Katya Brunelli*, Pietrogiovanni Cerchier*, Renato Bonora and Manuele Dabalà

Sonochemistry production of ZnO and zero-valent Fe nanoparticles from solutions of electric arc furnace dust leaching

Abstract: In this work, nanoparticles of ZnO and zero-valent Fe were sonochemically synthesised using a solution produced from electric arc furnace dust leaching as raw material. The leaching was previously carried out using ultrasound with various concentrations of sulphuric acid. The resulting solutions contained, in addition to varying amounts of Zn and Fe, elements such as Cr, Mn, Mg, Ca, and Si. Two methods were developed, one for Fe and one for ZnO, to obtain the nanoparticles and to avoid the precipitation of the additional elements during the nanoparticle production. The synthesis of ZnO nanoparticles was performed through the formation of a precursor by sonochemical reaction with NaOH, and the thermal decomposition of this precursor by heating in furnace. The production of Fe nanoparticles involved the precipitation of FeOOH, the dissolution of FeOOH in HCl solution, and the ultrasound-assisted reduction of the iron ions with $NaBH_4$. The nanoparticles were characterised by scanning and transmission electron microscopy, X-ray diffraction, X-ray fluorescence, and UV spectroscopy. The nanoparticles of Fe had a particle size of 6 nm and resulted in zero-valent Fe, whereas the ZnO nanoparticles were between 30 and 50 nm.

Keywords: electric arc furnace dust; nanoparticles; ultrasound; zero-valent iron; zinc oxide.

1 Introduction

Waste material produced in some industrial processes can be considered to be a source of various metals. It would be advantageous if it were possible to recover such metals in the form of nanoparticles using environmentally friendly processes.

Electric arc furnace (EAF) dust is one of the most critical waste products in the steelmaking industry. During the EAF production of steel from scrap, many elements are volatilised and subsequently cooled and collected as dust. The large volume of generated dust contains mainly Fe and Zn oxides, in addition to considerable amounts of harmful elements such as Pb, Cd, As, and Cr. The EAF dust, due to its chemical and physical characteristics, is classified as hazardous waste, and its disposal is not negligible [1]. Two different processes are used to manage EAF dust: pyrometallurgical and hydrometallurgical. Compared with conventional pyrometallurgy, hydrometallurgy is fast emerging as a preferred process, thanks to its lower energy consumption and lower smelter emissions. Moreover, it presents the possibility of obtaining the metals in the form of nanoparticles directly from the leaching solution.

Several hydrometallurgical processes have been proposed in the literature to recover zinc from EAF dust and involve mainly the use of acid or alkaline solutions [2, 3]. Acid leaching enables the extraction of almost all the zinc, but with the disadvantage to recover also iron.

In this work, nanoparticles of zero-valent Fe and ZnO were sonochemically synthesised using the solution coming from EAF dust acid leaching as a raw material. Formally, this work addresses two main problems: (i) the ions of the two metals in the solution were in a different form from those normally used in the production of these nanoparticles, and (ii) other metals were present in the solution, which could contaminate the nanoparticles.

In recent years, ZnO nanoparticles received attention for their properties, such as electric conductivity, optical transparency, and near-UV emission [4, 5]. Moreover, ZnO nanostructured materials are good candidates for the nanostructured part of dye-sensitised solar cells (DSSCs), which are attracting interest in the production of low-cost but efficient solar cells [6, 7]. ZnO is a large-band-gap semiconductor with similar electronic levels as TiO_2, which is the material actually chosen for DSSCs. A traditional method of synthesising ZnO nanoparticles is achieved by the preparation of ZnO sols in the liquid

*Corresponding authors: Katya Brunelli and Pietrogiovanni Cerchier, Department of Industrial Engineering, University of Padua, Via Marzolo 9, 35131 Padua, Italy, e-mail: katya.brunelli@unipd.it (K. Brunelli), pietro.cerchier@hotmail.it (P. Cerchier)
Renato Bonora and Manuele Dabalà: Department of Industrial Engineering, University of Padua, Via Marzolo 9, 35131 Padua, Italy

phase from homogeneous ethanolic solutions with precursors of lithium hydroxide and zinc acetate [8, 9]. Other methods to produce ZnO nanoparticles are hydrothermal synthesis, thermal decomposition, organo-zinc hydrolysis, alkali-precipitation, spray pyrolysis, emulsion, and sol-gel [10–12]. Among these methods, precipitation and thermal decomposition are generally preferred as they are economic and can provide large-scale production, without expensive raw materials and complex equipment.

