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Leaching of Zinc- containing converter sludge in sulfuric acid solutions

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Abstract. *With the reusing of galvanized scraps in the converter steelmaking process, zinc content in converter sludge increases gradually. The contents of Fe and Zn in Zinc-containing converter sludge are 48.77% and 3.65% respectively. In this study, the hydrometallurgical process of converter sludge in sulfuric acid solutions under atmospheric pressure is investigated in laboratory scale. Leaching behaviors and a sequence of elements from converter sludge were studied. The differences in leaching sequence, metal separation could be achieved by selective leaching.*

Keywords: *Converter Steelmaking, Zinc-Containing Converter Sludge, Leaching, Hydrometallurgy*

1. Introduction

Converter sludge is generated in the converter steelmaking process, accounting for a quarter of the total amount of dusts and sludges in a steelmaking plant. It is normally returned to sintering process as a smelting ingredient. In recent years, more and more galvanized scraps are used in steelmaking process, most of zinc from scraps is carried out with other particles into the off-gas cleaning system, and collected as dusts or sludges subsequently. Consequently, zinc content in the converter dust increases gradually. However, it is impossible to recycle these sludges directly as usual because of continuous zinc enrichment which would cause the zinc load on blast furnaces to exceed the limit, which would harm the stability and safety of long-term production eventually [1-2].

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Due to the low zinc content in converter dust, conventional technology for recovering iron and steel dust is not applicable [3-4]. Reduction smelting process is one of the most effective methods to recycle low zinc content converter dust and sludge. The converter dust and sludge would be reduced to metal pellets at 1100-1300℃ by reducing agents or in a reducing atmosphere. Zinc enters into flue gas in the form of vapor and will be collected as a form of impure zinc oxide in dedusting equipment. Some researchers have studied the hydrometallurgical leaching of other zinc-containing dust and sludge in steel plants such as blast furnace dust and electric furnace dust, but there are still few reports about the research on acidic leaching of low zinc content converter sludge.

The main objective of this study was to explore the feasibility of acid leaching recovery of zinc-containing convert sludge, especially focusing on the influences of the acid concentration, temperature of metal extraction into the acid solution and the behaviors of the main metals in convert sludge in hydrometallurgical process in acidic solutions.

2. Experimental

The chemical composition of converter sludge was determined by inductively coupled plasma (ICP) using Agilent 5110. The mineralogical phases of the converter sludge were determined by X-ray diffraction (XRD) using Bruker Phase D2. The scan ranges from 10 to 80° 2θ using a step size of 0.02° 2θ and a step time of 0.02s per step. The XRD analysis were conducted under the conditions of 30kV and 10 mA. Scanning electron microscopy (SEM) measurements using Phenom LE were performed to get information on the structure, morphology and chemical composition of converter sludge particles [5].

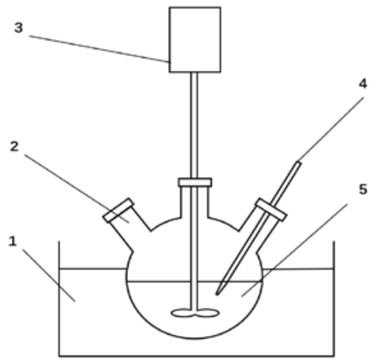

Figure. 1 Schematic diagram of the leaching apparatus (1. water thermostat; 2. flask with three necks; 3. mechanical stirrer; 4. thermometer; 5. Leaching solution)

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The leaching experiments were conducted using the apparatus shown in Figure.1. A 500 mL glass flask with three necks used as a leaching reactor was placed in a water thermostat. 3 g convert sludge sample was added to the flask and 300 mL lixiviant was poured into the reactor to make a L: S ration of 100. All the leaching tests were carried out with H_2SO_4 solutions of 0.05, 0.1, 0.5and 1.2 M at temperatures of 30, 50, 70 and 90^oC. The samples for metal concentration analysis were taken at the time interval of 5, 10, 15, 30, 60, 90, 120 min [6]. Analysis of the metal concentration in leaching solutions were conducted by inductively coupled plasma using Agilent 5110.

