

## Article

# Cost-Effective and High Purity Valuable Metals Extraction from Water Leaching Solid Residues Obtained as a By-Product from Processing the Egyptian Boiler Ash

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**Abstract:** The water leaching solid residues (WLSR) obtained from salt-roasting Egyptian boiler ash are considered an essential secondary resource for (13%) nickel and (5.6%) zinc extraction. Hence, the current study aims for the cost-effective and high purity Ni, Zn, Fe and Mg metal ion extraction from (WLSR) using a sulfuric acid leaching process. The factors affecting the percentage recovery of Ni, Zn, Fe and Mg from WLSR, including leaching temperature, time, acid concentration and solid/liquid ratio, have been investigated. The obtained leaching solutions were analyzed chemically using ICP, and the different precipitates were analyzed mineralogically using XRD and EDX analysis and chemically using XRF. The maximum percentage recovery of Ni, Zn, Fe and Mg was 95.02%, 90.13%, 66.29% and 75.73%, which was obtained under the optimum leaching conditions of 8% H<sub>2</sub>SO<sub>4</sub> concentration and 1/15 solid/liquid ratio at 85 °C for 240 min. The effect of pH, Fe<sub>2</sub>O<sub>3</sub> dosage as nucleating agent and the precipitation duration on iron removal and Ni and Zn loss have been thoroughly studied. It has been found that >95% of the contained iron impurity can be removed, while nickel and zinc losses are around 4.2% and 3.8%, respectively. Additionally, a pH of 6 and 0.45 mol/L concentration of H<sub>2</sub>C<sub>2</sub>O<sub>4</sub> was utilized to precipitate Mg as MgC<sub>2</sub>O<sub>4</sub>·2 H<sub>2</sub>O, demonstrating that the precipitation efficiency of Mg reaches 96.9%. Nickel and zinc precipitation efficiency was 92.25% and 85.51%, respectively, by raising the solution pH to approximately 9. The kinetic of Ni and Zn dissolution has been investigated to explain the mechanism prevalent and the factors influencing the leaching process. It has been found that the nickel leaching kinetic is controlled by both diffusion through an inert porous layer and by chemical reaction with an activation energy of 20.25 kJ·mol<sup>−1</sup>. Meanwhile, the kinetic of zinc leaching is controlled by solid product layer diffusion with an activation energy of 11.67 kJ·mol<sup>−1</sup>.

**Keywords:** extractive metallurgy; nickel; zinc; Egyptian boiler ash; waste recycling; sulfuric acid leaching; precipitation; leaching kinetics; activation energy

## 1. Introduction

Nickel has unique physical and chemical properties that enhance its utilization in a wide range of industrial and everyday applications including alloy production; food, military, electroplating and energy industries; and the production of nickel-cadmium batteries and automobiles [1–3]. Until now, stainless steel has been the primary use of nickel production by about 65% due to the mechanical and anticorrosive qualities of nickel when mixed with other metals [4–6]. On the other hand, there are two main categories of users in industrial applications of zinc first and end-users. Brass, die-casters, galvanizers manufacturers and comparatively modest applications such as chemical processing are among the first users. End-users of Zn, such as cathodes in batteries and those in the hardware, automotive, building, furniture, electronics, medical, toy and textile sectors,

utilize the product of the initial users as an input in their manufacturing processes [7]. The International Zinc Association has confirmed that over 70% of Zn production globally comes from mined ores, with the remaining 30% coming from recycled or secondary Zn resources. The production of Zn from natural sources is both expensive and complicated. Currently, the firstly mined Zn ores only contain 5%–15% Zn, and sphalerite mineral is the most abundant source of Zn. Oxidized ores containing Zn in various carbonate and silicate minerals have long been a significant source of Zn [8,9]. Ni-sulphide ore contains 0.2%–2% Ni and contributes approximately 60% of global Ni output, and it represents 30% of all known reserves. On the other hand, Ni laterites contain 1%–4% Ni, which accounts for 70% of all known resources, and are responsible for the remaining 40% of worldwide Ni output [10–13].

The depletion of Ni/Zn ores and the increasing global demand for these metals has necessitated extensive research on their extraction from secondary resources and/or low-grade ores [14]. Hence, its availability is a vital criterion for maintaining the output levels required to meet the demands of end customers [6,15]. Compared to the low content of Ni and Zn in the Ni/Zn-containing ores, Ni/Zn-containing wastes and scrap are considered a promising alternative to produce Ni and Zn due to their high Ni and Zn contents and easy extraction. Only around 40% of accessible nickel-bearing scrap is now recycled, indicating that nickel production from secondary materials containing (30%–72% Ni) has a lot of potential. The other 60%, in the form of solid wastes such as batteries, spent nickel-based catalysts, scrap metal, spent solutions, superalloys and non-land resources such as sea nodules, can be found and treated [16]. On the other hand, some industrial processes generate solid wastes in the form of ashes with relatively high amounts of vanadium (4.4%–19.2%), nickel (2.7%–8.5%) and zinc (1.3%–4.2%) [17–20], which makes it a beneficial and promising resource for the recovery of these important elements [14,21,22]. This material has no mining or grinding expenses, unlike other resources that are restricted and/or of low quality, because the material is generated on a regular basis as fine and agglomerate wastes from electricity stations [23].

