. All experiments were performed at room temperature.

2.3. Characterizations

The pH of all solution samples were measured by a pH meter (METTLER TOLEDO FE20-FiveEasy™, Switzerland). The concentrations of metal ions in the supernatant were determined by atomic absorption spectrophotometer (AAS: SHIMADZU AA-6880, Japan). X-ray diffraction (XRD: RU-200B/D/MAX-RB RU-200B, Japan) analysis was performed to identify the phases in the precipitated samples. To determine the existing states of elemental compositions before and after Cu treatment, XPS analysis was performed using the Thermo ESCALAB 250Xi spectrometer (Thermo Fisher Scientific, USA) with a single Al Kα X-ray source (Al Kα = 1486.6 eV) at room temperature. All binding energies were calibrated for C1 peak (284.8 eV). The surface morphology of the samples was characterized by scanning electron microscopy (SEM) equipped with energy dispersive X-ray spectroscopy (EDX) (Zeiss Sigma300, Germany). The samples were also analyzed by Fourier Transform infrared spectroscopy (FTIR) in the range of 400–4000 cm^{-1} (Therno Nicolet, USA).

The removal percentages of Cu and other metals were calculated by the following equation:

$$R\% = (C_0 - C_e)/C_0 \times 100\%$$

In the formula, C_0 represents the initial concentration and Ce the concentration after treatment. The unit of C_0 and Ce was mg/L.

3. Results and discussion

From its good reducibility, ZVS may has wide expectation in wastewater treatment. Challenge remains as to how use this potential because ZVS is easy to form oxidized passivation layer coated on the surface of shell core structure. In order to raise ZVS reduction performance, the passivation layer has to been stripped off to expose the fresh surface to pollutant target. Ball milling of ZVS was conducted in the solutions containing copper and other heavy metals to stimulate an in

Table 1
Real wastewater components of nickel sulfide leaching solution.

Ionic species	Ni^{2+}	$Fe^{2+/3+}$	Cu^{2+}	Co^{2+}
Ion concentration (g/L)	23.27	24.36	8.67	0.83

situ reduction reaction for copper ions and some quantitative data related to the milling operation are presented.

3.1. Cu removal experiments

The molar ratio of Si/Cu was first examined to check its effect when Si and $CuSO_4$ were comilled for 4 h at 300 r/min of ball grinding speed. Changes in removal percentage of Cu^{2+} and pH with Si/Cu molar ratio are shown in Fig. 1(a). It is obvious that with an increase in Si/Cu molar ratio, removal percentage of Cu^{2+} from solution increased rapidly and reached nearly 90% and 100% in the cases of 50:1 and 100:1, respectively, confirming clearly that it is possible to use ZVS to reduce copper ions into insoluble precipitate. Change in pH was in the range from 2 to 4, a relatively weak acidic solution. The pH value was measured of the washing solution by 200 mL, not directly measured datum in situ from the milling pot. It is clear that the acidity of the sample inside the milling pot, before diluted by the washing with large amount of water, would be very high, verifying the production of sulfuric acid from the reaction for copper precipitation. Reaction mechanism on copper reduction and sulfuric acid production will be discussed in the next section.

After confirmation of the obvious effect of Si/Cu ratio, examination of other parameters on the reaction was performed at a Si/Cu ratio of 20:1. Changes in removal percentage of copper ions and pH with milling time are shown in Fig. 1(b).When ZVS and Cu^{2+} were mixed evenly by hand in wet processing without introducing mechanochemical effect, there is no reaction between ZVS and Cu^{2+}, and copper still exists in the form of soluble ions, without any precipitation being removed. With an increase in ball milling time, removal percentage due to precipitation occurrence increases correspondingly and reaches over 50% by 4 h. Further increase in milling time to 5 h results in a very limited increase in removal percentage of copper up to 55.8% only. Extension in milling time only, as a result, is not able to complete the reduction reaction to have all copper precipitated. At the same time, pH change with milling time continues to decrease and reaches a very low value of 2.01 at 4 h milling, a very high acidity in milling pot. The pH value becomes levelled off with prolonged milling time to 5 h, consistent with the same change pattern as copper removal. This phenomenon implies that the reaction between ZVS and copper ions may be reversible, not easy to reach completeness, due to strong resistance by reaction product of sulfuric acid. On other word, the very strong acid may dissolve the precipitate to some degree, so that further milling time extension would not work reasonably for the purpose of copper precipitation. Therefore, ball milling time was fixed at 4 h in the following experiments.