One of the most important nanomaterials studied for soil and groundwater purification is Fe [13]. Among the nano-absorbents, iron covers the broadest range of environmental contaminants such as halogenated organics, pesticides, arsenic, nitrate, and heavy metals.

Several types of iron nanoparticles are already available in the market. However, the development of sustainable and responsible zero-valent iron nanoparticle production and a better information exchange with the remediation industry should be promoted.

The mechanism of reactivity for iron is similar to the mechanism of corrosion and involves the generation of electrons, which, in turn, reduces the organic species through dechlorination. Usually, the production of zero-valent iron involves the use of $FeCl_2 \cdot 4H_2O$ and $NaBH_4$, where $NaBH_4$ acts as a reducing agent of Fe^{3+} to produce zero-valent iron [14, 15].

2 Materials and methods

Two new methods, assisted by sonication, were developed to enable the synthesis of the nanoparticles from the leaching solution of EAF dust: one for Fe and the other for ZnO. All reagents were purchased from Sigma-Aldrich, St. Louis, USA.

The leach liquor produced from the ultrasound-assisted leaching with 0.5 M sulphuric acid at 80°C was used for the synthesis of ZnO nanoparticles. These leaching process parameters were derived

from a previous work of the authors, and were optimised to achieve a higher and more selective recovery of zinc, leaving iron in the solid residue [16].

The elemental composition of the initial EAF dust and of the leach liquor is reported in Tables 1 and 2, respectively. The concentration of Zn is found to be 5.6 g/l, whereas the amount of Fe is negligible. One of the advantages of using ultrasound during leaching with 0.5 M sulphuric acid was to obtain a higher recovery of Zn without the presence of Fe [16]. However non-negligible amounts of Mg, Ca, Mn, Na, K, Al, and Si were also present.

A precursor of ZnO was produced by adding drop-by-drop 0.5 M NaOH solution to 50 ml of the leach liquor, under ultrasound irradiation, for 3 min. The ultrasound irradiation was provided by a Ti_6Al_4V probe immersed in the solution, and linked to a mod. Sonopuls HD 2070 sonicator ultrasound generator of Bandelin (Berlin, Germany) which can supply ultrasonic power of 75 W/cm² at 20 kHz. The experiments were carried out at an amplitude of 80% in pulsated mode. In order to investigate the precipitation of Ca, Si, Mn, Mg, and Al, the addition of NaOH was interrupted at various pH values (pH 6–9). The precursor was separated from the solution by centrifugation. The extracted precursor was subsequently heated in a furnace for 150 min at 810°C. The powder obtained was characterised by using a Stereoscan 440 scanning electron microscope (SEM) (Cambridge Instruments, Cambridge, UK) equipped with a PV9800 energy dispersive spectroscope (EDS) (Philips, Amsterdam, Netherlands), and by X-ray diffraction (XRD) using a D500 diffractometer (Siemens, Berlin, Germany) with nickel-filtered CuKα (λ = 1.5405 Å), at 40 kV and 30 mA. Moreover, the size and the structure of the powder were characterised by a transmission electron microscope (TEM) with a JEOL 200CX. A solution containing the powders was also analysed by UV spectroscopy Model V-530 (Jasco, Easton, USA).

In order to produce Fe nanoparticles for each experiment, 100 ml of leach liquor from the 1 M sulphuric acid ultrasound-assisted leaching was used [16]. The composition of the leach liquor is reported in Table 2. The leach liquor was initially heated at 70°C, and some drops of HNO_3 were added to oxidise Fe(II) to Fe(III). Subsequently, the precipitation FeOOH was induced by adding drop-by-drop 33% NH_3 solution until a pH of 3.5 was obtained. The precipitate was separated from the solution by centrifugation, and then washed with deionised water. This step was repeated four times. A representative amount of the precipitate was dehydrated and analysed by SEM-EDS. Besides Fe and O, a non-negligible amount of Cr was detected. Therefore, an oxidation of Cr was performed by dispersing the precipitate in 5%

Table 1: X-ray fluorescence analysis of EAF dust.