Boiler ash is a solid waste formed by the combustion of heavy fuel oil (HFO) in power plants, from which several million tons of waste are produced annually. The generation of this ash has negative effects on the environment [24]. In order to reduce the environmental negative effects of this ash, the extraction of metals including nickel and zinc from boiler ash is of critical importance because: (1) nickel and zinc are two of the most hazardous metals and need to be reclaimed; and (2) their existence in this ash poses a serious hydrometallurgical and environmental conservation challenge [17,19,25]. Currently, there are many methods and techniques used for the processing of boiler ash, including salt roasting–water leaching and direct acidic leaching. One of the previously stated technologies, direct acidic leaching, has numerous drawbacks, such as the lack of selectivity in leaching the target metals, such as vanadium, nickel, zinc, iron, and magnesium, that are all dissolved in the solution. Additionally, the process uses large quantities of high acid concentration and generates leachate containing a lot of hazardous elements that cause some problems in the later precipitation and purification processes; the process also uses an oxidizing agent, which makes it costly [26–29]. On the other hand, salt roasting–water/acid leaching of boiler ash is a traditional way to recover vanadium and concentrate the ashes to increase its nickel and zinc content [30–35]. After the extraction of high-purity vanadium, the water leaching residue (WLSR) still contains a significant level of heavy metals and other important minerals, such as Ni, Zn and Pb; therefore, they are regarded as prospective resources for the extraction of Ni and Zn [36–38].

There are two principal methods for processing the solid waste to extract the valuable metals from it, including the following. (1) Hydrometallurgy, in which the valuable metal is leached from solid waste into a solution and then recovered from this solution. The main hydrometallurgical methods are classified according to the type of used leaching agent into three main groups of acidic leaching (i.e., HCl, H<sub>2</sub>SO<sub>4</sub> and HNO<sub>3</sub>), alkaline leaching (i.e., NaOH and Na<sub>2</sub>CO<sub>3</sub>) and a combination of acidic and alkaline leaching.

(2) Pyrometallurgy, in which the solid waste is heated to a high temperature to allow the separation of valuable metal [16,39,40]. Due to the cheap operational and energy costs, hydrometallurgical processing is frequently chosen as the preferred method for recovering nickel and zinc from fly ash [25]. Direct acidic leaching is used to dissolve almost all valuable metals into the solution from various types of solid wastes and then extract these metals separately by appropriate methods [41–56].

Due to the previous mentioned advantages, extracting nickel and zinc from boiler ash is a compelling alternative, as it allows the recovery and recycling of the metal values and, at the same time, avoids potential environmental damage or risks of these wastes. The main objective of the current study is the extraction of nickel, zinc, iron and magnesium with high purity from water leaching solid residue (WLSR) using a cost-effective and selective dilute sulfuric acid leaching process. The parameters affecting the leaching process, in addition to the mechanism of metal leaching in solutions and its subsequent precipitation, have been investigated. The kinetics of metal ion leaching process have been also studied.

## 2. Materials and Method

### 2.1. Materials

Water leaching solid residue (WLSR) containing high-grade nickel and zinc was obtained from the processing of Egyptian boiler ash (collected from one of the biggest Egyptian thermal power plants, which uses natural gas and heavy oil as a fuel, located in kuriemat, Egypt, supplied by Nuclear Material Authority) using salt roasting–water leaching processes for Vanadium extraction. The optimum conditions for roasting and water leaching processes have been optimized in the previous study as follows: 850 °C, 20 wt.% NaCl dosage, 2.5 h and 1/10 solid/liquid ratio for 90 min. The used water leaching solid residue (WLSR) sample was dried and ground to 63 µm and then mixed thoroughly to be processed in the subsequent leaching processes for the extraction of valuable metals including Ni, Zn and others.

