Low-Waste Recycling of CuO-ZnO-Al$_2$O$_3$ Spent Catalysts

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Abstract: CuO-ZnO-Al$_2$O$_3$ catalysts are designed for the low-temperature shift conversion in the process of hydrogen and ammonia synthesis gas production. The paper presents the results of research on recovery of copper and zinc from spent catalysts using pyrometallurgical and hydrometallurgical methods. Under reducing conditions, at high temperature, having appropriately selected the composition of the slag, more than 66% of copper in metallic form and about 70% of zinc in the form of ZnO can be extracted from this material. Hydrometallurgical processing of the catalysts was carried out using two leaching solutions: alkaline and acidic. Almost 62% of the zinc contained in the catalysts has been leached to the alkaline solution and about 98% of copper has been leached to the acidic solution. After the hydrometallurgical treatment of the catalysts, insoluble residue was also obtained in the form of pure ZnAl$_2$O$_4$. This compound can be reused to produce catalysts, or it can be processed under reducing conditions at high temperature to recover zinc. The recovery of zinc and copper from such a material is consistent with the policy of sustainable development and helps to reduce the environmental load of stored wastes.

Keywords: sustainable development; recycling; spent catalysts; zinc; copper

1. Introduction

Spent CuO-ZnO-Al$_2$O$_3$ catalysts are very important secondary resources for metal recovery and could be highly usable for copper and zinc recycling [1]. This type of catalysts is used in low-temperature processes of carbon monoxide conversion with steam and to obtain hydrogen as well as to obtain a synthesis gas to produce ammonia or methanol [2-5]. Manufacturers of catalysts define the content of the basic components in new products as follows: CuO–min. 50%, ZnO–min. 25%. Multiple variations of them are available on the market. They are different in terms of contents of Cu, Zn and Al oxides. The copper to zinc mass ratio in industrial catalysts manufactured using the co-precipitation method is usually 7:3 [6]. The presence of spinel structures is a feature specific to catalysts that are analyzed in the paper. In the literature, CuAl$_2$O$_4$ spinels on the surface of the catalysts and the ZnAl$_2$O$_4$ stoichiometry spinel structures in all their volume are most frequently reported [7-8]. X-ray diffraction studies in the literature [9] indicate that the ZnAl$_2$O$_4$ compound is present at a 1100°C temperature. Therefore, processing of spent catalyst with infusible spinel structures present in them, and complete recovery of zinc from this type of materials can be difficult using the pyrometallurgical method.

2. Experimental procedure

2.1 Properties of examined material

In the paper, decision was taken to examine, on a laboratory scale, pyrometallurgical and hydrometallurgical processing of the CuO-ZnO-Al$_2$O$_3$ spent catalyst. These studies were designed to copper and zinc recovery contained in the material processed.

The chemical analysis of the examined samples of spent catalysts indicates different content of copper and zinc in the materials analysed. With the detailed chemical analysis of the catalyst sample