Element	Fe_2O_3	ZnO	CaO	MnO	SiO_2	MgO	Cl	SO_3	F
wt.%	35.92	31.34	13.32	3.95	3.89	2.52	2.06	1.07	0.97
Element	Cr_2O_3	K_2O	Al_2O_3	CuO	Na_2O	P_2O_5	CdO	SnO_2	NiO
wt.%	0.85	0.77	0.46	0.25	0.23	0.16	0.09	0.05	0.05

Table 2: Concentration (g/l) of elements in the two leach liquors of sulphuric acid.

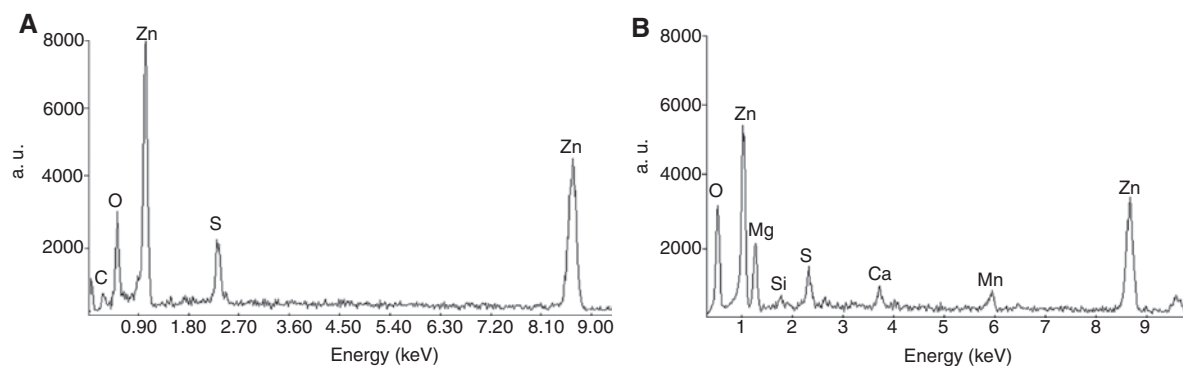| Element	Zn	Fe	Mg	Ca	Mn	Na	K	Al	Si	Cr
0.5 m acid	15.68	–	1.53	0.42	0.53	0.95	0.71	0.20	0.08	–
1 m acid	17.31	8.23	1.45	1.42	0.82	1.21	0.75	0.23	0.09	0.12

Figure 1: EDS spectra of the powder obtained at (A) pH 6.5 and (B) pH 8.

H_2O_2 aqueous solution, heated at 60°C for 2 h under vigorous stirring. The solution was then centrifuged, and FeOOH was separated from the solution. The solution was treated for Cr recovery.

Then, 3 g of precipitated FeOOH, without being dehydrated, was dissolved in 100 ml of 0.5 M HCl solution. The synthesis of the Fe nanoparticles was carried out by adding drop-by drop 0.1 M $NaBH_4$ under ultrasound irradiation, for 2 min. The solution turned from yellow to black colour, and the black powder was separated by centrifugation. The powder was washed thrice with ethanol each time and then held in a vacuum chamber.

The obtained powder was characterised as previously described for the ZnO powders, except that CrKα (λ = 2.2897 Å) was used instead of CuKα for the XRD measurements.
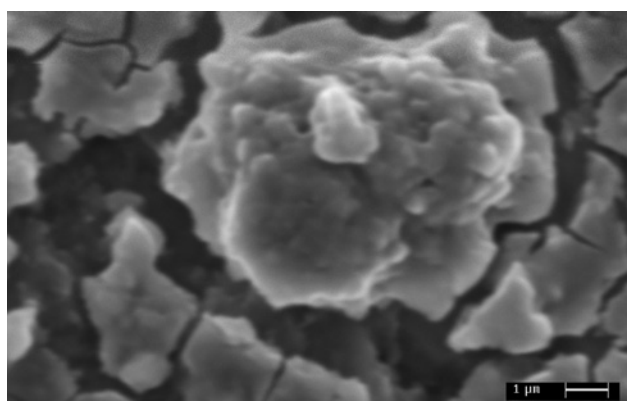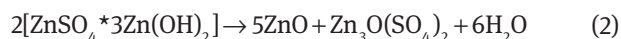
3 Results and discussion