### 2.2. Methods

#### 2.2.1. Acidic Leaching of Nickel and Zinc

In the leaching process, the WLSR sample was digested using a sulfuric acid solution in a 250 mL three-neck flask. The sulfuric acid solution with different concentration was prepared by adding the predetermined specific amount of H<sub>2</sub>SO<sub>4</sub> to the distilled water at atmospheric pressure, and all experiments were carried out using a constant weight of the solid sample of 20 g. The three-neck flask was designed so that one neck was fitted with a reflux condenser to maintain the concentration of the species in the solution, the second for a thermometer, and the last was used either for a mechanical stirrer or inlet/withdrawal of the samples or for pH measurements. The reaction suspension was agitated with a mechanical stirrer at a rate of 500 rpm, then heated directly to the specified temperature using a hot plate. After the completion of the leaching experiment, the obtained slurry was cooled and then filtered with a vacuum pump. The filter cake was washed with a small amount of warm distilled water to remove and separate the released Zn and Ni ion and then made up to volume; then, the washed spent cake was dried at 110 °C in a drying oven. The metals (Ni, Zn, Mg and Fe) content in the pregnant solution was analyzed by inductively coupled plasma–atomic mass spectrometry (ICP-MS, a Perkin Elmer ELAN model 9000, Waltham, MA, USA). To confirm the results obtained by (ICP-MS), the differences in the chemical compositions of the WLSR before leaching and their sulfuric acid solid residue (SASR) after leaching were measured using the X-ray fluorescence (XRF) data, which represent the Ni and Zn percentage recovery. The extraction of these metals was calculated according to Equation (1).

$$\eta (\text{Ni, Zn}) = \left( \frac{m_1 \cdot v_1}{m_0 \cdot v_0} \right) \times 100\% \quad (1)$$

where  $m_0$  and  $m_1$  are the mass of WLSR used in leaching experiments (g) and the concentration of metal ions (Ni, Zn, Mg and Fe) in the filtrate (g/L), respectively.  $v_0$  and  $v_1$  are the mass percentage age of metal ions (Ni, Zn, Mg and Fe) in WLSR (%) and the volume of filtrate (L), respectively.

### 2.2.2. Removal of Iron and Magnesium from Pregnant Solution

During sulfuric acid leaching, some impurities of Mg, Si, Fe and Al are transferred into the pregnant solution accompanied with Ni and Zn, which, in turn, affects the Ni and Zn precipitation rate and hence the purity of the final product, so that they need firstly to be removed from the pregnant solution.

Firstly, the iron contained in the leachate mainly exists in the form of  $\text{Fe}^{2+}$ , but  $\text{Fe}^{3+}$  ions are inevitable. To maximally improve the purity of the finally produced Ni-Zn, they had to be eliminated to the minimum possible level. Consequently, the leachate needed to be pre-treated with an excess of hydrogen peroxide to ensure that all the low valence  $\text{Fe}^{2+}$  were oxidized completely to  $\text{Fe}^{3+}$  and reduce the loss of nickel and zinc due to pH changes in the solution. Then, the iron ions in the pregnant solution were removed by the method of chemical precipitation method at room temperature. The pregnant solution pH value was adjusted at pH = 3 by using sodium hydroxide. Additionally,  $\text{Fe}_2\text{O}_3$  powder was added in amounts from 3 g/L to 15 g/L, which was used as nucleating agent. Then, this mixture was agitated for 10 min to precipitate the iron ions [57]. The obtained precipitate was filtered from the purified solution by vacuum filtration. Finally, the contents of Ni, Zn and iron in the purified solution were determined by using ICP-MS instruments. Then, the concentration of metal ion and the Ni and Zn loss rate were calculated by generalized Equation (2).

$$\rho = \left(1 - \frac{C_a \cdot \beta_a}{C_b \cdot \beta_b}\right) \times 100\% \quad (2)$$

where  $C_b$  and  $C_a$  refer to the concentration of metal ions (Ni, Zn, Mg and Fe) in the liquor before and after the precipitation experiment (g/L), respectively.  $\beta_b$  and  $\beta_a$  are volumes of the liquor before and after the precipitation experiment (L), respectively.

Additionally, the possibility of recovering magnesium from a solution using the oxalic acid precipitation method to obtain magnesium oxalate has been investigated, and the optimal conditions of precipitation have been investigated [57].

### 2.2.3. Nickle and Zinc Precipitation

After the iron and magnesium were precipitated and removed from the pregnant solution, the Ni and Zn concentrations in the purified solution increased. The recovery of Ni and Zn from the leachate was conducted by a direct precipitation method at pH 8.0 for 10 min at 25 °C. The Ni and Zn in the solution were subsequently precipitated as  $\text{Ni}(\text{OH})_2$  and  $\text{Zn}(\text{OH})_2$  until the solution settled. Then, the precipitate was filtered out, washed, dried at 60 °C and calcined at 450 °C for 2 h to obtain NiO and ZnO products.