Besides milling time as important factor influencing the reaction, it has been found that solid–liquid ratio in the ball milling pot is also very crucial. Changes in Cu removal percentage and pH with solid–liquid ratio are shown in Fig. 1(c). As a well known phenomenon, small amount of water as in the hydrated Cu sulfate will lead to a very heavy agglomeration so that milling operation cannot be carried out efficiently. Addition of certain amount water to the pot can avoid the agglomeration as a kind of wet milling. As shown in Fig. 1(c), copper removal can be obtained within less water addition up to solid–liquid ratio of 2:10. Copper removal is largely decreased by more water addition by the ratio up to 1:10. Addition of a small amount of water allows ZVS and $CuSO_4$ together in a high concentration solution in high viscous state, which is conducive to the full contact between ZVS and $CuSO_4$, thereby increasing the chance of collisions between atoms or ions. When the solution is too diluted with excess water addition, the contact chance between ZVS and Cu^{2+} during milling operation is largely decreased, correspondingly to barrier the reaction progression. The reaction mechanism gradually changes from the mechanical force collision in ball milling to simple stirring in a closed environment. Moreover, increase in dissolved oxygen from water addition will cause the fresh surface of ZVS exposed during ball milling to be oxidized into dense silicon oxygen compounds, which prevents the ZVS to play its reducing role. With the increase in the water added, the pH presents an upward trend, because the solution was gradually diluted and the reduction reaction tends to be weakened, without new formation of sulfuric acid, and gradually to reach the weak acid range resulting from copper sulfate itself.

3.2. Cu^{2+} removal mechanism

Fig. 2 shows the XRD patterns of precipitate samples, which were obtained by washing the slurry after ball milling with 200 mL water, filtered and dried at room temperature for 24 h. Fig. 2(a) shows the results by co-milling of ZVS and Cu^{2+} under different Si/Cu ratios. XRD patterns of the samples after reaction are compared with those of the ZVS ball milling alone. In addition to the remaining peaks of ZVS, new diffraction peaks of Cu_2O are observed clearly to appear, although with very low intensity. Formation of Cu_2O in the precipitate may be attributed also the fact of its resistance to acidity during milling operation. With an increase in Si/Cu ratio, the peak intensity of Cu_2O has become relatively obvious, due to the relative increase of Si content to promote the reductive ability for Cu^{2+} into Cu_2O. However, excess addition of Si at Si/Cu ratio of 100:1 makes the Cu_2O diffraction peak difficult to detect.

Fig. 2(b) shows the XRD patterns of the samples obtained at different milling time at a fixed Si/Cu ratio of 20:1. In the short time of ball milling at 1 h, there is no Cu_2O diffraction peak detectable in the filtered precipitate, which corresponds to the removal effect of Cu^{2+} less than 10%, shown in Fig. 1(b). With the prolongation of ball milling time, the diffraction peak of Cu_2O becomes more and more obvious, verifying that milling time plays an important role in the production of Cu_2O as the main mechanism of Cu^{2+} removal from solution. Although the prolongation of the reaction time will strengthen the reaction process, the

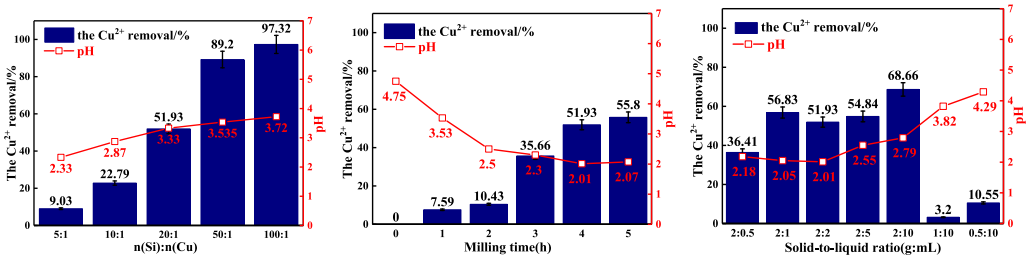


Fig. 1. (a). Changes in the removal percentage of Cu and pH with n(Si):n(Cu) (milling time: 4 h, solid-to-liquid rating: 2 g:10 mL, initial pH:5–6) (b). Changes in the removal percentage of Cu and pH with milling time (n(Si):n(Cu) = 20:1, solid-to-liquid rating: 2 g:10 mL, initial pH:5–6) (c). Changes in the removal percentage of Cu and pH with solid-to-liquid rating (n(Si):n(Cu) = 20:1, milling time: 4 h, initial pH:5–6).