3.1 Nanoparticles of ZnO

The precipitation of the precursor of ZnO was obtained by adding NaOH to the leaching solution, under sonication. The powders, precipitated at different pH values, were analysed by SEM-EDS in order to investigate the elemental composition. This analysis showed that it was necessary to stop the experiment at pH 6.5 to avoid the precipitation of the other metals. In Figure 1, the EDS spectra of the powder are shown, where it is possible to observe that, besides Zn, S, and O, also Mg, Si, Mn, and Ca were detected in the powder obtained at pH 8 (Figure 1B), whereas in the sample produced at pH 6.5 only Zn, S, and O were present (Figure 1A). It could be noted that the colour of the powder changed from pH 6. 5 to pH 8. At pH 6.5, the powder was white, whereas with increasing pH it became yellowish white, due to the contamination of other metals. The SEM image of the powder produced at pH 6.5 shows that the particles were agglomerated with a dried mud structure (Figure 2).

The inductively coupled plasma (ICP) analysis of a small amount of the dehydrated precipitate at pH 6.5 showed that it was possible to obtain Zn with high

Figure 2: SEM image of the powder obtained at pH 6.5.

purity. The powder produced by the experiment carried out at pH 6.5 was analysed by XRD, and the peaks of zinc sulphate hydroxide hydrate $ZnSO_4*Zn(OH)*4H_2O$ (ICDD n. 00-009-0204) were found (Figure 3A). This compound can be considered a precursor of ZnO, as zinc hydroxide sulphate hydrate can be transformed into zinc oxide by thermal transformation [17]. The thermal decomposition is thought to involve the dehydration, the dehydroxylation of the basal hydroxide, and the decomposition of sulphate groups in zinc oxide and various gases [Eqs. (1)–(3)] [17–19].

$$Zn_4(SO_4)(OH)_6 xH_2O \rightarrow ZnSO_4 3Zn(OH)_2 + xH_2O \qquad (1)$$

$$2[ZnSO_4*3Zn(OH)_2] \rightarrow 5ZnO + Zn_3O(SO_4)_2 + 6H_2O \qquad (2)$$

$$Zn_3O(SO_4)_2 \rightarrow 3ZnO + 2SO_2 + O_2 \qquad (3)$$

After heat treatment at 80°C for 150 min, the obtained powder was probed with SEM, and EDS analysis was performed (Figure 4A,B). The particles were found to be agglomerates of approximately 300 nm and constituted of O and Zn, suggesting that ZnO was produced. The XRD analysis confirmed that the precursor zinc sulphate
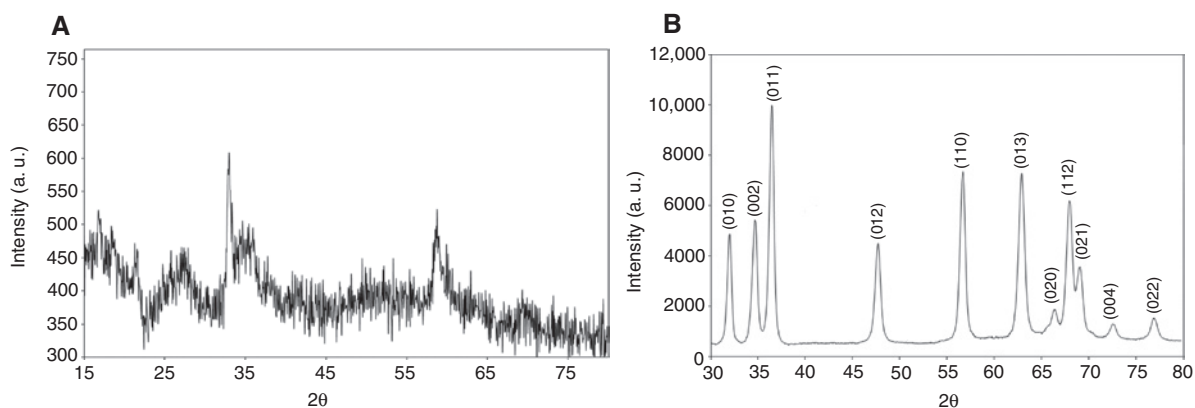
A