## 2.3. Sample Characterization

The chemical compositions of the original water leaching solid residue (WLSR) sample and the chemical changes that resulted from the acidic leaching process were determined and measured by the method of X-ray fluorescence (XRF), using a Shimadzu XRF-1800 analyzer (XRF-1800, 90 mA, 40 kV, Re anode, Kyoto, Japan). The changes in the mineralogical composition of WLSR, microstructural compositions during the phase transformations of the WLSR as well as sulfuric acid solid residue (SASR) and the final precipitate of nickel and zinc were determined by the method of X-ray diffraction (XRD) (Analytical X-Ray Diffraction equipment model X'Pert PRO with Monochromator, Cu-K $\alpha$  radiation ( $\lambda = 1.542 \text{ \AA}$ ) at 50 KV, 40 mA and scanning speed 0.02/s). In order to determine the phase transformation during the leaching process, different products were also prepared and carefully investigated using a scanning electron microscope (SEM) Tescan TS 5130MM equipped with an energy dispersive X-ray (EDX) detector (prepared by Oxford Instruments,

Abingdon, UK, active crystal area—50 mm<sup>2</sup>) in addition to a microanalysis system and YAG crystal as a backscattered electron (BSE) detector. Inductively coupled plasma atomic mass spectrometry (ICP-MS, a Perkin Elmer ELAN model 9000, Waltham, MA, USA) was also used to determine metal content accurately on the obtained pregnant solutions after the acidic leaching process and chemical precipitation.

### 3. Results and Discussion

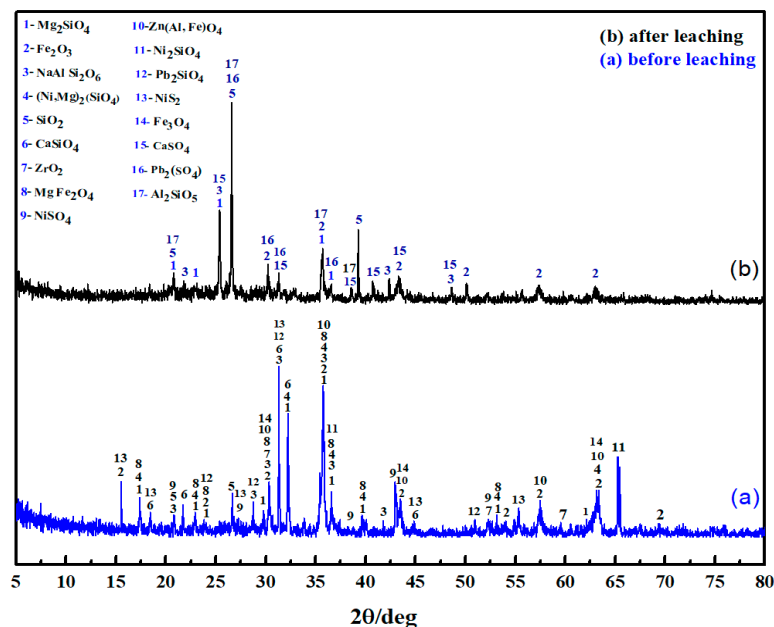
#### 3.1. Chemical and Mineralogical Composition of the Used WLSR

The chemical composition of the water leaching solid residue (WLSR) using X-ray fluorescence analysis (XRF) tabulated in Table 1.

**Table 1.** Overall chemical analysis of water leaching solid residue (WLSR).

| Compound wt. %               | Fe <sub>2</sub> O <sub>3</sub> | NiO   | SiO <sub>2</sub> | ZnO  | V <sub>2</sub> O <sub>5</sub> | CaO  | Na <sub>2</sub> O | Al <sub>2</sub> O <sub>3</sub> | TiO <sub>2</sub> | MnO   | MgO   | K <sub>2</sub> O | P <sub>2</sub> O <sub>5</sub> | SO <sub>3</sub> | PbO  | L.O.I | Others |
|------------------------------|--------------------------------|-------|------------------|------|-------------------------------|------|-------------------|--------------------------------|------------------|-------|-------|------------------|-------------------------------|-----------------|------|-------|--------|
| Water Leaching Solid Residue | 24.83                          | 13.23 | 15.04            | 5.67 | 1.25                          | 4.54 | 1.04              | 4.67                           | 0.552            | 0.628 | 14.21 | 0.106            | 0.302                         | 1.38            | 1.61 | 1.09  | 9.85   |

