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Studies on the Extraction of Copper and Zinc from Waste Catalysts resulted from Catalytic Conversion of CO

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Abstract: The paper presents studies on the extraction of copper and zinc from the solid waste catalyst resulted from the conversion of CO with water steam. In order to find the optimum conditions for the extraction we studied the influence of several parameters on the copper and zinc extraction degree: the nature of the acid used as extraction agent (HCl, HNO₃, and H₂SO₄), the concentration of the acid solutions (5, 10, 15, 20 and 30%), the stirring time (2.5, 5, 7.5, 10, 12.5, 15, 30, 45 and 60 minutes) and the size of catalyst particles (< 0.5 mm, 0.5–1 mm, 1–2 mm, 2–4 mm). The copper and zinc recovered from the waste catalyst can be used at the obtaining of complex mineral fertilizers with microelements.

Keywords: waste catalyst, copper recovery, zinc recovery

1. Introduction

The homogeneous conversion of CO with water steam $(CO + H_2O = CO_2 + H_2)$ occurs slowly even at high temperatures (up to 1000°C). In order to increase the reaction rate, in industry one use two types of catalysts: medium temperature and low temperature catalysts.

Lately, an important attention is accorded to the low temperature catalysts for the conversion of CO with water steam. These catalysts are based on copper oxide, zinc oxide and chromium oxide, and aluminum oxide. The high catalytic activity of the low temperature catalysts is due to the presence of copper and increases with the increase of copper content [1-4].

In the reduction process, the copper oxide is reduced to metal and the other oxides remain as they are. The reduced catalyst has a specific surface of 50-150 m² g⁻¹ and can be used for about two years. After that it becomes a solid waste that should be reused.

A way to reuse the waste catalyst could be the extraction of the component metals using various acids and their use at the obtaining of complex mineral fertilizers with microelements. That can be done if the amount of the extracted metals is sufficient.

The aim of the studies presented in the paper was to find the optimum conditions for the extraction of copper and zinc from the waste catalyst resulted from the conversion of CO with water steam [5-10].

2. Experimental

In order to determine the initial content of copper and zinc, the catalyst samples were brought into solution using concentrated HCl and HNO₃ solutions (3:1) [5].

In view of copper and zinc ions extraction, various fractions of catalyst (< 0.5 mm, 0.5–1 mm, 1–2 mm, 2–4 mm) have been treated with HCl, HNO₃ and H_2SO_4 solutions of various concentrations (5,10, 15, 20 and 30%).

A certain amount of catalyst was treated with 20 mL acid solution (ratio S:L = 3:1) under continuous stirring (for 2.5, 5, 7.5, 10, 12.5, 15, 30, 45 and 60 minutes), at a temperature of 20°C. After stirring, the samples were filtered.

The concentrations of copper and zinc ions in the solutions have been determined by atomic absorption spectrophotometry using an VARIAN Spectr AA 110 spectrophotometer [11].

3. Results and discussion

In order to find the optimum conditions for the extraction of metal ions from the catalyst, we studied the influence of concentration of the acid solutions, stirring time and fraction of the catalyst on the copper and zinc extraction degree.

3.1. The assay of copper and zinc content of the catalyst samples

Following the chemical analysis, we found the values for copper and zinc content of the catalyst samples presented in Table 1.

TABLE 1. The copper and zinc content of the catalyst samples

Fraction, mm	Cu [%]	Zn [%]
< 0.5	31.75	21.88
0.5-1	39.59	21.35
1–2	36.43	21.78
2-4	32.51	20.68

The experimental data show a high content of copper and zinc that allows us to conclude that this catalyst can be used for studies on the copper and zinc extraction. 3.2. Studies on the influence of the concentration of the acid solutions and of the catalyst fraction on the copper and zinc extraction degree

Figures 1-3 illustrate the influence of the concentration of the acid solutions and of the catalyst fraction on the copper and zinc extraction degree reached

after 15 minutes of stirring. One observes that the extraction degree of both copper and zinc increases as the concentration of the acid solution and the size of the catalyst particles increase. A high extraction degree can be reached using \sim 30% acid solution and the fraction 2–4 mm.