B

Figure 3: XRD pattern of (A) the precursor and (B) ZnO nanoparticles.
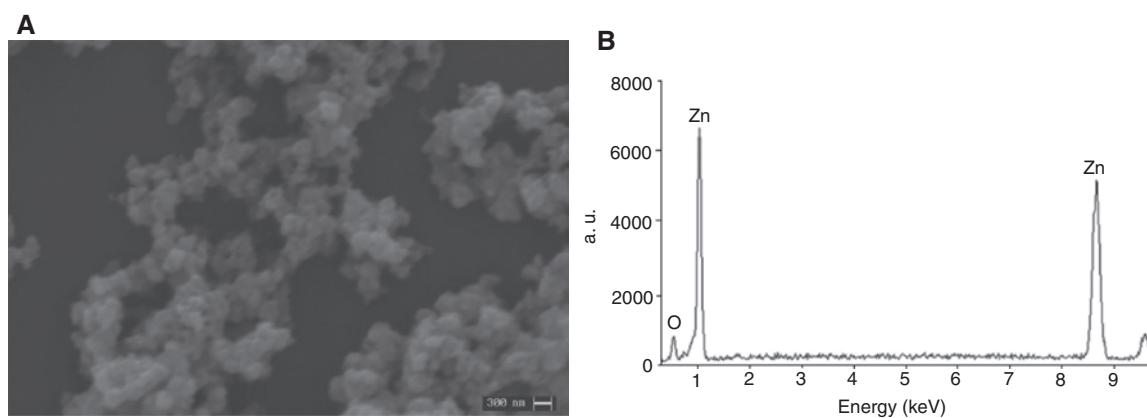
A

B

Figure 4: SEM image and EDS spectrum of the ZnO nanoparticles.

hydroxide hydrate was transformed completely to ZnO (ICSD n. 98 002 5119), as shown in Figure 3B.

The mean size of ZnO particles was calculated to be approximately 20 nm using Sherrer's equation:

$$D = \frac{0.9\,\lambda}{\beta\cos\theta}, \tag{4}$$

where D is the mean crystalline size (nm), λ is the wavelength of CuKα (0.154 nm), β is the full width at half maximum intensity in radians, and θ is the Bragg angle.

From TEM analysis, the particles were found to be spherical in shape and were agglomerated with a particle size of approximately 30 nm (Figure 5). Compared to results obtained in the literature with thermal decomposition, the use of ultrasound in the presented work was found to produce nanoparticles with a lower mean size. For example, Darezereshki et al. [19] produced ZnO nanoparticles with a particle size of 80 nm, when using $ZnSO_4 \cdot 7\,H_2O$ and Na_2CO_3 as the raw materials to form the precursor of $Zn_4(SO_4)(OH)_6 \cdot 0.5\,H_2O$. The reaction between
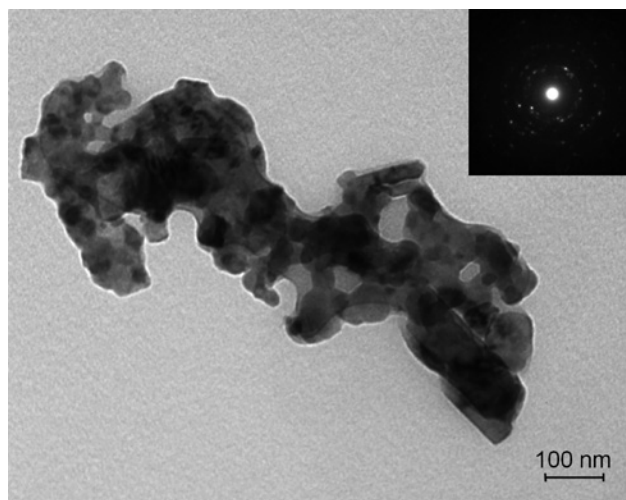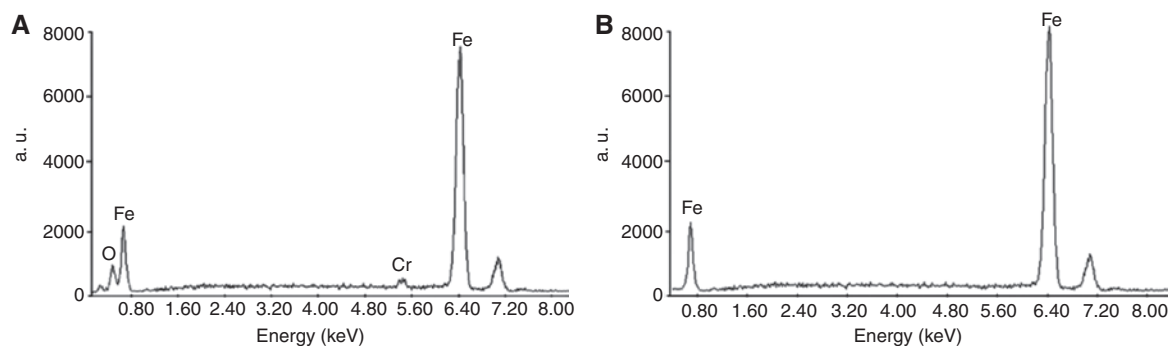