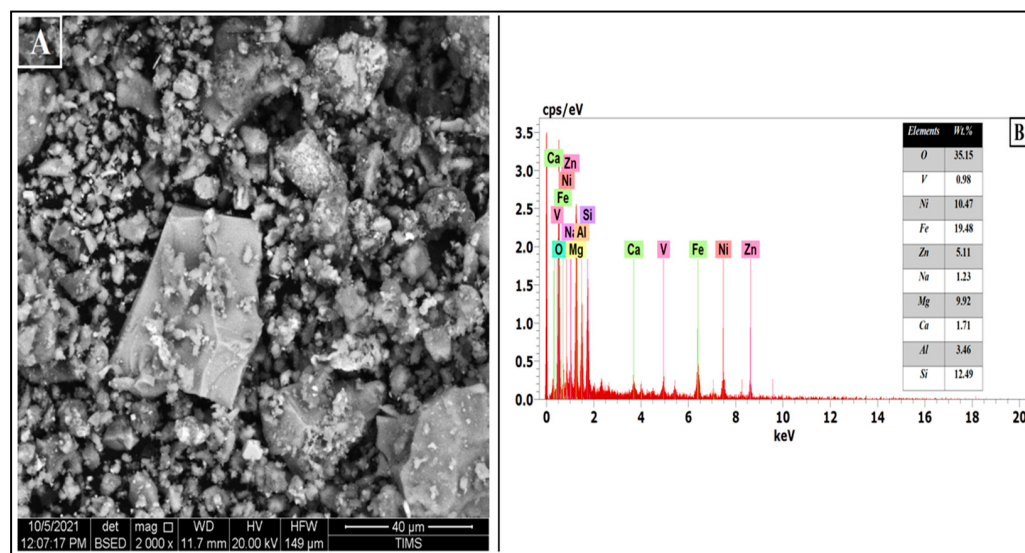
The mineralogical phase composition of the WLSR analyzed by X-Ray Diffraction analysis is presented in Figure 1a,b. The results revealed that the WLSR was composed mainly of the following phases: hematite Fe<sub>2</sub>O<sub>3</sub>, magnesioferrite MgFe<sub>2</sub>O<sub>4</sub>, nickel magnesium silicate (Ni, Mg)<sub>2</sub>(SiO<sub>4</sub>), zinc aluminum iron oxide Zn(Al, Fe)O<sub>4</sub>, calcium silicate (Ca<sub>2</sub>SiO<sub>4</sub>) and jadeite (NaAlSi<sub>2</sub>O<sub>6</sub>). Meanwhile, the minor phases were nickel sulfide (NiS<sub>2</sub>), lead silicate (Pb<sub>2</sub>SiO<sub>4</sub>) and nickel sulfate oxide (NiSO<sub>4</sub>).



**Figure 1.** XRD patterns of water leaching solid residue (WLSR) of boiler ash (a) before and (b) after leaching with H<sub>2</sub>SO<sub>4</sub> at the optimum operating conditions.

Further investigation of the water leaching solid residue (WLSR) was carried out using the backscattered electron image and the corresponding EDX microanalysis results of the whole area, as shown in Figure 2. The leaching residue had increased roughness and degradation with irregular semi-circular and cube surface and exhibited very different morphology from those of the ash roasting process obtained at the optimum operating

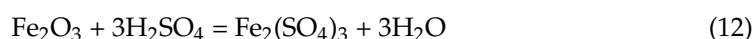
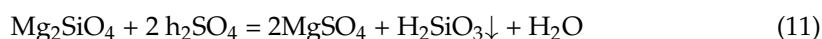
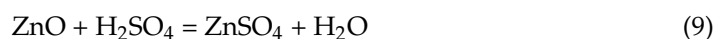
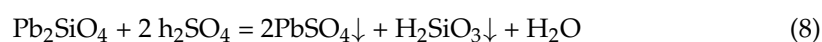
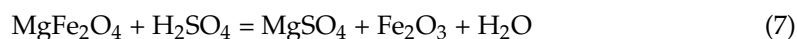
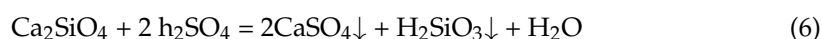
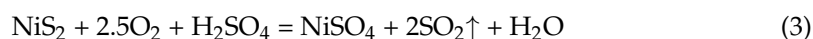
conditions optimized in a previous study by the research group, as shown by Figure 2A. This confirms that most of the vanadium was leached, leaving nickel and zinc in WLSR. The EDX results in Figure 2B show that the particles mainly consisted of Ni, 10.47 wt.%; Fe, 19.48 wt.%; Si, 12.49 wt.%; Zn, 5.11 wt.%; and O, 35.15 wt.%, in good agreement with the data obtained by XRF analysis.