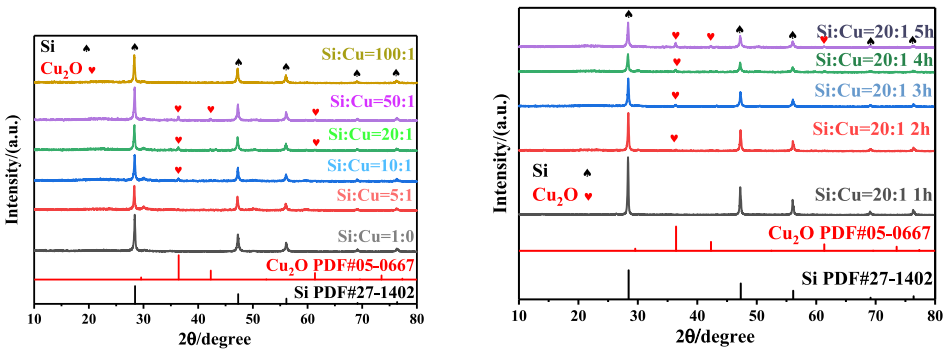


Fig. 2. (a). XRD patterns of the precipitates obtained at different n(Si):n(Cu) ratios (milling time: 4 h, solid-to-liquid rating: 2 g:10 mL, initial pH:5–6)(b). XRD patterns of the precipitates obtained at different ball milling times (n(Si):n(Cu) = 20:1, solid-to-liquid rating: 2 g:10 mL, initial pH:5–6).

optimal reaction time at 4 h is reasonable, considering the energy consumption and the trend of growth percentage. Qualitative characterization by XRD and quantitative analysis of soluble copper ions in the solution matches well to understand the reduction reaction between ZVS and divalent copper ions during their direct milling operation.

The filter residue obtained after washing the co-ground sample between Si and $CuSO_4$ was analyzed by Fourier infrared spectroscopy (FTIR) and the spectrum is shown in Fig. 3. Several obvious vibration modes of OH at 3500 cm^{-1} and 1589 cm^{-1} are observed [6], implying the existence of hydrated products, possibly amorphous silicon and copper oxides. Amplification of the spectrum was carried out in the range from 1400 cm^{-1} to 800 cm^{-1}. Several weak peaks are observed to transfer very important information: the vibration peak at 1144 cm^{-1} from Cu-O bonding [16,15], as well as the vibration peaks at 1067 and 829 cm^{-1} from Si-O bonding [26]. The Cu-O bond vibration peak at 1144 cm^{-1} further proves the formation of Cu_2O, confirming the results by XRD analysis. The occurrence of Si-O bonding as the results of silicon oxidation is another evidence for the reaction between ZVS and divalent copper, with copper reduced and at the same time silicon oxidized, to which XRD analysis does not offer direct information.

XPS analysis of valence state of related elements is very important to understand the reduction reaction between Si and Cu. Spectrum of Cu (2p) of the residue sample after washing is shown in Fig. 4(a). Two diffraction peaks at 952.0 eV and 932.2 eV have been found, confirming not only the existence of copper in the residue sample, but also the

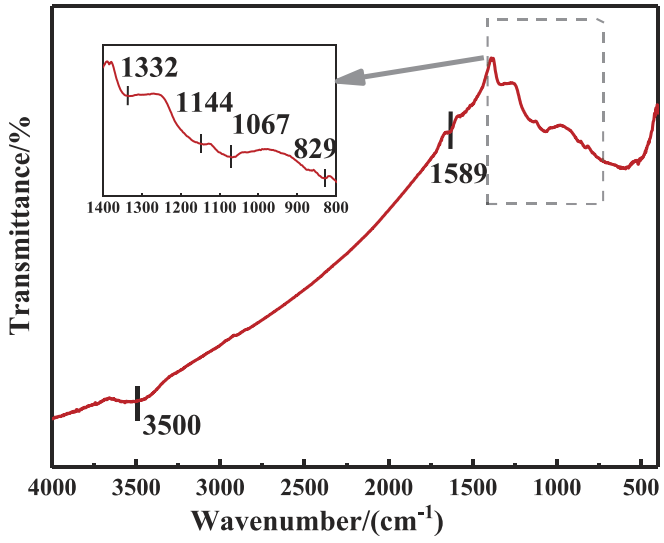


Fig. 3. FT-IR spectrum of the filtered residue after co-grinding of silicon and copper sulfate (n(Si):n(Cu) = 20:1, milling time: 4 h, solid-to-liquid rating: 2 g:10 mL, initial pH:5–6).