Figure 5: TEM bright-field image and selected-area electron diffraction (SAED) of ZnO nanoparticles.

$ZnSO_4 \cdot 7\,H_2O$ and Na_2CO_3 occurred at 70°C for 45 min. The obtained precursor was calcinated in air in a muffle furnace at 825°C for 1 h.
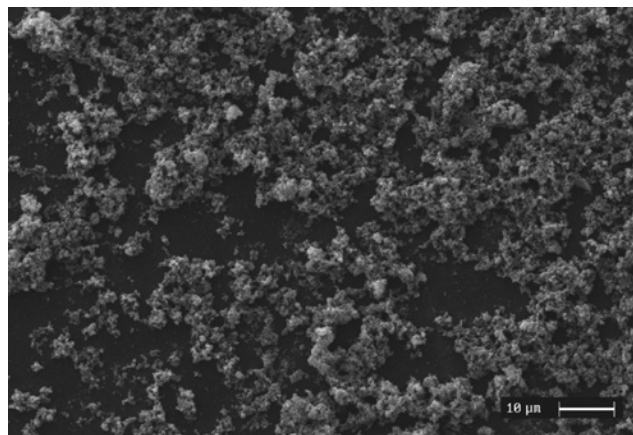
Figure 6: EDS spectra of (A) FeOOH precipitated from the leaching solution and (B) FeOOH after the oxidation of Cr.
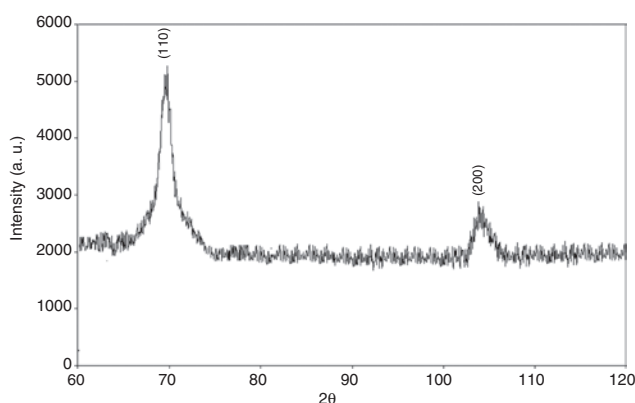
3.2 Nanoparticles of zero-valent Fe

The Fe powders were obtained by reduction with $NaBH_4$ of the iron present in the solution where FeOOH was previously dissolved. The EDS analysis showed that Fe powders contained a non-negligible amount of Cr (Figure 6A). The method adopted to remove it, described in the experimental part, was efficacious. In fact, after the oxidation of Cr, this element was no longer present, as shown in Figure 6B and confirmed by ICP analysis. The SEM image of the iron powder shows that the particles were agglomerated (Figure 7).

The XRD analysis confirmed that nanoparticles synthesised were effectively zero-valent Fe, as no peaks of iron oxides were observed and only peaks due to α-iron were found (Figure 8). The two peaks were indexed as α-iron (ICDD n. 00-087-0722). The mean size of Fe nanoparticles calculated using Sherrer's equation [Eq. (4)] was approximately 5 nm. The TEM image of the iron nanoparticles is shown in Figure 9. The particles resulted in a spherical in shape, and the size was between 5 and 7 nm, in agreement with XRD analysis.