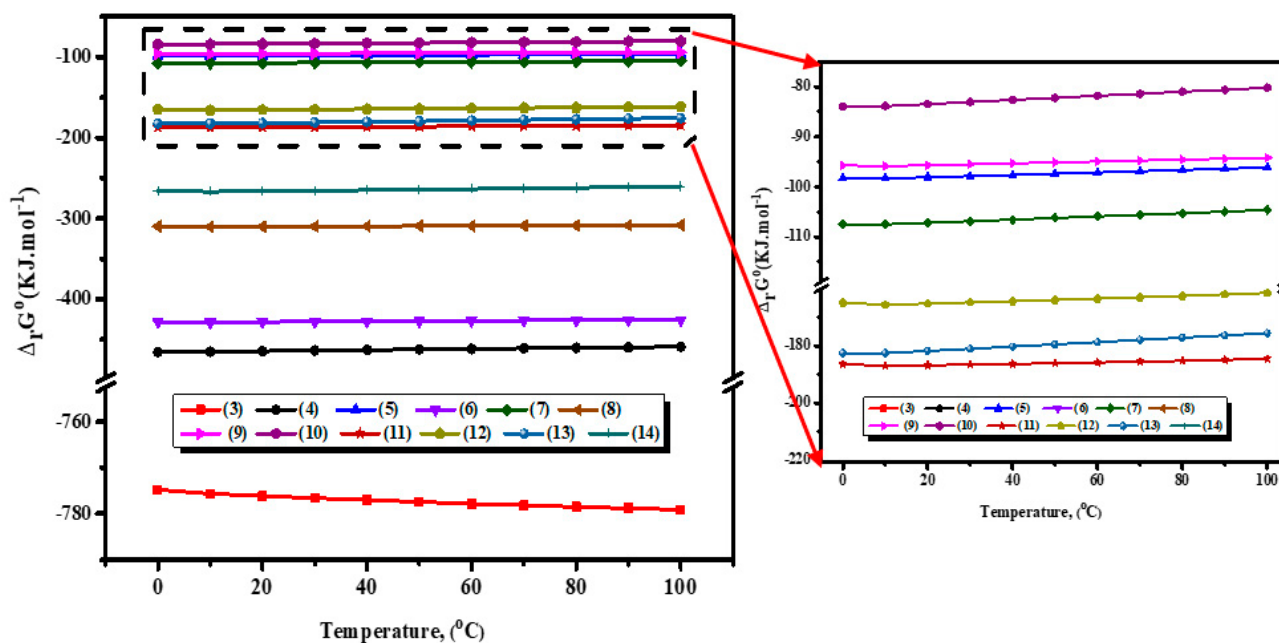
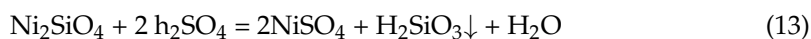


**Figure 2.** SEM images of used water leaching solid residue (WLSR) obtained under optimum leaching conditions of the Egyptian boiler ash (A) and EDX element analysis (B).

### 3.2. Thermodynamics Analysis of Leaching Process

The reactions of the components in WLSR with  $H_2SO_4$  according to Equations (3)–(14) are presented in the thermodynamic diagrams (Figure 3). The original crystal structure of the residue has been totally changed by means of sulfuric acid leaching. The metallic components such as iron, zinc, nickel and magnesium in the WLSR were converted into the corresponding sulfate and leached by the sulfuric acid solution; on the other hand, calcium, lead and silicon were converted into lead sulfate ( $PbSO_4$ ), calcium sulfate ( $CaSO_4$ ) precipitate and metasilicic acid ( $H_2SiO_3$ ) as colloidal precipitate, respectively. The thermodynamic results shown in Figure 3 illustrate the feasibility of this method for leaching water leaching solid residue (WLSR) with sulfuric acid to obtain dissolved metal sulfate because the Gibbs free energy change ( $\Delta G$ ) of the above Equations (3)–(14) had negative values in the range from 0 to 100 °C [57,58]. The free energy change of the metals varies in the sequence of dissolution of  $Ni > Fe > Mg > Zn$ .