monovalence state of copper, because 952.0 eV from $2p_{3/2}$ orbital and 932.2 eV from $2p_{1/2}$ orbital are typical ones of Cu_2O, not from divalent copper [4,10,3]. No appearance of shake-up peaks in the spectrum typical for divalent copper is also an evidence for ruling out the existence of divalent copper in the residue sample, further verifying that soluble Cu^{2+} are reduced to insoluble Cu_2O under the strong reduction of ZVS to achieve the purpose of copper removal from solution.

XPS spectrum of Si(2p) is shown in Fig. 4(b). Different binding energies of 102.77 and 98.69 eV have been observed, corresponding to different valence states of silicon in the residue sample. Peak at 98.69 eV is the information from Si-Si bonding, due to the zero-valent silicon remaining in the sample from the excess use of silicon. It is interesting to note that peak at 102.8 eV appears in the spectrum resulting from the Si-O bonding, confirming the occurrence of silicon oxidation, consistent with the result by FT-IR analysis [34,17,21]. This value does not reach the high value around 104 eV, typical one of silicon dioxide, in the form of SiO_2. Together with a binding energy at 99.74 eV resulting from a highly reactive Si-O bonding, an intermediate state between ZVS and SiO_2, it may be understood that the oxidation of silicon during Si and Cu reaction is partially achieved to give an unstable state of silicon. Unfortunately, there is still a large amount of ZVS left at silicon form after the reaction and further investigation is needed to facilitate the efficiency for reduction ability of silicon.

SEM analysis was carried out on the residue sample together with element identification by EDS and the results are shown in Fig. 5. It can be clearly seen from the SEM image that there exist two different substances, of which the lighter color is Cu_2O, and the darker color is ZVS, coexising in the form of mixture. It also proves that the Cu^{2+} removal mechanism is realized by reducing soluble Cu^{2+} into insoluble Cu_2O as precipitate to achieve the copper removal, rather than simply Cu^{2+} adsorption on the surface ZVS. Actually it is not possible to have copper ions adsorbed on some solid particles within a strong acidic atmosphere.

From the reaction product of Cu_2O and the high pH value after the reaction, it can be considered that the reaction is a process of producing acid, namely the change of sulfate into H_2SO_4. The main reaction equation may be proposed as following:

$$Si + 2CuSO_4 + 2H_2O == Cu_2O + 2H_2SO_4 + SiO \quad (1)$$

Reaction equation occurs in the ball milling pot, and water, as a reactant, also participates in the reaction, which can also be explained by the fact that the reaction progresses steadily with the increase of solid–liquid ratio within certain range. The silicon oxide compound produced after the reaction is unstable such as SiO in an intermediate state, which may change in valent state depending on atmosphere during sampling operation. Due to the excess addition of ZVS, the reducing ability of the sample will be maintained by the low valent state, far from the fully oxidized state as silicon dioxide of tetravalence.

