Studies Regarding the Recovery Possibilities of Heavy Metals from Waste Catalysts Resulted from CO Conversion

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During CO conversion with water steam, the reaction occurs very slowly even at higher temperatures. In order to increase the reaction rate, catalysts of slow temperature based on copper oxide, zinc oxide, chrome oxide and aluminium oxide are used. A way to reuse these waste catalysts is the extraction of the heavy metals with different acids. In this paper we carried out studies in order to establish the optimum conditions of copper and zinc extraction from waste catalysts. The waste catalyst was separated in four fractions (< 0.5; 0.5 – 1; 1 – 2 and 2 – 4 mm). For the extraction we used HCl, HNO_3 and H_2SO_4 solutions of various concentrations (5, 10, 15, 20 and 30 %), at various stirring times (2.5, 5, 7.5, 10, 12.5, 15, 30, 45 and 60 minutes) and various stirring speeds (200, 400, 600 and 800 rot/min). For all used acids, the optimum conditions for zinc and copper ions extraction from waste catalyst are: dimension of the catalyst particles: <0.5 mm; stirring time: 15 minutes; acid concentration: 30%; stirring speed: 600 rot/min.

Keywords: waste catalysts, extraction, copper extraction, zinc extraction and absorption spectrophotometry

During CO conversion with water steam, the reaction occurs very slowly even at higher temperatures (1000°C). In order to increase the reaction rate, catalysts of slow temperature based on copper oxide, zinc oxide, chrome oxide and aluminium oxide are used [1-3].

The higher catalytic activity of these catalysts is due to the presence of copper and increases with the increase of copper content. The catalysts are used for maxim two years and then become solid waste which must be reused.

A way to reuse these waste catalysts is the extraction of the heavy metals with different acids. The extracted metals can be reused for the obtaining of fertilizers with micronutrients, or at the obtaining of various salts [4-6].

In this paper we studied the establishment of the optimum conditions of copper and zinc extraction from waste catalysts.

Experimental part

The waste catalyst was separated in four fractions: I < 0.5 mm, II = 0.5 – 1 mm, III = 1 – 2 mm, IV = 2 – 4 mm. The catalyst fractions were mineralized and in the resulted solutions it was determined the zinc and copper concentration in order to find the initial content of heavy metals in the catalyst.

For the extraction of heavy metals were used the stoichiometric quantities of waste catalyst needed and a well determined volume of HCl, HNO_3 and H_2SO_4 solutions, of various concentrations (5, 10, 15, 20 and 30 %), at various stirring times (2.5, 5, 7.5, 10, 12.5, 15, 30, 45 and 60 min) using various stirring speeds (200, 400, 600 and 800 rot/min) of the glass agitator. After stirring, the samples were filtered and it was determined the residual concentration of the heavy metals in the solutions.

The heavy metals concentrations were determined through atomic absorption spectrophotometry using an atomic absorption spectrophotometer Varian SpectrAA 110.

In order to establish the optimum conditions of heavy metals extraction from catalyst has been considered the dependence of heavy metals separation degree versus the concentration of the used acid, versus the dimensions of the particles of the catalyst, time and stirring speed.

Results and discussion

The chemical composition of the waste catalyst

The experimental data regarding the initial composition of the waste catalyst, separated on the four fractions are presented in table 1.

The initial composition of the catalyst is almost the same for all four fractions.

The influence of the acid concentration used for extraction [7-9]

The experimental data regarding the dependence of the heavy metals separation degree on of the acid

Table 1

THE INITIAL COMPOSITION OF THE WASTE CATALYST

Fraction	Heavy metals ions concentrations [%]	
	Zn	Cu
I	20.7	31.8
II	21.4	32.5
III	21.8	36.4
IV	21.9	39.6

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concentration of the acid used for extraction and on the particles dimension of the catalyst particles, at the stirring time of 15 min and at the stirring speed of 600 rot/min are presented in figures 1-6.

