

## SYNTHESIS OF ZnO NANOPARTICLES FROM ELECTRIC ARC FURNACE DUST

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### Abstract

This paper presents a hydrometallurgical treatment of electric arc furnace (EAF) dust taken from a Vietnamese steelmaking plant to obtain zinc oxide (ZnO) nanoparticles by using aqueous ammonium carbonate solution as a leaching agent. Characterization of the EAF dust was conducted by XRD technique, SEM observation, and manual wet chemical analysis. The results showed that total zinc (Zn) of the dust was 42.69 wt.% and existed mainly in the forms of zincite - ZnO, simonkolleite -  $Zn_3(OH)_8Cl_2H_2O$ , and franklinite -  $ZnFe_2O_4$ . The leached condition, in which the ammoniac carbonate concentration was 300 g/l and the time was 90 minutes, was found to provide the highest leaching efficiency of 85.29 % when the temperature was fixed at 60 °C and the ratio of solid/liquid was 1/6. After some steps of the subsequent treatment, the ZnO nanoparticles with the purity of 99.5 % and the size of 100 nm were obtained from thermal decomposition of zinc carbonate hydroxide -  $Zn_3(CO_3)_2(OH)_6$ .

**Keywords:** EAF dust; Hydrometallurgy; Zincite; Franklinite; ZnO nanoparticles

### 1. Introduction

As the galvanized scrap is remelted in electric arc furnace (EAF), zinc (Zn) evaporates and transforms into dust. In average, production of one ton of the EAF liquid steel generates about 15-25 kg of dust, in which the Zn content widely changes from 5-40 wt.% or more [1]. EAF dust needs to be recycled for recovery of Zn element and minimization of the environmental impact [2, 3]. Many recycling methods based on the pyrometallurgical and/or hydrometallurgical processes have been proposed and developed to recover Zn so far [3-5]. For example, the acidic leaching treatment can dissolve the constituent elements of Zn in the aqueous solution for subsequent electrolytic step [3-5]. Other processes are also under development, but they mostly depend on dissolving the dust and recovering Zn metal from solution. Coke/anthracite is used as a reductant in the carbothermic reduction method, in which the ZnO is obtained to supply for the Zn production and the residue can be supplied for the steel industry [6, 7]. Another methodology enables the EAF dust to be mixed with a given flux and then heated to a certain temperature for obtaining an amorphous glassy structure or a red ceramic [8-9]. Some of these processes have been developed for the pilot plant or

on a small commercial plant scale. Alternative EAF dust treatment routes with a high economically efficiency have been studied.

In Vietnam, EAF dust recycling has been considered for years because of the strict regulations on the environmental protection. There have been many efforts to recover the Zn amount in EAF dust, but it is still a very interesting issue because of involving several factors such as investing cost, recovery product, and environmental protection. Pyrometallurgy is used in most industrial installations for the dust processing, in which ZnO is recovered by heating the mixture of the dust and carbonaceous materials at high temperature [10]. This process can apply for the EAF dust containing low or high Zn content, but one of the disadvantages is that the purity of the ZnO product is not higher than 70 wt.%. Thus, the EAF dust recycling by hydrometallurgical techniques is more interesting. All solutions have been performed towards the environmental protection and improvement of the recovered product's value; however, hydrometallurgical methods are considered not to recover zinc completely and require a further treatment [11, 12].

Currently, ZnO nanomaterials have been used for many applications, e.g. sensor, biomaterials, ceramics, etc. The aim of this research is to propose a

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treatment route to recover the high purity ZnO nanoparticles from EAF dust using aqueous ammoniac carbonate solution. The characterization of the deployed EAF dust and the recovered ZnO nanoparticles was investigated. The leached condition including the ammonium carbonate concentration, the leaching time and others were also presented and discussed.

## 2. Materials and Method

The EAF dust was taken from a steelmaking plant in Vietnam, Figure 1. After drying at 105 °C for 24 hours, the dust was used for the investigation. Characterization of the EAF dust and the obtained ZnO nanoparticles was performed with the use of some analytical methods. Namely, the total Zn content was determined by the manual wet chemical analysis that used the so-called royal water (Aqua regia) to dissolve the samples, the mineralogical composition was investigated by X-ray diffraction (XRD, AERIS 600) using Cu-K $\alpha$  radiation ( $\lambda = 1.540598 \text{ \AA}$ ), and the morphology was observed by scanning electron microscopy (SEM, JEOL 7600F). In addition, the EDS method was used to micro-analyze the compositions of the EAF dust and the synthesized ZnO powder.