selected to be examined, the following results were obtained: 35.1% of Cu, 29.9% of Zn and 9.2% of Al. A sample of the material was also examined using X-ray phase analysis and microscopic observation combined with the qualitative chemical analysis. Results of the phase analysis are shown in Fig. 1. CuO and ZnO oxides are the main phase components. Additionally small quantities of Cu_2O and hydroxy-carbonate complexes of zinc and copper are present.
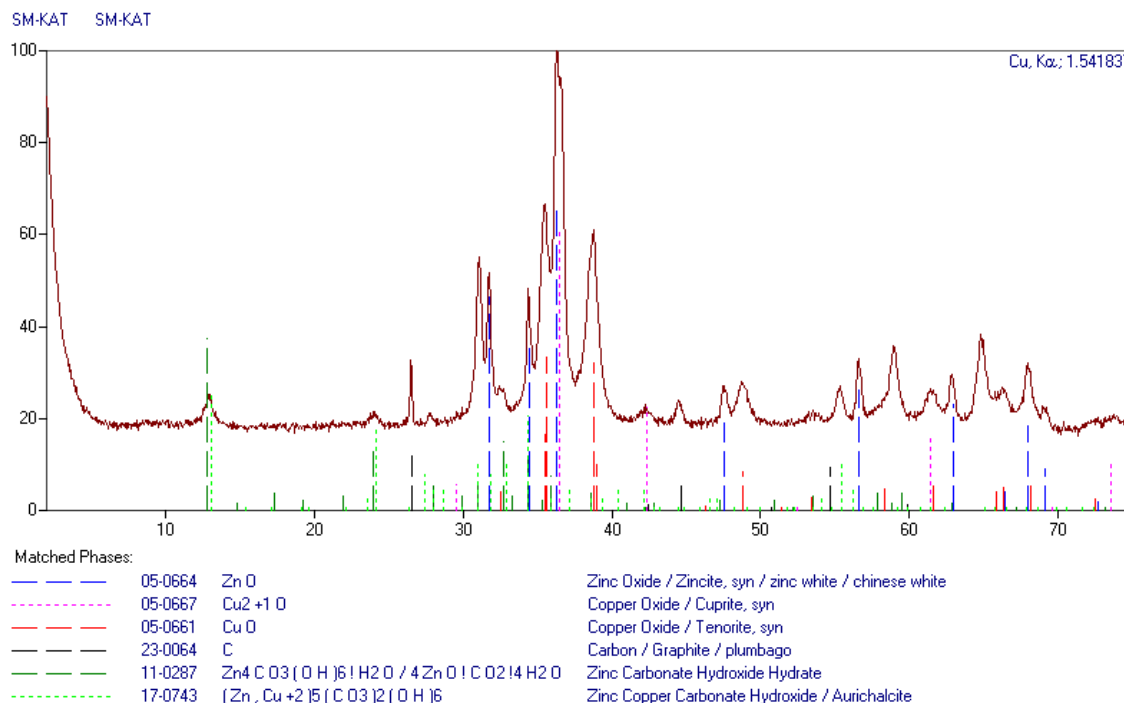
Figure 1. XRD pattern of catalysts sample.

In Fig. 2 and 3, respectively, an image of a sample of fragmented catalysts and EDS analysis of the area presented are shown. The elements identified are copper, zinc, aluminium, carbon and oxygen. This is a only a confirmation of the phase analysis.
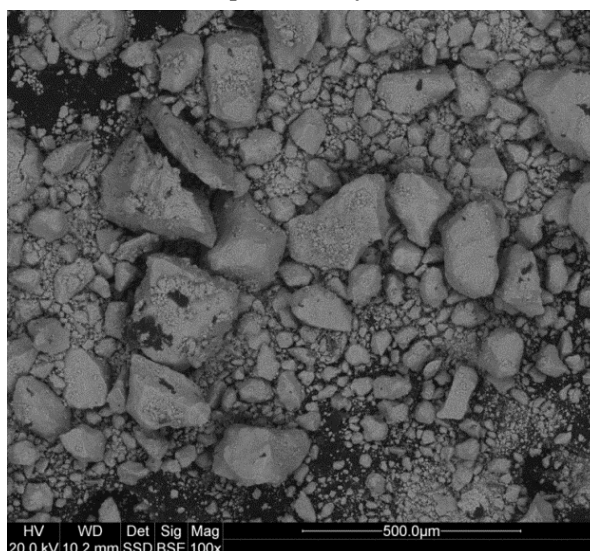
Figure 2. The microscopic image of sample of the fragmented catalysts material.
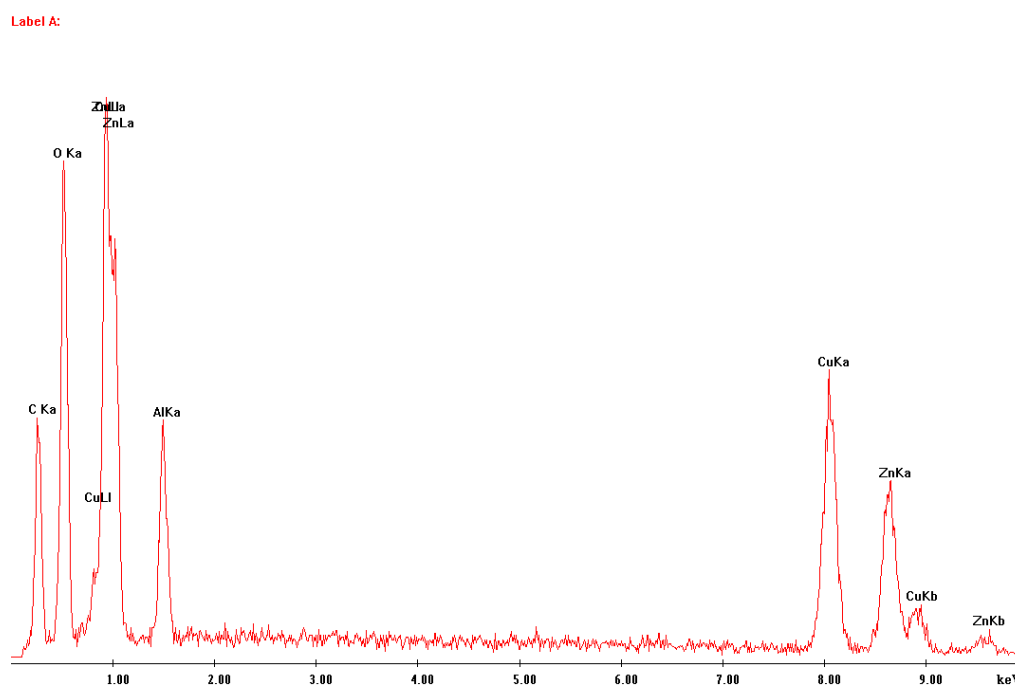
Figure 3. EDS analysis of the area of the sample.