3. Results and discussion

3.1 Characterization of convert sludge

The flue gas generated from converter is at a high temperature of 1500-1600℃. It is cooled to about 900℃ through heat exchange flue, and then it enters spray washing tower for spraying which could cool it to 90℃ as fast as possible. The mixture of dust and water is discharged from cyclone dehydrator and enters a gravity sedimentation tank for sedimentation. Then convert sludge (as shown in Figure.3) is collected through pressure filtration. A sample of convert sludge with chemical composition listed in Table.1, was used infurther experiment [7].

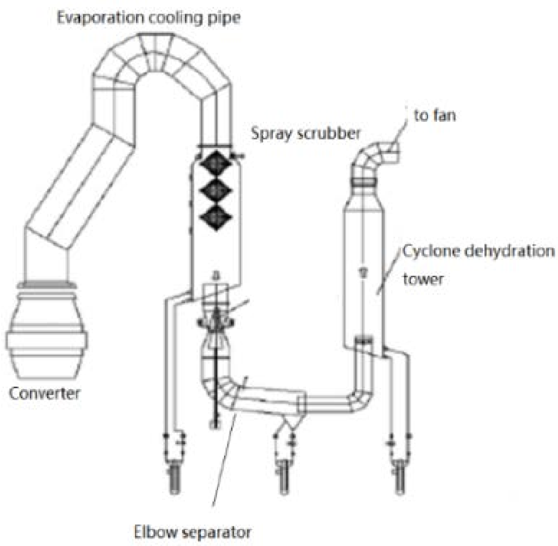

Figure. 2 Converter off-gas cleaning system flow sheet

Figure. 3 Containing Converter Sludge

Table 1 Chemical Composition of convert sludge %

element	Al	Ca	Cr	Fe	Mg	Mn	Na	Pb	Zn
%	0.062	9.00	0.04	48.77	1.11	0.65	0.07	0.08	3.65

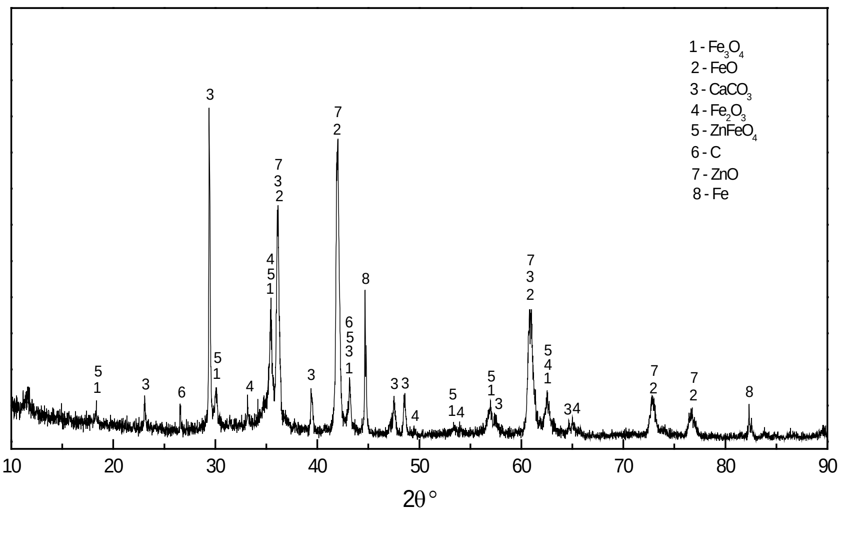

Figure. 4 X-ray diffraction pattern for converter sludge

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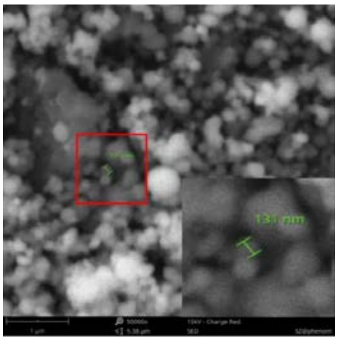

Figure. 5 Scanning electron micrograph of converter sludge particles

For the X-ray diffraction pattern, major phases were identified as magnetite (Fe_3O_4), hematite (Fe_2O_3), wustite (FeO) and so on. Zinc in the examined converter sludge is in various forms as zinc ferrite ($ZnFe_2O_4$) and zinc oxide (ZnO).Figure.5 shows the scanning electron micrograph of converter sludge particles. It is obvious that most of the converter sludge particles appear as spherical fine-grained particles which are almost submicronic and smaller than 1 μm. Most of the fine particles are present in agglomerated morphology.