Figure 1. Image of the EAF dust

Experimental procedure was carried out through several steps to obtain the ZnO nanoparticles: (1) Leaching the EAF dust to get the Zn-containing solution, (2) Precipitating the crude zinc hydroxide, (3) Removing the Fe compound to get the fine zinc hydroxide, and (4) Calcining to obtain the high purity ZnO nanoparticles.

Ammonium carbonate -  $(\text{NH}_4)_2\text{CO}_3$  powder (DC Chemical) was used to prepare the leaching solution. A 100 g of the dried EAF dust was leached in the 600 g of aqueous ammoniac carbonate solution, which had various concentrations of 200, 250, 280, 300, and 320 g/l. The leaching time was predetermined from 60 to 180 minutes. Since ammonium carbonate becomes

unstable and is decomposed as temperature is higher than 60 °C, the leaching temperature was fixed at 60 °C for all experiments. During the leaching process, agitation was created by using a magnetic stirrer (Joan Lab HS-12), and the pH of the solution was measured continuously by using a pH meter (Hanna HI 2210-02). The pH changed from 8 to 10 dependent on the ammonium carbonate concentration. Two experiments with the same parameters were performed for average calculation in each leaching conditions. After the leaching step, the aqueous solution was separated from the residue by the filtration. The Zn content of the filtered solution was analyzed to calculate the leaching efficiency ( $\eta$ ), equation (1). The leaching process was carried out in various conditions to find out the highest  $\eta$  for the present EAF dust. After leaching treatment, the residue was dried at 105 °C for 24 hours, and then examined by XRD technique.

$$\eta = \frac{\text{Zn in the filtered solution (g)}}{\text{Zn in the EAF dust (g)}} \times 100 (\%) \quad (1)$$

A few drops of the hydrochloric acid (35 wt.%) were added in the filtered solution until the pH was reduced to 7.0 at which a complex compound containing both Zn and Fe was precipitated in the solution. After being separated by the filtration, this precipitate was dissolved again in the aqueous ammonia solution with the  $\text{NH}_3$  concentration of 25 wt.%. Consequently, the red-brown iron hydroxide -  $\text{Fe}(\text{OH})_3$  remained and then was removed by the filtration. Afterward, the filtered Zn solution was boiled until the white precipitation of zinc carbonate hydroxide -  $\text{Zn}_5(\text{CO}_3)_2(\text{OH})_6$  remained. This precipitation was rinsed repeatedly with the distilled water, and finally calcined in a resistant furnace, under the air atmosphere. After being slowly cooled down to the room temperature, the ZnO nanoparticles were obtained and subjected to the characterization. In this research, three times of the manual wet chemical analysis have been done to determine the Zn content of the given samples (e.g. the EAF dust, the leached solution and the ZnO nanoparticles).

## 3. Results and Discussion

### 3.1. Characterization of the EAF dust

Figure 2 shows the SEM image and EDS analysis of the EAF dust. It can be seen that the distribution of the dust particles was homogenous, and the sizes of the particles were mostly below 1  $\mu\text{m}$ . The EDS result of the EAF dust sample suggested that the Zn content was about 45 wt.%; and some other elements were also present in the EAF dust. According to Vieira et al. [9], the Zn content was very important for the economic recycling of EAF dust. Therefore, the high



Zn content and the fine particles was expected to be an advantage for improving the leaching efficiency of the EAF dust.

XRD result of the EAF dust is shown in Figure 3(a), where the peaks were analyzed according to the crystallography open database (COD) for phase identification. Although some observed phases showed overlapping peaks, almost all of them were composed of zinc-iron oxides whose main crystalline phases were identified. The dominant compounds corresponded to the zincite - ZnO (No. 96-900-8878),

simonkolleite -  $\text{Zn}_5(\text{OH})_8\text{Cl}_2\text{H}_2\text{O}$  (No. 96-900-4684), and franklinite -  $\text{ZnFe}_2\text{O}_4$  (No. 96-900-5108). Other compounds such as magnetite -  $\text{Fe}_3\text{O}_4$  and dicalcium silicate -  $\text{Ca}_2\text{SiO}_4$  were found in the EAF dust. Based on each relative peak intensity of the XRD patterns, content of the identified phases was estimated based on the quantitative phase analysis. The results are given in Table 1 where the  $\text{ZnFe}_2\text{O}_4$  was in the range of 8 - 10 wt.%, equivalent to 2.2 - 2.7 wt.% of the Zn content. According to other literature, the  $\text{ZnFe}_2\text{O}_4$  content which could change up to 60 wt.% in EAF