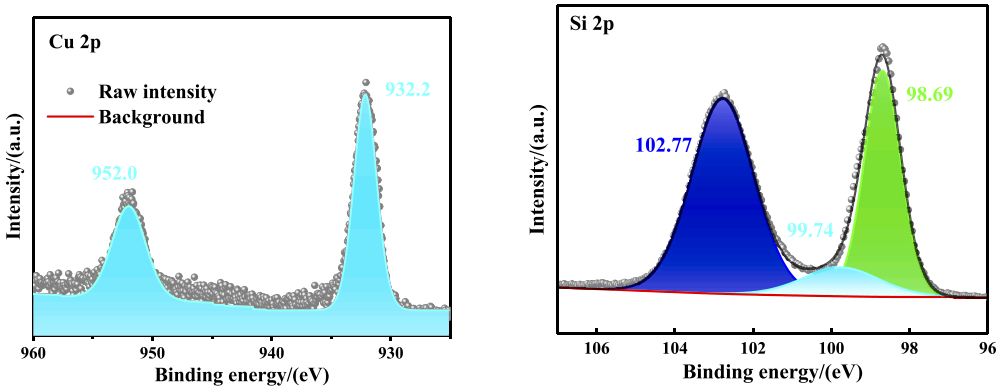


Fig. 4. XPS spectra of Cu(2p) (a) and Si(2p) (b) of the residue sample from the co-milled Si and $CuSO_4$ (n(Si):n(Cu) = 20:1, milling time: 4 h, solid-to-liquid rating: 2 g:10 mL, initial pH:5–6).

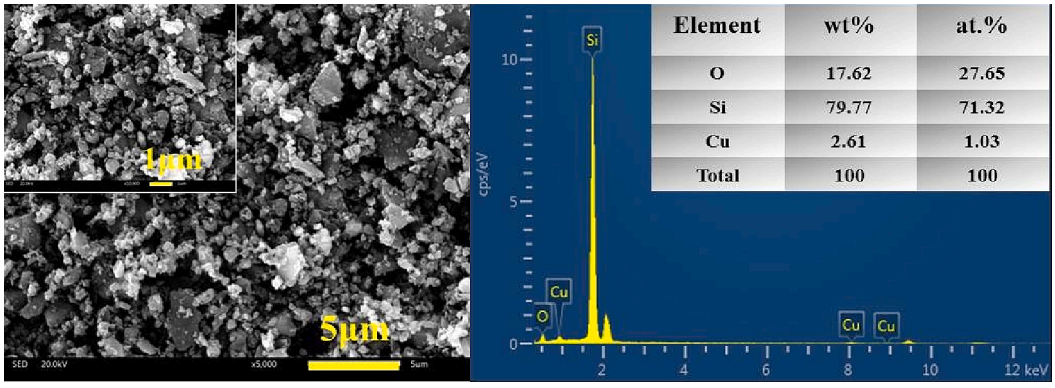


Fig. 5. SEM image of residue sample after washing co-milling of Si and $CuSO_4$ SEM image; b.EDS pattern and element distribution) (n(Si):n(Cu) = 20:1, milling time: 4 h, solid-to-liquid rating: 2 g:10 mL, initial pH:5–6).