2.3 Pyrometallurgical processing of spent catalysts

With information about the contents of the most valuable components in the material processed, it was decided to perform the test melting in order to extract copper and zinc in the form of zinc oxide from spent catalysts and to optimise the process for maximum yields of Cu   and ZnO as mentioned above. Having in mind the oxidic nature of catalysts, in order to lower the melting point (softening point) of the slag created and, if possible, to decrease its viscosity, it was decided to carry out the recovery process under reducing conditions and to apply slag-forming additives (e.g. CaO, SiO_2, Na_2O). Therefore, in order to determine the amount of additives ensuring the lowest melting point of the slag, the relevant binary and ternary systems were analysed. In the case of a binary ZnO-SiO_2 system, the liquid phase occurs at a temperature of 1432oC, with the content of about 52% ZnO by weight [10], while in the Na_2O-SiO_2 system, the liquid phase occurs in a wide range of concentrations and temperatures close to 1000oC [11]. Therefore, it can be assumed that in the Na_2O-ZnO-SiO_2 ternary system, compositions, for which the melting point of the respective ternary phase will be low enough to melt the catalysts processed, are likely. The above hypothesis is confirmed by reports in the literature [12], which indicate that once the concentration level of (weight percent) 21.5% Na_2O, 12.0% ZnO, 66.5% SiO_2 in this system is reached, the minimum melting point is 680oC. On the base of available information about the CaO-ZnO-SiO_2 and CaO-ZnO-Al_2O_3-SiO_2 systems [13-14], it was assumed that the lowest melting points can be obtained at similar concentration levels of the relevant components.

The catalysts were processed in an induction furnace, operable at a temperature range between 1100–1300oC. This temperature was to ensure maximum stripping of zinc and obtaining liquid copper by reducing its oxide. The amount of coal for the reduction of CuO and ZnO was determined assuming the formation of CO and CO_2. As a result, the amount of reductant added varies between 6-12%. For further studies, the mean value was taken increased by 10% due to the ash content in coal. Carried out initial testing allowed to determine that at 10% of added reductant degree of stripping the zinc is at a level of approx. 65%. Remaining part of zinc goes into the slag and metal phase. It should be noted that tests were carried out in a graphite crucible, which additionally improved the

reduction conditions. Based on these results it was possible to determine the test plan to optimize the amount of slag-forming additives.