3.2 Leaching sequence of metals

The leaching sequence of metals from convert sludge was studied in sulfuric acid concentration (0.05, 0.1, 0.5and 1.2 M) at 50^{o}C for 120 min. During the sulfuric acid leaching process, the following chemical reactions are assumed[8]：

$$Fe_3O_4 + 4H_2SO_4 = Fe\ (SO_4)\ (aq) + Fe_2(SO_4)_3(aq) + 4H2O \quad (1)$$

$$Fe_2O_3 + 3H_2SO_4 = Fe_2(SO4)_3(aq) + 3H_2O \quad (2)$$

$$FeO + 4H_2SO_4 = Fe\ (SO_4)\ (aq) + 4H_2O \quad (3)$$

$$2CaCO_3 + 2H_2SO_4 = CaSO_4(s) + CaSO_4(aq) + 2CO_2 + 2H_2O \quad (4)$$

$$ZnO + H_2SO_4 = ZnSO_4(aq) + H_2O \quad (5)$$

$$ZnFe_2O_4 + 4H_2SO_4 = ZnSO_4(aq) + Fe_2(SO_4)_3(aq) + 4H_2O \quad (6)$$

The phases of other elements such as Al, Na, Mn, Cr, Mg were hardly able to be identified by XRD due to their low contents. Based on the sludge formation mechanism, it is inferred that most metals may exist in the form of oxides while a small amount may exist in the form of soluble salts. Therefore, compounds of other metals may dissolve or react with acid like oxides of main elements.As can be seen from Figure.1(a), only Ca, Na, Mg were leached in the case of low acid concentration 0.05 M. With an increasing of reacting time, the leaching efficiencies

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of Mg and Na increasedwhile the leaching efficiency of Ca decreased. Because of the stronger alkalinity than other metals, Ca, Na, Mg elements would react with acid first in the case of low acid concentration. Since these alkaline metals exist in the form of oxides in the sludge, alkaline oxides will continue to dissolve into solution resulting in the precipitation of previously leached Ca and the decrease of leaching efficiency [9].