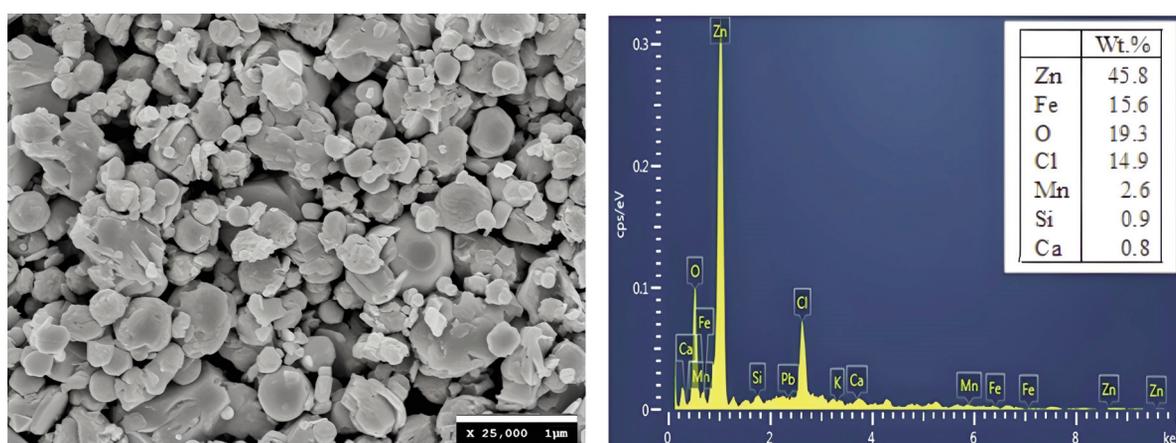


Figure 2. Morphology and EDS analysis of the EAF dust

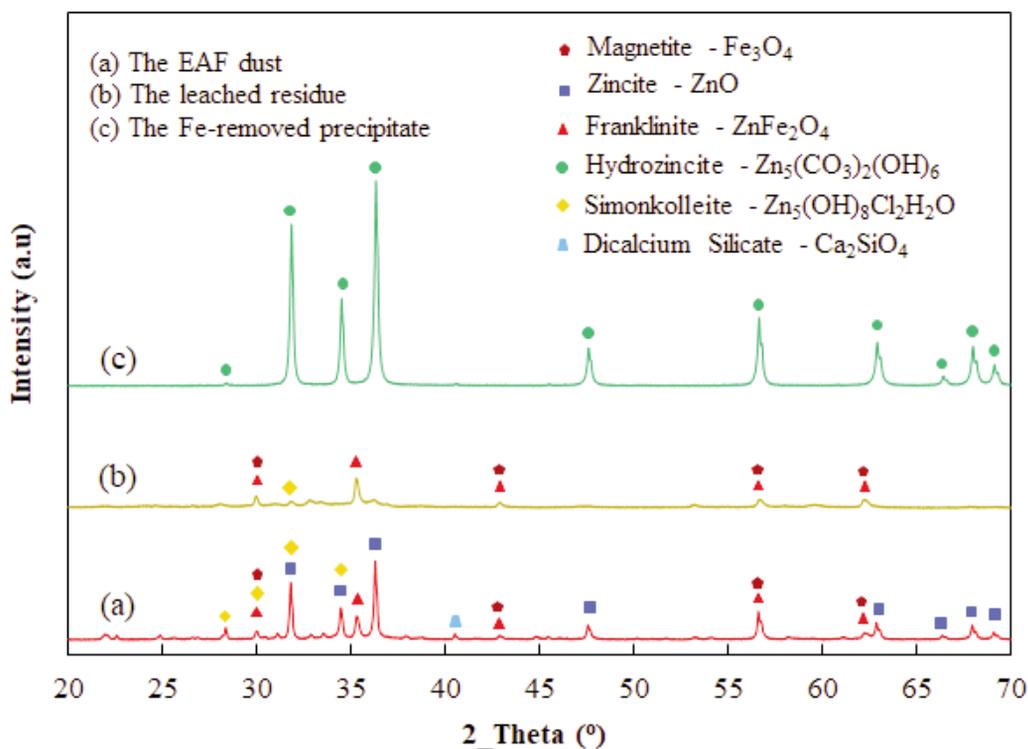


Figure 3. XRD patterns of the EAF dust, the leached residue and the Fe-removed precipitate