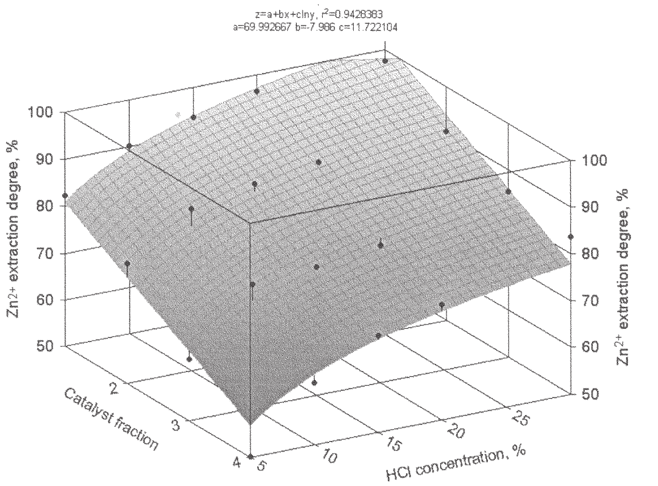

Fig. 1. Dependence of the zinc ions separation degree on the HCl concentration and on the catalyst fraction, at 15 min and 600 rot/min

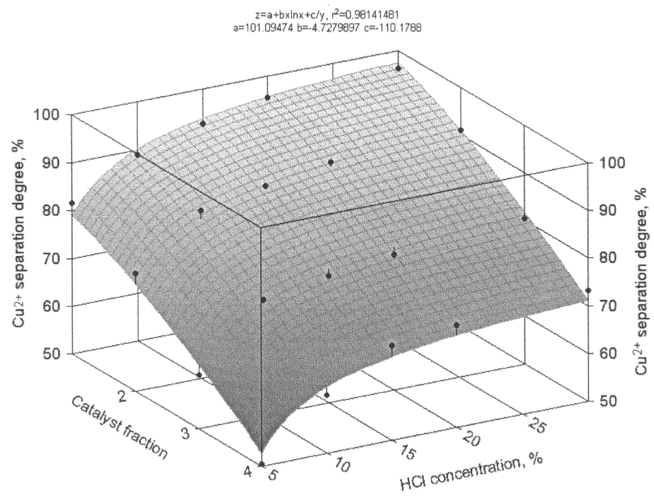

Fig. 2. Dependence of the copper ions separation degree on the HCl concentration and on the catalyst fraction, at 15 min and 600 rot/min

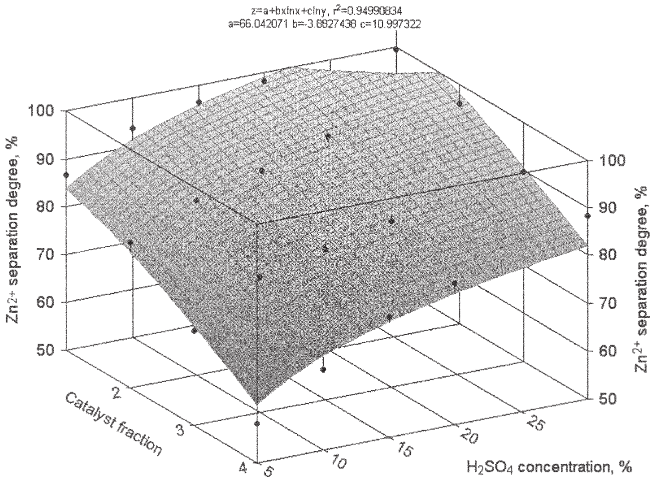

Fig. 3. Dependence of the zinc ions separation degree on the HNO_3 concentration and on the catalyst fraction, at 15 min and 600 rot/min

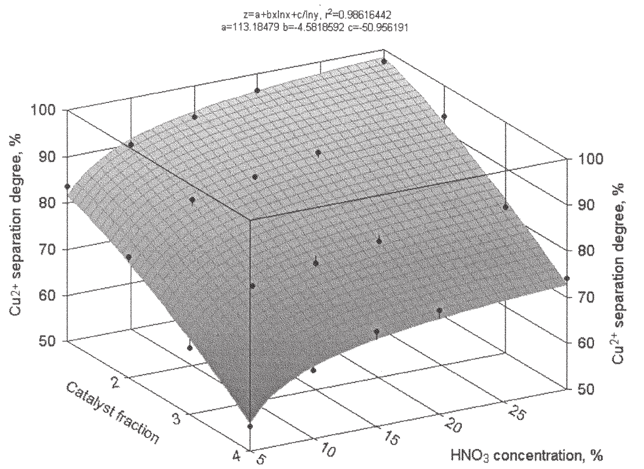

Fig. 4. Dependence of the copper ions separation degree versus the HNO_3 concentration and versus the catalyst fraction, at 15 min and 600 rot/min