Four variants of laboratory tests were performed. The tests were different from each other in terms of quantity of slag-forming components added. The optimal process parameters were sought in order to obtain the lowest melting points of slag, thereby, to minimise the loss of metals extracted from the catalysts to slag. 100 g of   uncrushed catalysts were used for each of the tests. The weights of copper and zinc contained in them were 35.1 g and 29.9 g, respectively. Reducing conditions of the process were secured by adding 10 grams of coal and by the fact that the melting was carried out in the graphite crucible. Once the melting was completed, the liquid products contained in the crucible were cooled, separated, weighed and chemical analyses of the materials obtained were performed. The following part presents the detailed description of each test, and in Tab. 1, the most important information obtained from experiments conducted are summed up.

Test No. 1

100 g of catalysts were mixed with 10 g of carbon, 50 g of SiO_2 and 15 g of CaO. The whole feed was placed in a graphite crucible and heated until a temperature of 1300°C was reached. At the beginning, intensive reduction of ZnO to Zn was observed and the metal was lifted in the gas phase and re-oxidised. After about 45 minutes, this process has been definitely halted (no emission of ZnO white films), and hence the decision was taken to terminate the test after this time. After cooling the crucible, its contents were separated into three fractions, and 26 g of metal, 62 g of glassy slag and about 17.5 g of unmelted fine fraction were yielded. This phase is, most likely, unreacted slag-forming components and unmelted $ZnAl_2O_4$ spinel structures. Additionally, in the experimental system, it was impossible to identify the amount of dust produced. It should be added that in the slag phase, not sedimented tiny metallic copper inclusions were visible.

Test No. 2

100 g of catalysts, 10 g of carbon, 60 g of SiO_2 and 20 g of NaOH were the feed for smelting. Temperature of the process was 1300 ^{o}C, duration-50 minutes. Like in the previous test, during the first 45 minutes of the process, stripping of zinc in the form of ZnO was very intense. Upon its completion, products cooling and separation, 25 grams of metal, 95 g of glassy slag and 7.5 g of free-flowing phase (slag-forming components and spinels) were found. Also, in this test, metallic copper inclusions were seen in the slag.

Test No. 3

100 g of catalysts, 10 g of carbon, 31 g of Na_2CO_3 and 55.4 g of SiO_2 were the feed for the process. The feed was melted at a temperature 1250°C, and the melting time was 90 minutes. After this period, stripping of zinc drastically decreased and hence the decision to terminate the smelting was taken. 25 g of metal and 107 g of glassy slag with minor copper inclusions were yielded.

Test No. 4

100 g of catalysts, 10 g of carbon, 16 g of Na_2CO_3 and 28 g of SiO_2 were melted. The melting time was 90 minutes and the process temperature was 1250°C. 20 g of metal and 61 g of glassy slag with a certain amount of copper drops were yielded.

The smelting products, namely slag and metallic alloy were subjects of chemical analysis for the content of copper and zinc. Summary of test results in Tab. 1 takes into account the fact that the unbalanced portion of zinc is transferred to the dust phase.

Table 1. List of parameters of processing the spent catalysts conducted on a laboratory scale according to smelting variants.

	smelting variant

	I	II	III	IV
FEED				
Mass of catalysts [g]	100	100	100	100
Mass of silica [g]	50	60	55.4	28
Mass of carbon [g]	10	10	10	10
Mass of CaO [g]	15	-	-	-
Mass of Na_2CO_3 [g]	-	-	31	16
Mass of NaOH [g]	-	20	-	-
Smelting time [min]	45	50	90	90
Process temperature [^{o}C]	1300	1300	1250	1250
PRODUCTS				
The overall mass of the alloy [g]	26	25	25	20
Mass of Cu in the alloy [g]	23.2	22.1	22.0	17.7
Mass of Zn in the alloy [g]	2.5	2.7	2.8	2.3
Mass of slag [g]	62	95	107	61
Mass of copper in the slag [g]	6.4	7.5	7.6	11.9
Mass of zinc in the slag [g]	6.0	6.1	6.7	6.3
The copper yield in the alloy [%]	66.1	63.0	62.7	50.4
The estimated yield of zinc in the dust [%]	71.6	70.6	68.2	71.2

The results of the pyrometallurgical test of catalysts recycling do not give grounds for optimism. Too low yield of copper may cause that the processing will be less cost-effective. This is due to the problem of obtaining a low viscosity slag. Probably, the presence of zinc aluminate causes high viscosity of slags. Correction of the slag composition results in the formation of large amount of slag, and even at a lower copper content in it, total losses are significant.