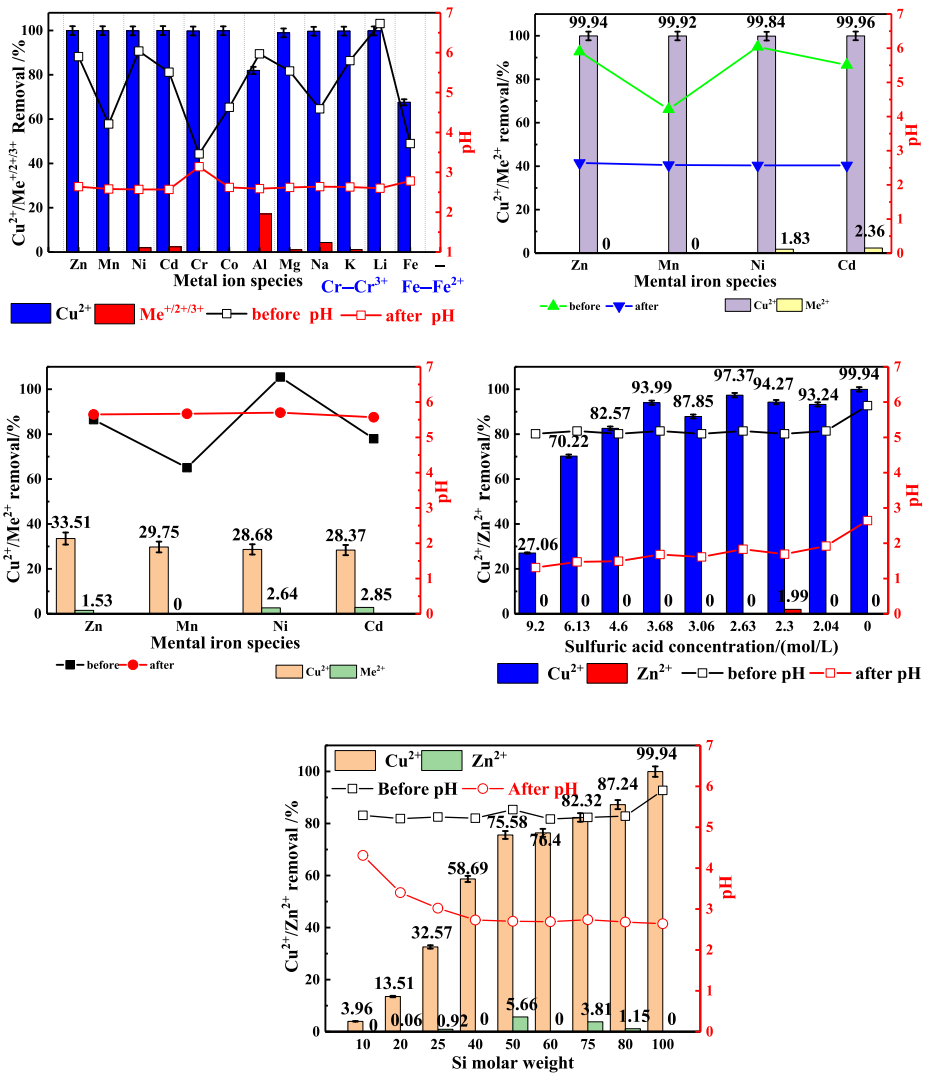
3.3. Application for copper recovery

By using the strong reducibility of ZVS and taking advantage of the intermediate valence state of copper element with +1 valence, soluble $CuSO_4$ can be reduced to insoluble Cu_2O through a simple ball milling operation. Many industrial production processes discharge waste solutions with usually mixed existences of different heavy metal cations, particularly from hydrometallurgical processing of sulfide minerals of copper, zinc and lead etc. For the enrichment and recovery of a specific metal, the coexistence state of a variety of heavy metals increases the difficulty in its purification. Through the above reported experimental results, Cu^{2+} can be reduced to Cu_2O, and Cu^{2+} in a waste solution with coexistence of other metal cations is expected also to be reduced to Cu_2O. If other divalent metal ions remain soluble at cationic states in the solution, there exists a chance for copper removal from these ions, to achieve enrichment and purification of copper as secondary resource.

Fig. 6 summarizes the quantitative data of copper removal at various conditions. Fig. 6(a) shows the changes in copper removal and pH of the solutions, of which 12 kinds of sulfates such as Zn, Cd, etc. heavy metals, and K, Na etc. were added separately with $CuSO_4$ to examine each effect on copper precipitation and removal. Except two cases of Al and Fe, where copper removal has been decreased to some degree, copper removals are achieved nearly completely without observable interference by the coexisting ions, which remain soluble in the solution without evident precipitation. These elements usually does not undergo valence change even with ZVS, allowing an efficient separation of copper from the solution by reduction to monovalent state. In the case of Al, copper removal performance is affected negatively to a low value and the decrease in Al solubility is also observed. Precipitation of Al on the surface of ZVS may be one reason to act as barrier to the reduction reaction for copper removal. As to the case of Fe, the situation is complicated and specific mechanism is not clear. Quite possibly the reduction of Fe by ZVS may occur to induce valence change in Fe together with Cu to interfere the reaction between ZVS and Cu. Detailed investigation should be performed on the effect of Fe coexistence.

The effect of solution volume in the milling pot, namely solid–liquid ratio on the reaction performance for copper removal was examined and the results are shown in Fig. 6 (b1 at 2 g:2mL; b2 at 2 g:10 mL, respectively) with changes in copper removal and pH during the co-milling ZVS, $CuSO_4$ and sulfates (Zn^{2+}/Mn^{2+}/Ni^{2+}/Cd^{2+}). First of all, in Fig. 6b1, no differences are observed within four sulfate salts of Zn^{2+}/Mn^{2+}/Ni^{2+}/Cd^{2+}, and all the coexisting four heavy metal ions are remaining in the solutions regardless of changes in the solid–liquid ratio. On the other hand, the removal percentage of Cu^{2+}changes largely with the change in solid–liquid ratio, regardless of the type of coexisting heavy metal. When the water volume inside the milling pot was 10 mL, in the figure of b2, copper removal percentage gives a low level around 30% with all four metals, due to low reaction performance in the diluted solution as shown in Fig. 1(c). In case of 2 mL water used, copper removal percentage gives a high level close to 100%, namely a nearly complete precipitation. A high solid–liquid ratio is similarly conducive to the reduction of copper ions by ZVS to achieve the purpose of transforming soluble copper ions into insoluble cuprous oxide even with the coexistence of other heavy metals. As to the changes in pH, a low value around 2.5 is obtained at the use of water volume of 2 mL, corresponding to the high copper removal percentage.