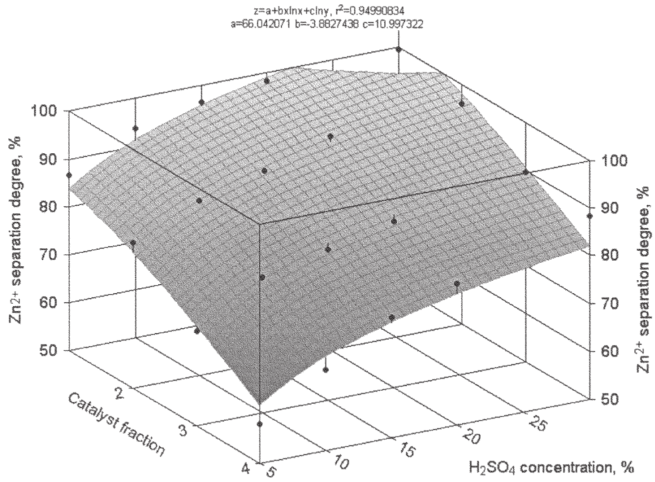

Fig. 5. Dependence of the zinc ions separation degree on the H_2SO_4 concentration and on the catalyst fraction, at 15 min and 600 rot/min

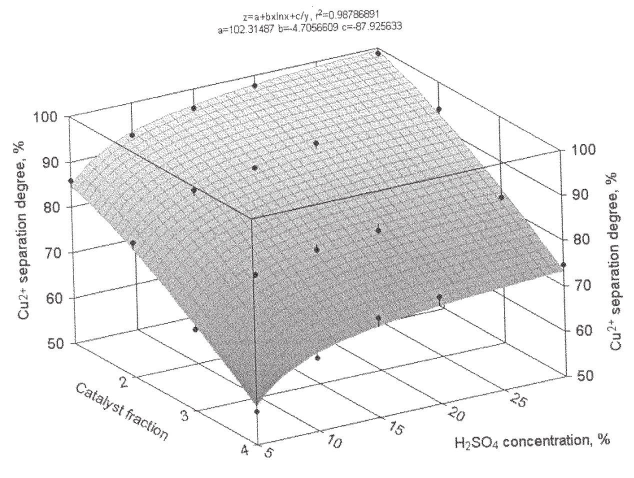

Fig. 6. Dependence of the copper ions separation degree on the H_2SO_4 concentration and on the catalyst fraction, at 15 min and 600 rot/min

From the experimental data can be observed that for all three acids used for extractions, the metals ions separation degree increases with the increase of the acid concentration. One may also notice that the metal ions separation degree decreases with the increase of the dimensions of the catalyst particles, due to the decrease of the surface contact. The optimum concentration of the acids used for extraction of zinc and copper ions from the catalyst is 30 % and the optimum dimension of the catalyst particles is < 0.5 mm.

The influence of the stirring time

The experimental data regarding the dependence of the metals ions separation degree on the stirring time for the optimum concentration of the acids and for the optimum dimension of the catalyst particles at a stirring speed of 600 rot/min are presented in figures 7-8.

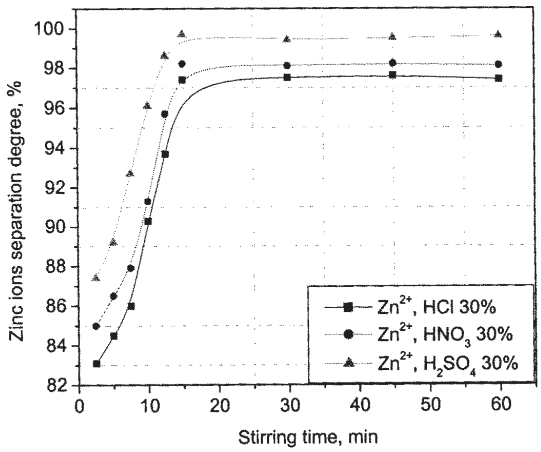

Fig. 7. Dependence of the zinc ions separation degree on the stirring time for the catalyst fraction <0.5 mm, an acid concentration of 30%, and a stirring speed of 600 rot/min

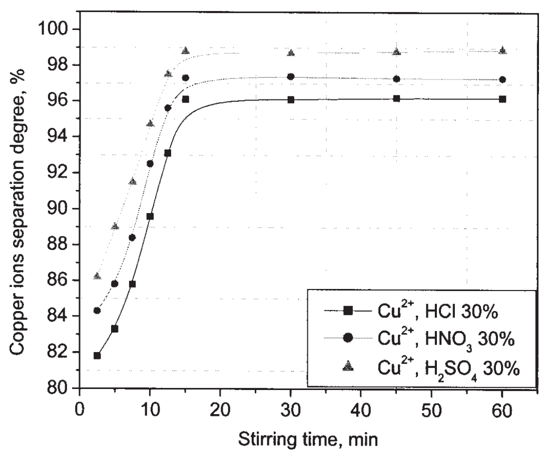

Fig. 8. Dependence of the copper ions separation degree on the stirring time for the catalyst fraction <0.5 mm, an acid concentration of 30%, and a stirring speed of 600 rot/min