Figure 8: XRD pattern of Fe nanoparticles.
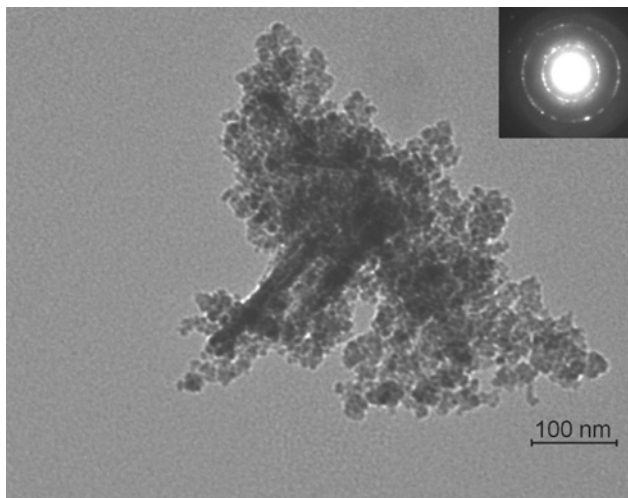
Figure 9: TEM bright-field image and SAED of Fe nanoparticles.

It should be noted that the size of zero-valent iron nanoparticles produced in this work was smaller than those obtained by other researchers, using $NaBH_4$ as reducing agent. Sun et al. used the ferric iron reduction by sodium borohydride to synthesise zero-valent iron, and

Figure 7: SEM image of Fe nanoparticles.

nanoparticles with a size of about 60 nm were formed [15]. Jamei et al. investigated an ultrasound-assisted method that involved the reduction of $FeSO_4$ with sodium borohydride [20]. The smaller nanoparticles obtained were characterised by a mean size of about 30 nm.

4 Conclusions

In this work, the possibility of synthesising nanoparticles with high purity using as raw materials the acid leaching solution of EAF dust was demonstrated. Two methods were developed to produce ZnO and Fe nanoparticles and to avoid the precipitation of other metals present in the initial leaching solution.

ZnO nanoparticles and zero-valent Fe with particle sizes of approximately 30 and 5 nm, respectively, were obtained. The use of ultrasound decreased both the particle size of the nanoparticles and the reaction time.

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Bionotes

Katya Brunelli

Ing. Katya Brunelli is a fellowship postdoc in metallurgy at the Department of Industrial Engineering, University of Padova (UoP). She received a degree in chemical engineering in 2000 and her PhD in metallurgical engineering in 2004 from UoP. Her scientific activity is addressed at the recovery of metals from different types of waste, reuse of steel slag, surface treatments of light alloys, microstructural evolution of steels, intermetallic compounds, amorphous metals, corrosion of metals, and hydrometallurgy. She is an author of about 90 scientific and technical papers.

Pietrogiovanni Cerchier

Ing. Pietrogiovanni Cerchier received a degree in materials engineering in 2014 and is now a PhD student at the Department of Industrial Engineering, University of Padova. The theme of his research is the recovery of strategic materials from wastes. In particular, his study concerns green synthesis of nanoparticles (NPs) from printed circuit boards: silver NPs, tin oxide NPs, gold NPs, copper NPs, and iron NPs; plasma eletrolytic oxidation coating containing silver or copper powder; full recycling of photovoltaic panels; recovery of tantalum from end-of-life capacitors; and recovery of neodymium from permanent magnets.

Renato Bonora

Ing. Renato Bonora is a professor at the Department of Industrial Engineering, University of Padova (UoP). He received a degree in

chemical engineering and a PhD in separation processes, both from UoP. For over 15 years, he worked as a scientist for a leading international company in the recovery and refining of precious metals. For his master's degree in chemical engineering, he is currently teaching recovery of contaminated sites. His research projects and contracts concern innovative technology design, and development for recovery and refining of precious and strategic metals.

Manuele Dabalà

Ing. Manuele Dabalà is a professor at the Department of Industrial Engineering, University of Padova (UoP). He received a degree in industrial chemistry in 1992 from University of Venice and his PhD in metallurgical engineering in 1998 from UoP. He was a researcher from 2001 until 2009. His research topics are the evolution of microstructure for high-temperature alloys, the recovery metals from wastes with hydrometallurgy, the synthesis of metallic nanoparticles, corrosion tests and techniques to improve corrosion resistance, and advanced coatings for metals like plasma electrolytic oxidation or atmospheric plasma.