Processing of catalysts using the hydrometallurgical method

The results of using the described pyrometallurgical method to recycle the spent catalysts are not fully satisfactory. Therefore, to process them, the decision to use a hydrometallurgical method was taken for their processing. With knowledge about the structure of catalysts, their chemical composition and their phase composition, as well as being familiar with how they are produced, an innovative method to process them was developed. Zinc aluminate ($ZnAl_2O_4$), that is present in catalysts, is a compound highly resistant to both acids and alkalines [15]. Therefore, it has been recognised that after leaching copper oxides and zinc oxides, will be left as insoluble residue. First, catalysts in form of pellets were fragmented to reach the size of less than 90 μm.   In order to separate zinc and copper, zinc oxide and copper oxide leaching process was carried out selectively and consisted of two stages:

- Leaching in NaOH solution (temperature 75°C, process duration 120 min., NaOH concentration = 200 g/dm^3),
- Leaching in H_2SO_4 solution (temperature 60°C, process duration 120 min., H_2SO_4 concentration = 180 g/dm^3).

The process conditions were adjusted based on previous experience in alkaline leaching [16], and pilot tests. After each leaching process, the slurry was filtered to separate the deposit. The filtration process is difficult because the deposit consist of very fine grains. During the leaching using NaOH, just zinc was transferred to the solution. In fact, after the acidic leaching, the solution contained just copper. The amount of zinc in the solution was 100 to 150 times less than the amount of copper. Additionally, in order to facilitate transferring copper to the solution, as acidic leaching was conducted, small amounts of hydrogen peroxide solution were added. A small quantity of it may in fact be present in metallic form. This procedure allowed to obtain the following products from 100 g of catalysts recycled:

- Zn solution – 0.8 dm^3 (Zn-23 g/dm^3),
- Cu solution – 0.8 dm^3 (Cu-43 g/dm^3),

- ZnAl$_2$O$_4$ deposit in the amount of 33 g.

After leaching, the solutions still contain highly concentrated leaching agent, and should be returned to the initial leaching of subsequent batches. In order to recover as much metals as possible, the final leaching must be carried out using highly concentrated leaching agent. The zinc aluminate deposit was of dark gray colour, since it contained a certain amount of carbon. An attempt carried out to burn it out resulted in weight reduction by about 10% and the colour was changed into light gray. The sample obtained this way was analysed using the X-ray phase analysis. The results are presented in Fig. 4.
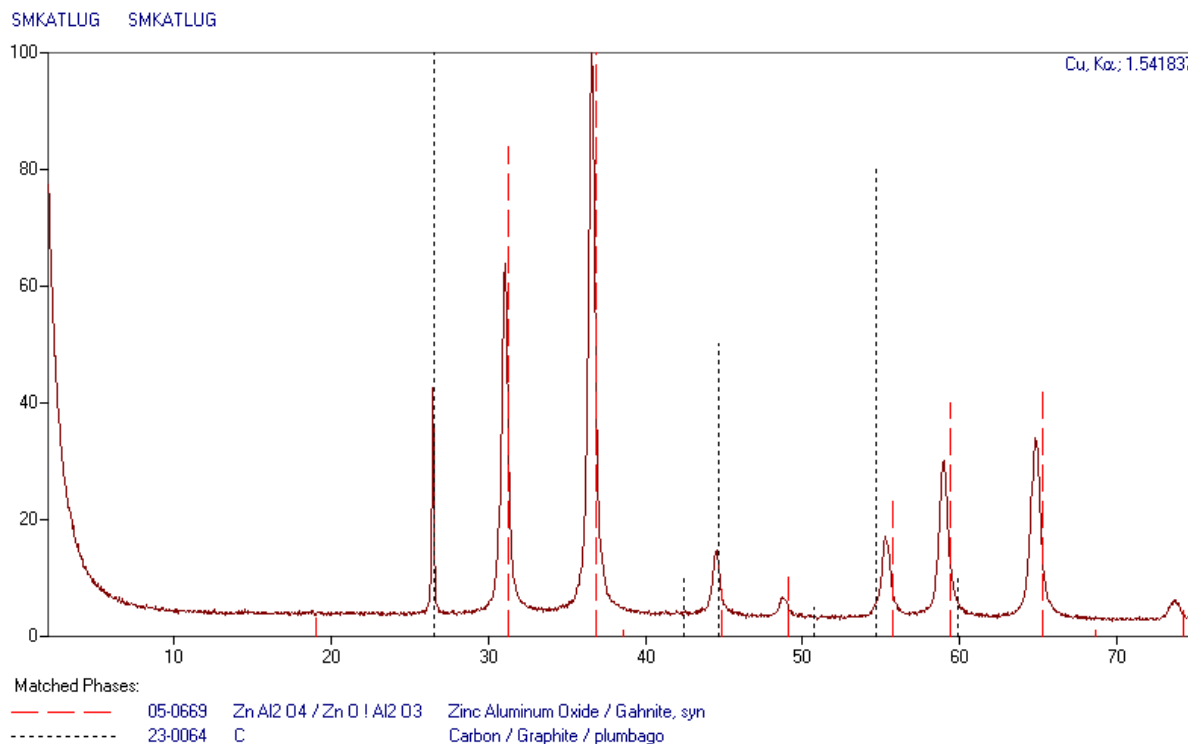
Figure 4. XRD pattern of zinc aluminate obtained from recycling catalysts.