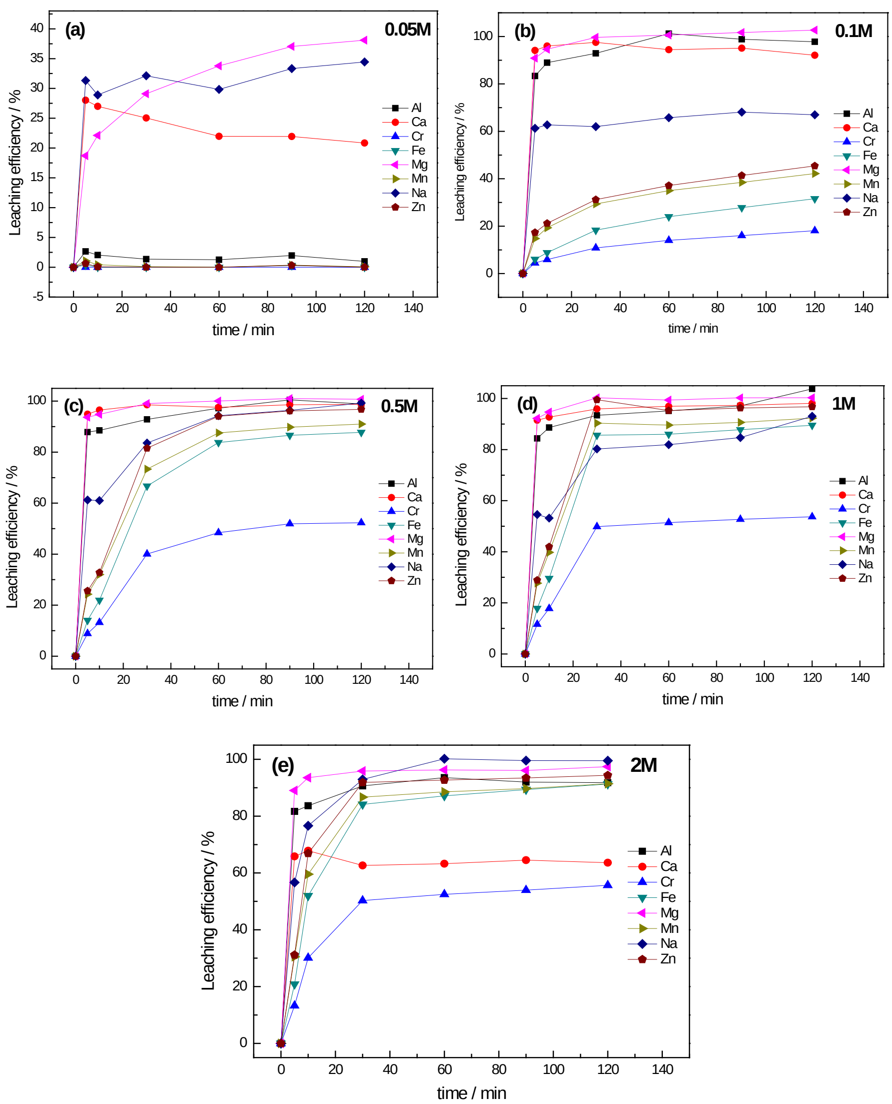

Figure. 6 Leaching sequence of main metals in convert sludge

(3 g, 300 mL, 0.05, 0.1, 0.5, 1, 2 M sulfuric acid, 50^{o}C)

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As shown in Figure.1(b), when the acid concentration reaches 0.1 M the reactions of alkaline metals Na, Ca, Mg and Al are completed rapidly in 30 minutes and other elements began to enter the solution. Although Na is an alkaline element, Na leaching efficiency is only 60% which is more less than Mg, Ca, and Al over 90%. It is inferred that the part of Na not leached might exist as a form combined with other undissolved elements. After the reaction of these element compounds, Na would be leached simultaneously. With an increase of acid solution to 0.5 and 1 M, most Zn, Mn, and Fe are involved in the reaction achieving efficiencies higher than 80%. Based on thermodynamic data, Zn will react with acid more easily than Fe and will be leached preferentially.

When acid concentration increases to 2 M, all elements are dissolved sufficiently, and metal leaching efficiencies get higher than 85%, except Ca and Cr. The reason for the decrease of Ca's leaching efficiency is that the sulfate ion concentration is too high in the 2 M sulfuric acid solution, which leads to combinations with previously leached Ca^{2+} ,resulting in precipitation in the form of $CaSO_4 \cdot 2H_2O$. According to the references, the phases of chromium in convert sludge are probably of Cr_2O_3 and $FeCr_2O_4$, which are difficult to be leached completely, especially for $FeCr_2O_4$, which is a relatively stable spinel structure. Based on the studies above, the elements are leached in the following order: Na, Ca, Mg → Al → Zn → Mn→ Fe→ Cr.

3.3 Leaching behavior of Fe

Figure.7a to Figure.7d show the extraction curves of Fe expressing the percentage of Fe passing into the solution. These experiments were carried out under following conditions: sulfuric acid concentrations: 0.05-2M, temperatures: 30, 50, 70and 90°C, L:S ratio:100. The highest Fe leaching efficiency of 94.0% was achieved by applying 1 M sulfuric acid at 90 ℃ for 120 min reaction. As shown in Figure.7, sulfuric acid concentration has a considerable effect on the amount of Fe leached into the solution. It is obvious that Fe is hardly leached under low acid concentration condition such as 0.05 M. Iron compounds begin to react when the acid concentration reaches 0.1 M, but the reaction could not be completed owing to the insufficiency of acid. Whereas a high concentration sulfuric acid will be a certain oxidation property at high temperature, which may produce passivation on the mineral surface, resulting in incomplete leaching. In this case, the leaching rate of 2 M sulfuric acid solution at 70 and 90℃ is lower than those of 0.5 and 1 M ones. Temperature is also an important factor for the dissolution of Fe. The leaching reaction rate is accelerated obviously with the increasing of temperature. And a significant leaching efficiency could also be reached under a high concentration acid condition if leaching time is sufficient [10].