From the experimental data one observes that for all three acids the metals ions separation degree increases with the increase of stirring time up to 15 min, and after this value the increase of the stirring time has no influence on the separation degree of the heavy metals. The optimum stirring time for the extraction of zinc and copper ions from the catalyst for all used acids is of 15 min.

The influence of the stirring speed

The experimental data regarding the dependence of the heavy metals separation degree on the stirring speed in the case of the catalyst fraction < 0.5 mm, the acids concentration of 30% and the stirring time of 15 min are presented in figures 9-10.

From the experimental data one observes that for all three acids used for extraction the metals ions separation degree increases with the increase of stirring speed up to the value of 600 rot/min. At a higher stirring speed, the influence is insignificant. Therefore the optimum stirring

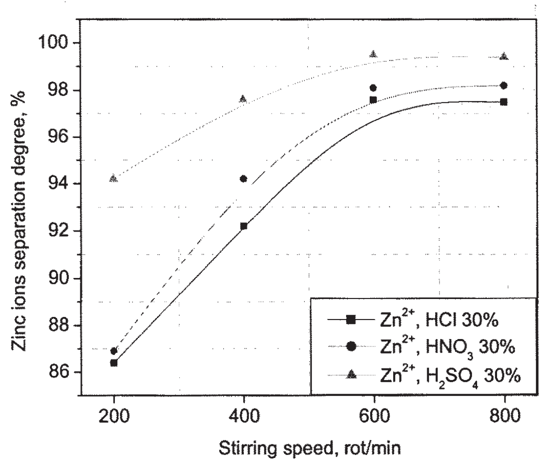

Fig. 9. Dependence of the zinc ions separation degree on the stirring speed, for the catalyst fraction <0.5 mm, an acid concentration of 30%, and a stirring time of 15 min

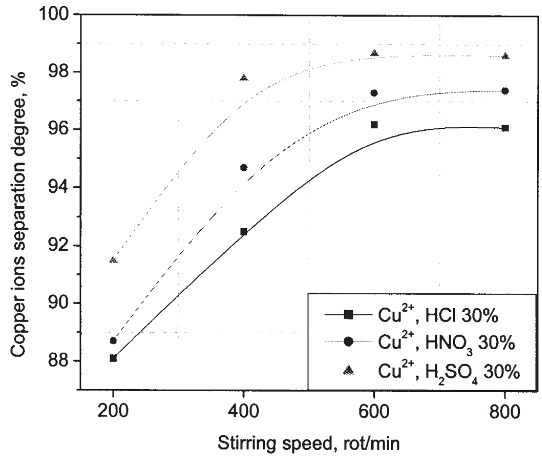

Fig. 10. Dependence of the copper ions separation degree on the stirring speed, for the catalyst fraction <0.5 mm, an acid concentration of 30%, and a stirring time of 15 min

speed for the extraction of zinc and copper ions from the waste catalyst is that of 600 rot/min.

Conclusions

This paper established the optimum conditions for the extraction of zinc and copper ions from waste catalyst resulted from the CO conversion. After two years of use, this catalyst loses his efficiency and becomes a solid waste. For this reason is important to find a way to reuse the heavy metals ions from its composition.

For the extraction of the heavy metals ions HCl, HNO_3 and H_2SO_4 solutions were used.

In order to establish the optimum conditions for heavy metals extraction, we determined the dependence of the heavy metals separation degree on the acid concentration, dimension of the catalyst particles, stirring time, stirring speed and the nature of the acid used for extraction.

From the experimental data one can conclude that for all acids used for extraction, the heavy metals separation degree increases with the increase of all studied parameters with the exception of the dimension of the catalyst particles.

The optimum conditions for zinc and copper ions extraction from waste catalyst are:
- dimension of the catalyst particles: <0.5 mm;
- acid concentration: 30%;
- stirring time: 15 min;
- stirring speed: 600 rot/min.

The solution resulted after extraction can be used for the obtaining of fertilizers with the microelements copper and zinc, or after a further separation the metals ions salts can be obtained.

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Manuscript received: 21.10.2008