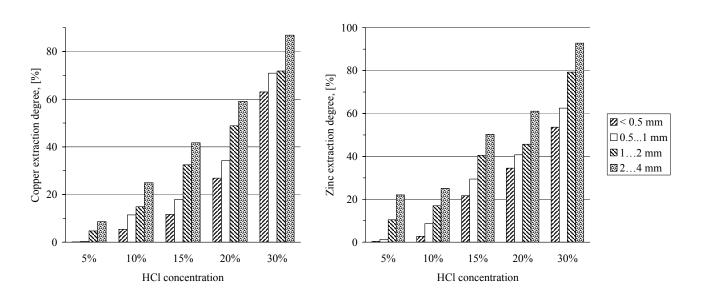


Fig. 1. The influence of the concentration of HCl solution and of the catalyst fraction on the copper and zinc extraction degree

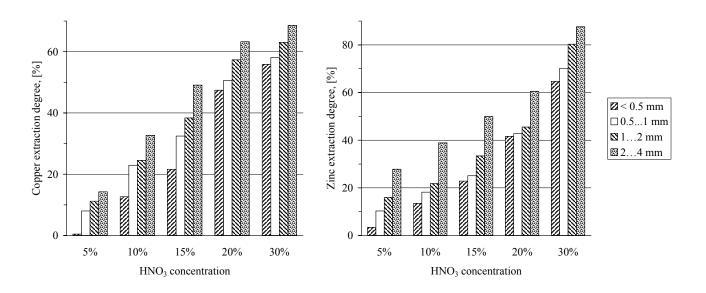


Fig. 2. The influence of the concentration of $\rm HNO_3$ solution and of the catalyst fraction on the copper and zinc extraction degree

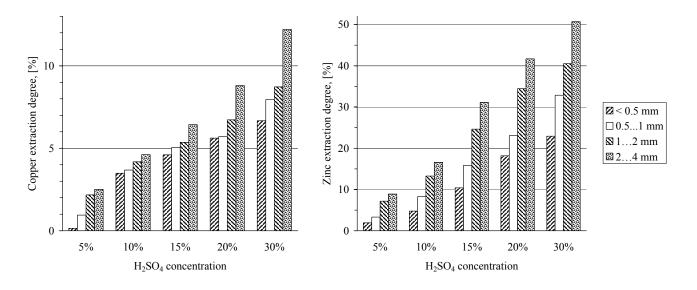


Fig. 3. The influence of the concentration of H_2SO_4 solution and of the catalyst fraction on the copper and zinc extraction degree

3.3. Studies on the influence of the stirring time and the nature of the acid on the copper and zinc extraction degree

Figure 4 shows the influence of the stirring time on the copper and zinc extraction degree when 30% acid solutions and the fraction 2–4 mm of the catalyst were used. One notice that for both copper and zinc the extraction degree

increases with the increase of stirring time up to 5 minutes, after that remaining practically the same. The figure also shows that the extraction degree depends strongly on the nature of the acid used as extraction agent. In both cases of copper and zinc a higher extraction degree was reached using 30 % HCl solution.

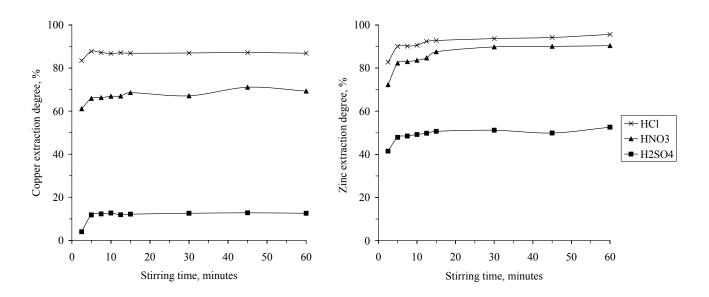


Fig. 4. The influence of the stirring time on the copper and zinc extraction degree

4. Conclusions

The purpose of the studies presented in the paper was to find the optimum conditions for the extraction of copper and zinc ions from the solid waste catalyst resulted from the conversion of CO with water steam. We studied the influence of several parameters on the copper and zinc extraction degree: the nature of the acid used as extraction agent, the concentration of the acid solutions, the stirring time and the size of catalyst particles.

We found that at a temperature of 20° C and a ratio L:S = 3:1, the separation degree of both copper and zinc increases with the increase of acid concentration and also with the increase of the size of catalyst particles.

The separation degree increases with the increase of stirring time up to 5 minutes. A longer stirring period has no influence on the extraction degree.

One can conclude that the optimum conditions for the extraction of copper and zinc ions from the solid catalyst waste are as follows:

- size of the catalyst particles: 2-4 mm;
- stirring time: 5 minutes;
- temperature: 20°C;
- ratio L:S = 3:1;
- acid concentration: 30%.

In both situations a higher extraction degree was reached using 30 % HCl solution (87.7% for copper and 90.1% for zinc).

The copper and zinc recovered from the waste catalyst can be used at the obtaining of complex mineral fertilizers with microelements.

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