Results of the phase analysis indicate just the presence of zinc aluminate and carbon. The presence of carbon is a result of analysis method.

The balance of the processing performed is as follows (100 g of catalysts):

- Amount of zinc in alkaline solution – 18.5 g
- Amount of copper in acidic solution – 34.5 g
- Zinc aluminate – 30 g
- Carbon   – 3 g

Material balance and analysis of the solutions allowed to determine the yield of copper in solution at the level of 98%. The yield of zinc to the alkaline solution is 61.9%. Because the residue after leaching is actually pure ZnAl$_2$O$_4$, it can be treated as a product of the process. In this case zinc yield increases to 97.5%, and the yield of aluminum is 96%.

Conclusions

Laboratory tests carried out indicate that pyrometallurgical method can be used to recover copper and zinc contained in the spent catalysts processed. However, after the tests conducted, some amounts of the alloy in the slag in the form of small inclusions were noted. This may be a result of high viscosity of the slag and a result of difficult sedimentation conditions under the test conditions. The process should be carried out at temperatures above 1200°C and a reductant should be used in the form of coal in an amount of about 10% by weight of catalysts. Liquid copper and ZnO in the

form of dust are products of the process. Silica and CaO or NaOH or Na_2CO_3 are an indispensable technological additive in processing catalysts for slag adjustment. This allows to obtain a glassy slag and minimise copper losses in the process. Laboratory tests conditions made it possible to carry out the process of copper recovery with a yield of up to 66%. The Zn yield for dust was estimated based on the amounts of zinc contained in the alloy obtained and in slag. It can be assumed that under proper process conditions (reducing atmosphere, ~1300°C, enough time for Zn stripping) transferring to dust more than 70% of zinc contained in the spent catalysts is very possible.

Hydrometallurgical processing, based on the selective leaching allows to accurately separate the components of spent catalysts. More than 96% degree of metal recovery is reached. In the case of zinc and aluminum, this value is relative to the overall yield. It also includes the content of these metals in the leach residue. This residue may be the product of the process because it contains actually pure $ZnAl_2O_4$. Solutions obtained as a result of applying acidic and alkaline leaching allow to perform the selective extraction of Cu and Zn they contain. These metals can be recovered from solutions in the form of compounds by precipitation or in a metallic form by electrolysis. The residue (mainly $ZnAl_2O_4$) that is left after leaching may be returned to produce new catalysts or may be thermally processed to recover zinc it contains.

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