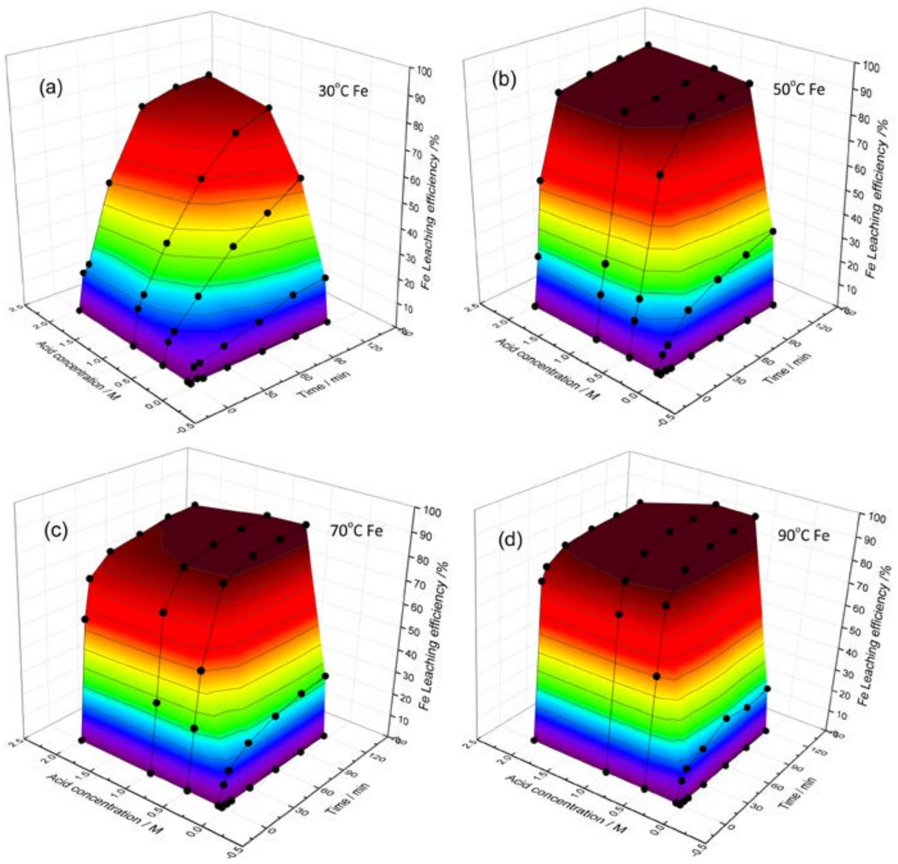

Figure. 7 Effect of sulfuric acid concentration on the Iron extraction at various temperatures (3g, 300ml, 0.05, 0.1, 0.5, 1, 2M sulfuric acid, 30, 50, 70, 90oC)

3.4 Leaching behavior of Zn

Figure.8a to Figure.8d illustrate the leaching curves for Zn under the same experimental conditions. Most of zinc in convert sludge exists in the form of a chemical combination with iron, which leads to a similar leaching behavior with that of iron.