**Table 1.** Estimated content of the Zn compounds in the EAF dust

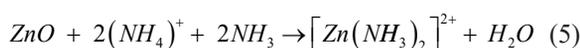
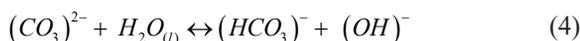
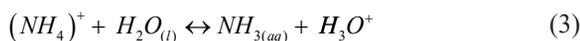
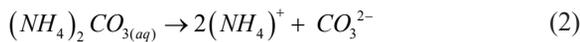
No.	Type of the compounds	Estimated content (wt.%)	Equivalent Zn content (wt.%)
1	Zincite - ZnO	26 – 28	20.8 – 22.4
2	Simonkolleite - $Zn_5(OH)_8Cl_2H_2O$	18 – 20	10.6 – 11.8
3	Franklinite - $ZnFe_2O_4$	8 – 10	2.2 – 2.7
4	Amorphous	~ 45	No estimation

dust was stable and insoluble except in the case of leaching in hot and/or strong acid, as a result, Zn recovery from the  $ZnFe_2O_4$  compound was usually low [11, 13]. The fact that the estimated  $ZnFe_2O_4$  was low suggested it would increase the leaching efficiency for this study.

Chemical analysis showed that the total Zn content of the present EAF dust Zn was 42.69 wt.%. Taking in account the calculation in Table 1, a small amount of the Zn must exist in the amorphous compounds. It is acknowledged that the chemical composition of EAF dust is different and depends on each specific steelmaking melts such as the input scrap, the type of steel product, technological requirements, operating conditions [3, 9, 14-16]. In this study, the chemically analyzed Zn content was consistent with the estimated results from the XRD and EDS investigation. All these results showed that the EAF dust contained a relatively high content of Zn, the mineralogical and the chemical compositions were quite similar with the published results.

### 3.2. Synthesis of ZnO nanoparticles from the EAF dust

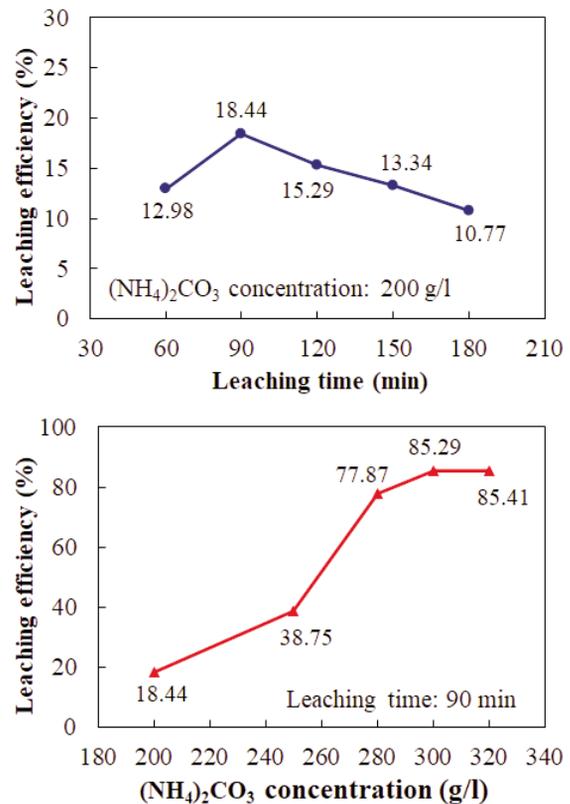
As ammonium carbonate solution was not stable at the given condition, it could be decomposed through reactions from (2) to (4) [1]. Once excess ammonia was present in the solution, the ZnO in the EAF dust dissolved into the leaching solution by reaction (5). Consequently, a colorless solution containing zinc compound was obtained.