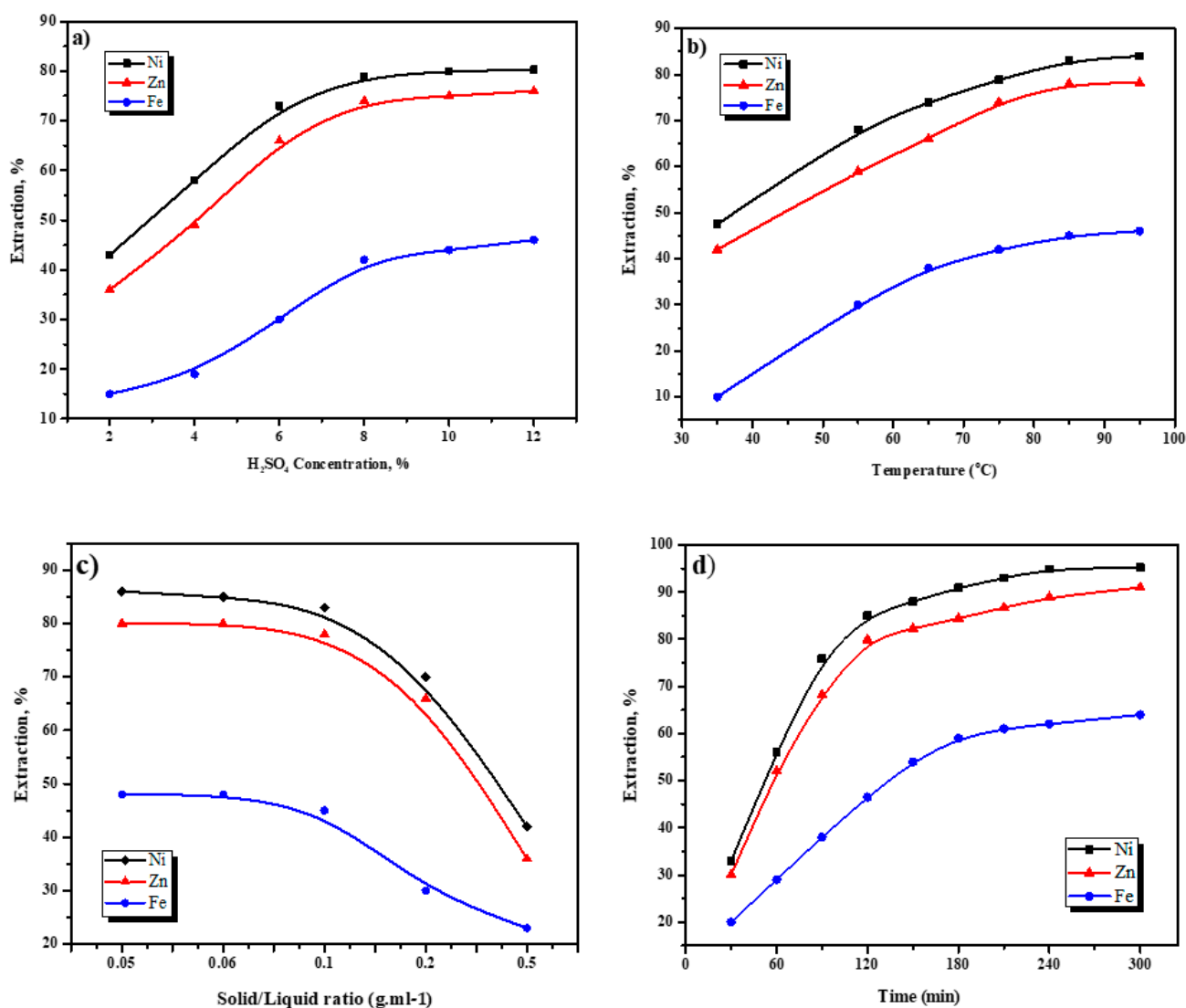


**Figure 3.** Relationship between  $\Delta_r G^0$ -T for main reactions in  $\text{H}_2\text{SO}_4$  leaching process of WLSR.

### 3.3. Optimizing the Factors Affecting the Leaching Process of WLSR

The factors affecting the leaching process of WLSR and hence the percentage recovery of Ni, Zn and Fe have been investigated to obtain the maximum recovery. These factors include the acid concentration, the leaching temperature, solid/liquid ratio and leaching time.

The effect of sulfuric acid concentration on the extraction of Ni, Zn and Fe has been investigated by using different acid concentrations in the range 2%–12% (vol%), for 120 min leaching time, 75 °C leaching temperature, 1/10 solid/liquid ratio and 500 rpm rotation speed [17,20]. The results indicate that the WLSR sample is easily amenable to sulfuric acid leaching, as shown in Figure 4a. Hence, by gradually increasing acid concentration from 2% to 8%, the dissolution percentage of Ni, Zn and Fe increased almost linearly from 43%, 36% and 15% until they reached 79%, 74%, 42%, respectively. This means that low acid concentration is insufficient to dissolve metal ions from WLSR sample, while at 8% acid concentration, the participation of a large part of the acid in the internal reactions has been noted in Equations (10)–(13), which improves the extraction of metal ions. Otherwise, by increasing the acid concentration more than 10%, the metal leaching efficiency remained stable due to more generation of colloidal silicic acid and solid  $\text{CaSO}_4$ , which prevent unreacted particles and hinder the dissolution of more desirable ions [14,19,59]. In consideration of reducing the acid consumption cost, a sulfuric acid concentration of 8% was selected as the best value and used in the subsequent leaching experiments.



**Figure 4.** Effect of  $H_2SO_4$  acid concentration (a), leaching temperature (b), solid/liquid ratio (c) and leaching time (d) on Ni, Zn and Fe extraction.

The effect of leaching temperature on the dissolution of Ni, Zn and Fe has been studied by varying the leaching temperature range from 35  $^{\circ}C$  to 95  $^{\circ}C$ , and the other leaching conditions were fixed as mentioned above. The results presented in Figure 4b reveal the important effect of leaching temperature on obtaining a reasonable dissolution of Ni, Zn and Fe from WLSR. Leaching at a low temperature (35  $^{\circ}C$ ) under the above conditions gives a low recovery of Ni, Zn and Fe of no more than 47.9%, 42% and 10%, respectively. Further increasing the leaching temperature to 85  $^{\circ}C$  increases the dissolution of Ni, Zn and Fe to 83%, 78% and 45%, respectively. This can be attributed to the fact that the increased temperature leads to the breaking of the boundary founded in surface of WLSR particles by increasing the diffusion of  $H^+$  ions on their surfaces, which increased the activity of the molecules, thereby increasing the collision probability between WLSR and  $H_2SO_4$  molecules [14,20,22]. The further increase in the leaching temperature above 85  $^{\circ}C$  had no significant effect on the extraction of the different metal ions; therefore, 85  $^{\circ}C$  was selected to be the best leaching temperature in the subsequent leaching experiments.