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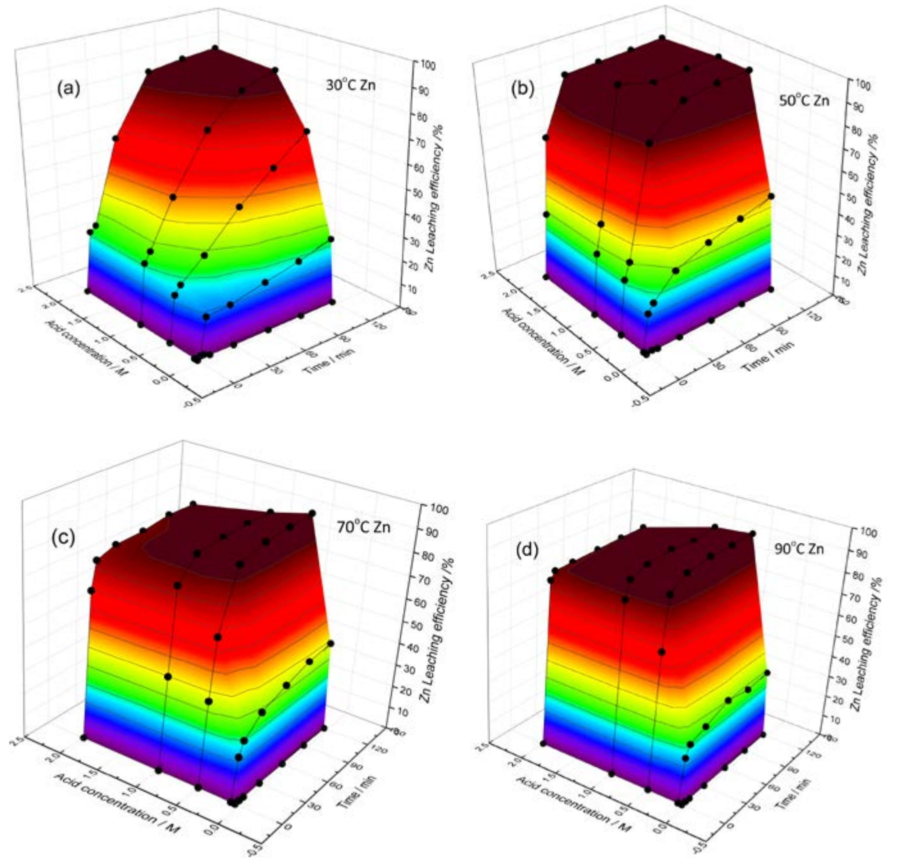

Figure. 8 Effect of sulfuric acid concentration on the Zinc extraction at various temperatures (3g, 300ml, 0.05, 0.1, 0.5, 1, 2M sulfuric acid , 30, 50, 70, 90^{o}C)

According to converter sludge formation mechanism, zinc combined with iron is located on the surface of dust particles, so the leaching rate of zinc is higher than that of iron and reaches plateau within 60 minutes at temperature of 50, 70 and 90^{o}C. The higher the reaction temperature, the shorter it takes to reach leaching equilibrium. Based on thermodynamic parameters, zinc is prior to iron to react with acid, as a result, complete leaching of zinc does not require so high temperature and high acid concentration. The maximum value for Zn leaching efficiency of 99.1% is obtained at a temperature of 50 ^{o}C, in a reaction time as 30 min, and at a sulfuric acid concentration of 1 M. Zn leaching efficiency is not improved with a further increase of temperature, even slightly decreased at 70 and 90^{o}C though [11-12].