Since pH of the solution in mining wastewater and some industrial wastewater, such as electroplating wastewater and metal pickling wastewater, is in strong acidic range, the removal performance and pH changes of Cu^{2+} and Zn^{2+} by co-milling ZVS, $CuSO_4$ and $ZnSO_4$ at



(d)

Fig. 6. (a). Copper removal percentage and pH change under different ion species (n(Si):n(Cu) = 20:1, milling time: 4 h, solid-to-liquid rating: 2 g:10 mL/2g:2mL) (b). Copper removal percentage and pH change under solid-to-liquid rating (n(Si):n(Cu) = 20:1, milling time: 4 h, b1 solid-to-liquid rating: 2 g:2mL, b2 solid-to-liquid rating: 2 g:10 mL) (c). Copper removal percentage and pH change under initial acid concentration (n(Si):n(Cu) = 20:1, milling time: 4 h, solid-to-liquid rating: 2 g:10 mL) (d). Copper removal percentage and pH change under silicon dosage (milling time: 4 h, solid-to-liquid rating: 2 g:10 mL, initial pH:5–6).

different initial acidity regulated by H_2SO_4 were examined as example and the percentages are shown in Fig. 6(c). 2 mL pure water was replaced with sulfuric acid at different concentrations to simulate the acidity in acidic wastewater. It can be found that the acidity of the solution has no effect on the fixation effect of Zn^{2+}, that is, Zn^{2+}remains soluble under any acidic conditions. Fixation effect of Cu^{2+} basically changes with lowering trend with an increase in sulfuric acid concentration. However, even at a high concentration of 4.6 mol/L, the fixation percentage of copper ions can still be maintained at a high value over 80%, which has a great application prospect in the treatment of actual wastewater.

The effects of ZVS dosage on Cu^{2+} and Zn^{2+} removal percentage and pH change are shown in Fig. 6(d). Consistent with the above results of the removal percentage of $Cu^{2+}$by ZVS and the change of pH, copper removal increases largely with an increase in silicon dosage. At the dosage of 100:1 Si/Cu, Cu^{2+}can achieve nearly 100% removal effect, and Zn^{2+}remains almost completely in the solution.

Table 2 summarizes the reported copper enrichment and removal mainly on adsorption and compares with our method by ZVS reduction in an acidic system. Every reported method has advantages and

Table 2
Comparison of previously reported Cu^{2+} removal from strongly acidic with our research by ZVS.

Removal method	Removal percentage	pH	Reaction mechanism	Optimum reaction time	Maximal adsorption capacity (mg/g)	References
Lemon peel	89%	3	adsorption	15 min	13.2	[19]
Electroosmos	10%	2	Reduction	2 h	–	[11]
Molybdenum sulfide modified dipyrrolidine chelating resin	>99%	<3	adsorption	24 h	329	[9]
Zeolite and cellulose composites	32.4%	>4	adsorption	2 h	12.74	[7]
ZVI	99.99%	4	Reduced to Cu	30 min	99.77	[31]
ZVS	89.2%	<2	Reduced to Cu_2O	4 h	46.36	This study

disadvantages. ZVS reduction as a novel choice presents not only excellent performance with high removal capacity of 46.36 mg/g, but also high selectivity relying on a unique formation of copper monoxide, which is usually difficult to achieve on the common adsorption operation. Application in the future will promote the recovery of the highly required copper through processing suitable waste solution/solid.

This study provides the data as the fundamental basis as a new approach for the reduction and precipitation of copper ions to achieve selective separation by mechanochemical means of zero-valent silicon. When heavy metal ions and organic compounds are complexed, the removal performance of heavy metal ions by zero-valent silicon will change largely, and it is should be confirmed to what range the proposed process could be applied particularly with the existences of organic compounds. Continuous investigation on real wastewater from a mining company of hydrometallurgical process containing various kinds of heavy metals but less influence of organic compounds has been under planning to confirm the feasibility for possible application.