The fact that pH of the leaching solution was constant during the treating process indicated that there was no loss of the ammonia ( $NH_3$ ) in the

solution for all experiments. Effects of the leaching time and the ammonium carbonate concentration on the efficiency are shown in Figure 4, where the time of 90 minutes was suitable for the leaching process. If the time was less than 90 min, the Zn compound had not dissolved completely into the ammonium carbonate solution. In case of the increased time, the ammonium carbonate solution would have dissociated and reduced the  $NH_3$  concentration. Thus, the ammoniac carbonate concentration clearly affected the leaching efficiency of the EAF dust. The efficiency increased strongly from 18.44 to 85.29 % as the concentration raised from 200 to 300 g/l, but the efficiency did not increase significantly for the concentration of 320 g/l. Therefore, the parameters such as 300 g/l and 90 min were used for selectively leaching the EAF dust in this study. The leached solution that was obtained in this experimental condition was treated subsequently to synthesize the ZnO nanoparticles.

XRD result of the residue leached in the condition of 300 g/l and 90 min is shown in Figure 3(b), where almost all of the identified peaks represented the franklinite. Therefore, it can be speculated that all the zinc present in the ZnO and the  $Zn_5(OH)_8Cl_2H_2O$  compounds was transferred to the leached solution; and



**Figure 4.** Effect of the leaching time and the ammonium carbonate concentration on the leaching efficiency

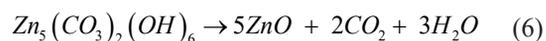


most of the franklinite remained in the leached residue.

Because the ZnO and the  $Zn_5(OH)_8Cl_2H_2O$  of the EAF dust reacted completely and  $ZnFe_2O_4$  reacted partially, the filtered solution contained both Zn (majority) and Fe (minority). When the hydrochloric acid (HCl) was added in the filtered solution, the pH decreased to the value of 7.0; consequently, the mixture of Zn and Fe compounds was precipitated. After the filtration, this precipitation was collected and subjected to remove the Fe compound by dissolving in the aqueous ammonia solution. It is acknowledged that this Zn compound can dissolve easily in a highly basic solution, as a result, the iron hydroxide particles in red-brown color remained and was removed by the filtration. The filtered solution that contained only Zn compound was boiled until the white precipitates remained. The XRD result of this precipitation is shown in Figure 3(c), in which all the identified peaks were indexed as zinc carbonate

hydroxide -  $Zn_5(CO_3)_2(OH)_6$  (No. 96-900-7482).

According to Kanari et al., thermal decomposition of zinc carbonate hydroxide to zinc oxide occurred via the reaction (6) in the range of 150-400 °C [18]. In this study, the calcination was performed at 400 °C for 3 hours. Finally, the white ZnO powder was obtained, as in Figure 5, and characterized.



### 3.3. Characterization of the obtained ZnO nanoparticles

As the observed SEM micrograph in Figure 5, the particle size of the ZnO powder was homogenous and approximately 100 nm. According to the XRD investigation of the obtained ZnO powder as shown in Figure 6, all peaks were identified to ZnO with a hexagonal wurtzite crystal structure (No. 96-900-8878).