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3.5 Leaching behavior of Ca

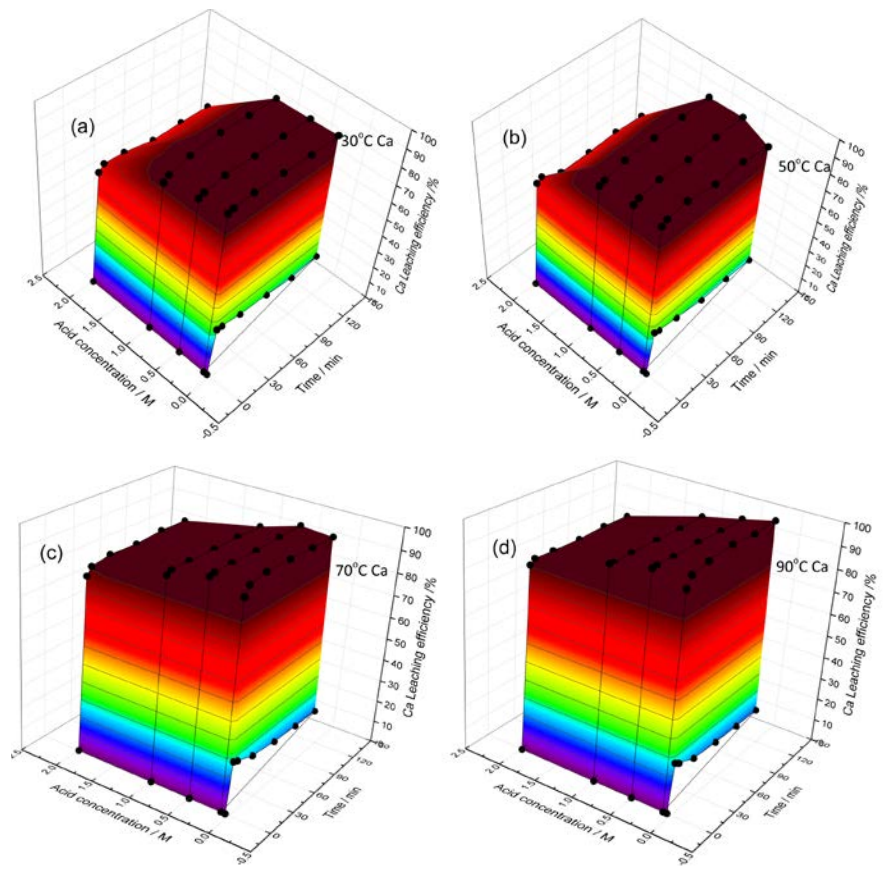

Figure. 9 Effect of sulfuric acid concentration on the Calcium extraction at various temperatures

(3g, 300ml, 0.05, 0.1, 0.5, 1, 2M sulfuric acid, 30, 50, 70, 90^oC)

Figure.8a to Figure.8d demonstrate the leaching curves for Ca under the same experimental conditions as that of Fe and Zn. Since calcium is alkaline metal, leaching equilibrium can be achieved within 10 minutes. Acid concentration (acid amount) is the most important factor for calcium leaching. Insufficient acid amount leads to a low leaching efficiency in the case of acid concentration as 0.5 M. However, under a higher acid concentration condition of 2 M, a large number of sulfates will combine with Ca^{2+}, resulting in precipitation as $CaSO_4 \cdot 2H_2O$, leading to a decrease of leaching efficiency of 70%. Therefore, only at an appropriate acid

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concentration of 0.1-1M, Ca could be completely leached achieving a high leaching efficiency nearly 100%. Due to the high reacting rate, the temperature has little effect on the leaching of Ca. However, the solubility of $CaSO_4 \cdot 2H_2O$ is improved when temperature is increased. Ca leaching efficiencies at 70 and 90^oC are over 80% much more than that at 30 and 50^oC. In this case, the precipitation of $CaSO_4 \cdot 2H_2O$ is reduced and the leaching efficiency of Ca rises.

4. Conclusion

Leaching of metals from converter sludge was studied in sulfuric acid medium. The leaching sequence of metals is as follows: Na, Ca, Mg → Al → Zn → Mn→ Fe→ Cr.

Based on the differences in metal leaching behavior, multi-stage leaching might be a reasonable and recommended method for metals recovery of converter sludge. Using water or low concentration acid as the lixiviant in the first leaching stage, the alkaline elements are able to be leached and separated by filtration. Then the second leaching stage is reached by applying 1 M sulfuric acid at 50^oC for 30 min, while more than 99% of the Zn will be leached into the solution.

Separation of most main metals is achieved by selective leaching. However, part of iron is still leached during zinc leaching, which is inevitable under this condition. Complete separation of zinc and iron may be a great obstacle of this recovery method. Due to the amphoteric chemistry of zinc, the separation of zinc and iron is better in an alkaline reaction system which could be considered to be a more appropriate method for treating this kind of sludge with high iron and low zinc content.

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