As to the treatment of the sludge with copper selectively precipitated and possible method to recover copper to serve the purpose of circular economy, we are considering two approaches to recover copper from the sludge. Based on the existing state of copper suboxide, namely copper(I) oxide, and that silicon is stable in acid, one way is to recover copper at monovalent state by dissolving copper suboxide directly into a concentrated HCl as product $HCuCl_2$ without change in valence. Another choice is to recover copper at divalent state to serve as a source for copper electrolysis by dissolving the sample in sulfuric acid solution. In order to increase the dissolution of copper suboxide and at the same time to avoid a disproportionation reaction happening between it and sulfuric acid, the sample will be oxidized by air with moisture to transform copper suboxide into copper oxide (CuO) before the acidic dissolution. The research plan is under consideration for confirming which approach is feasible and reliable so that the copper can be recovered at high purity as secondary sources for circular economy.

3.4. Practical application for copper recovery

Based on the basic data of 3.3, removing copper ions from mixed heavy metal ion solutions with other ions remaining in the solution, verifying test was conducted on a real wastewater from the sulfide mineral leaching. The experimental results are shown in Fig. 7. Cu^{2+} could achieve a removal rate of 92.25%, while Ni^{2+} and $Fe^{2+/3+}$ were basically remaining in the solution, with a small amount of Co^{2+} being removed, with a removal rate of 5.31%, confirming the possibility of separating copper from the mixed heavy metal ions. The ball milling environment was conducted in a strong acidic atmosphere with a pH value of 1.64, demonstrating that the technical means can resist strong acidity.

4. Conclusions

Alkali precipitation is widely used in the removal of heavy metal ions, but for mine wastewater and some industrial wastewater with strong acidity, the addition of a large amount of alkali will undoubtedly increase a lot of economic cost. In this paper, co-milling ZVS and $CuSO_4$ to remove specifically Cu^{2+} from solution by reduction precipitation has been carried out in strong acidic environment to develop a new process. Cu_2O produced by reduction exists stably in a relatively strong acidic environment and has positive significance for subsequent enrichment and recovery from the high selectivity. At the same time, this technology can also achieve the goal of separating copper element from nickel, iron etc. in a real mixed heavy metal ion wastewater obtained by leaching sulfide mineral. This research work also serves the purpose of using the recycled Si from the end-of-life solar panels close in 2030. Using the advantage of the formation of Cu_2O in the intermediate valence state of copper elements, the separation and purification of Cu^{2+} from other metal ions at stable divalent state have a wide application prospect in the recovery and purification of secondary Cu sources.

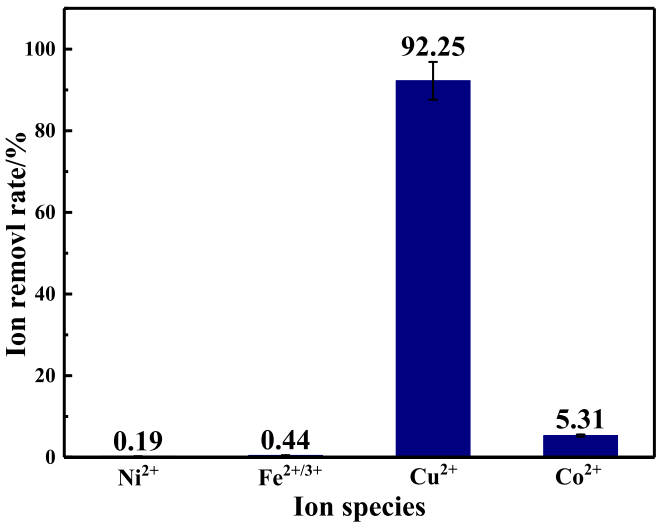


Fig. 7. Different ion removal rates in actual wastewater (ball milling time: 4 h, ball milling speed: 300 rpm, solid–liquid ratio: 2 g: 2 mL, ZVS additive amount: 3 g).

CRediT authorship contribution statement

Kai Li: Investigation, Methodology, Formal analysis, Writing – original draft. **Chao Wang:** Visualization, Writing – review & editing. **Huimin Hu:** Visualization, Writing – review & editing. **Qiwu Zhang:** Conceptualization, Supervision, Funding acquisition, Writing – review & editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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