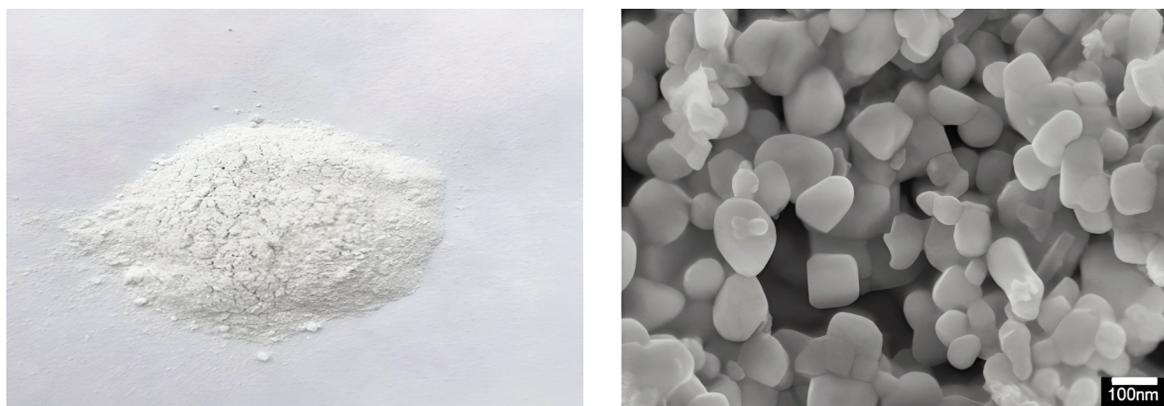


Figure 5. The obtained ZnO powder and SEM micrograph

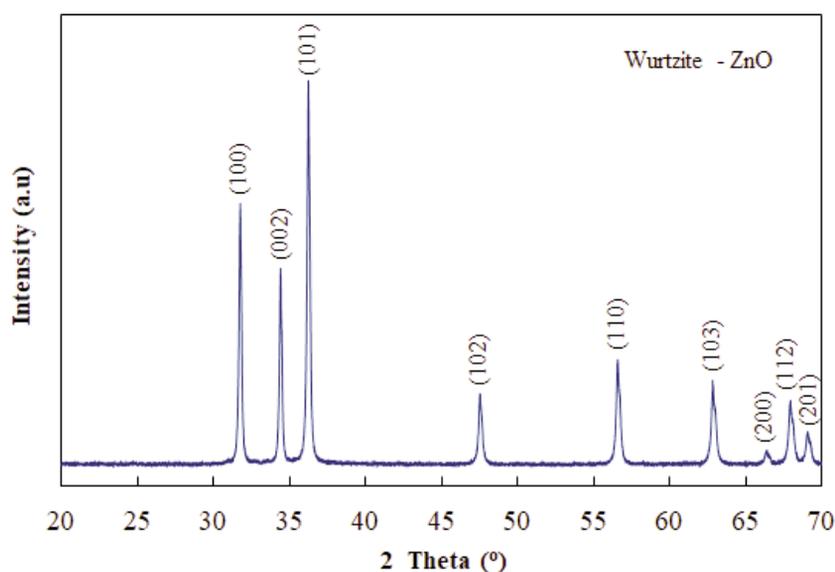


Figure 6. XRD pattern of the synthesized ZnO nanoparticles

The EDS results of the ZnO nanoparticles are shown in Figure 7, in which the mass ratio of the Zn and O elements was close to the theoretical value (80.2/19.8). This EDS result was consistent with the chemical analysis of the ZnO nanoparticles, of which the total Zn content was determined as 79.85 wt.%. Therefore, the purity of the ZnO nanoparticles was calculated as 99.5 %. Taking into account all the results of the XRD, EDS, and manual wet chemical analysis together, it can be confirmed that the high purity of the ZnO nanoparticles were synthesized from the EAF dust.

#### 4. Conclusions

A new EAF dust treatment process was carried out to synthesize ZnO nanoparticles using aqueous ammonium carbonate solution as a selectively leaching agent. The total Zn was chemically analyzed at about 42.69 wt.% and presented mainly in the forms of zincite - ZnO, franklinite - ZnFe<sub>2</sub>O<sub>4</sub>, and simonkolleite - Zn<sub>5</sub>(OH)<sub>8</sub>Cl<sub>2</sub>H<sub>2</sub>O. The leached condition, including ammonium carbonate concentration of 300 g/l, ratio of the solution and the dust of 6/1, the leached time of 90 min, and the temperature of 60 °C, was found to be suitable and provided the highest efficiency of 85.29 %. The XRD result of the leached residue

indicated that the franklinite of the EAF dust almost did not dissolve in the leaching solution. The characterization of the synthesized ZnO nanoparticles showed that the purity was 99.5 %, and the average particle size was approximately 100 nm. It can be concluded that this proposed treatment is technologically feasible to recycle EAF dust containing low ZnFe<sub>2</sub>O<sub>4</sub> content for obtaining ZnO nanoparticles.

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#### Authorship contribution statement

A.-H. Bui: Methodology, Supervision; D.-C. Le: Data analysis; T.-T. Nguyen: Experimental work.

#### 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.

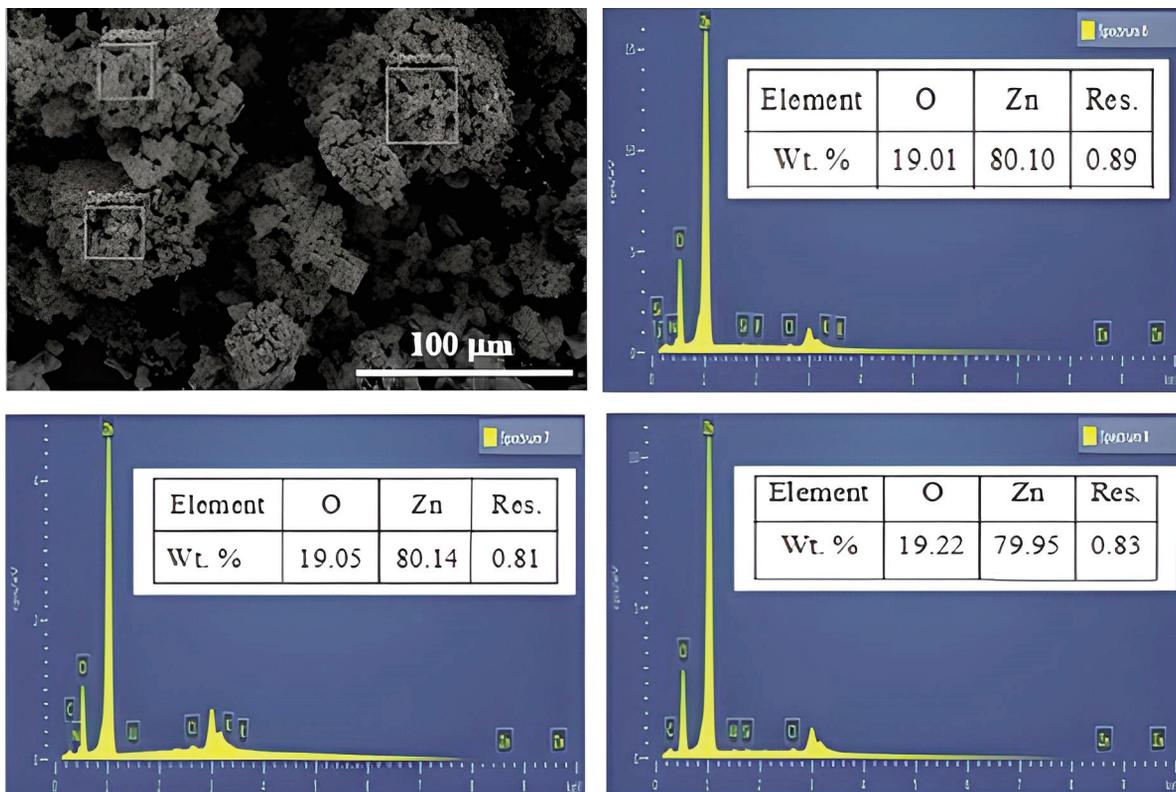


Figure 7. EDS results of the obtained ZnO nanoparticles

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## SINTEZA NANOČESTICA ZnO IZ PRAŠINE DOBIJENE IZ ELEKTROLUČNE PEĆI

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### Apstrakt

Ovaj rad predstavlja hidrometalurški tretman prašine dobijene iz elektrolučne peći uzete iz vijetnamske fabrike čelika za dobijanje nanočestica cink-oksida (ZnO) u prisustvu rastvora amonijum karbonata kao agensa luženja. Za karakterizaciju EAF prašine je korišćena XRD, SEM i analiza mokre hemije. Rezultati su pokazali da je ukupni cink (ZnO) u prašini iznosio 42.69 wt.% i da je bio uglavnom u obliku cinkita – ZnO, simonkolete -  $Zn_5(OH)_8Cl_2H_2O$  i franklinit -  $ZnFe_2O_4$ . Uslovi prilikom luženja su bili sledeći: koncentracija amonijum karbonata je iznosila 300 g/l tokom 90 minuta. Ovi uslovi su obezbedili najveću efikasnost prilikom luženja, 85,29%, kada je temperatura bila konstanta i iznosila 60 °C, a odnos č:t je iznosio 1:6. Nakon nekoliko naknadnih tretmana, termičkim razlaganjem cink karbonat-hidroksida  $Zn_3(CO_3)_2(OH)_6$  dobijene su nanočestice ZnO čistoće 99,5% i veličine 100 nm.

**Cljučne reči:** EAF prašina; Hidrometalurgija; Cinkit; Franklinit; ZnO nanočestice