The effect of the solid/liquid ratio on the dissolution percentage of Ni, Zn and Fe was studied using 1/2, 1/5, 1/10, 1/15 and 1/20 S/L ratios, while other leaching parameters have been fixed. The obtained results presented in Figure 4c show that the solid/liquid ratio has a considerable effect on the percentage recovery of Ni, Zn and Fe from WLSR.

The dissolution of the metal ions increases with decreasing the pulp density to 1/15 S/L ratio, which leads to an increase in the recovery to 85% Ni, 80% Zn and 46% Fe. This can be attributed to a sufficient amount of acid present in the liquid to attack the solid particles. However, by increasing the S/L ratio to higher values, the Ni, Zn and Fe percentage recovery decreases [9,20]. This effect could be attributed to the increased solid percentage in the solution, which decreases the interaction between the ions, thus reducing the proton ions' concentration in the solution. Therefore, the best S/L ratio has been selected to be 1/15.

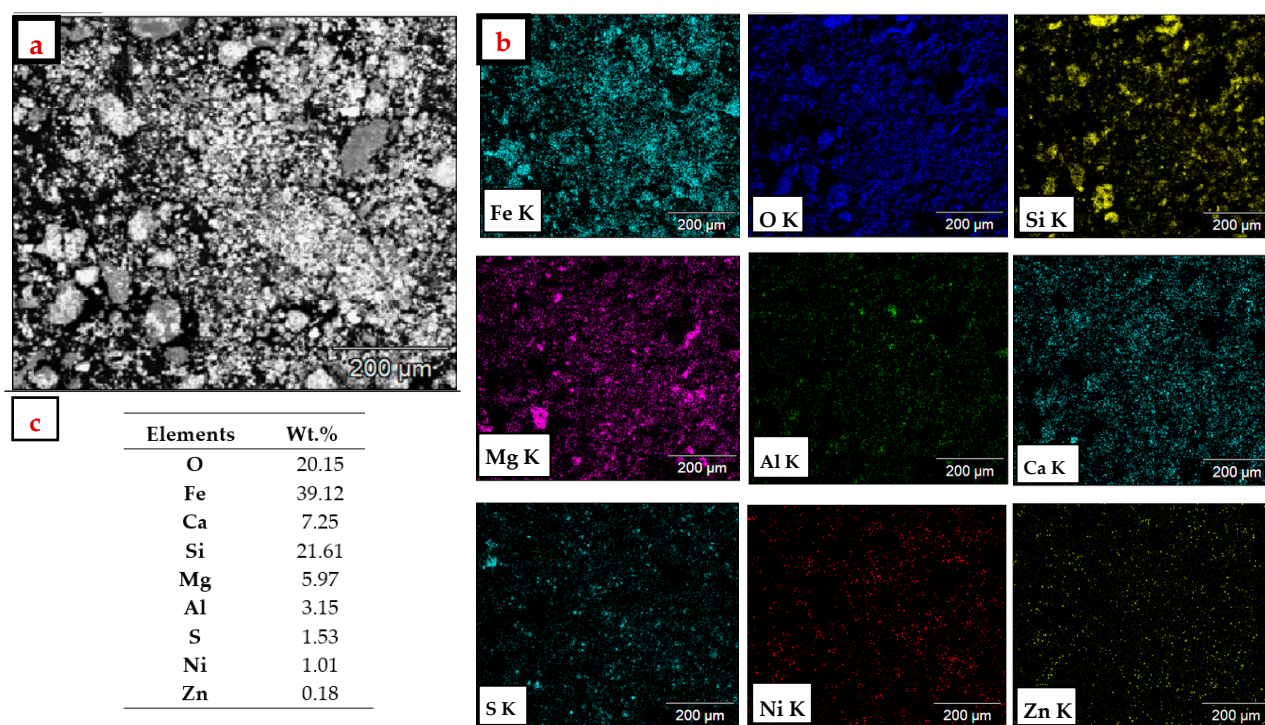
The effect of leaching time on Ni, Zn and Fe percentage recovery has been investigated by varying the leaching time from 30 to 300 min with all other leaching parameters fixed. The obtained results presented in Figure 4d indicate that the dissolution percentage of Ni, Zn and Fe increases as the leaching time increases to 240 min, to maximum values of 95.02% Ni, 90.13% Zn and 66.29% Fe. Hence, the leaching time of 240 min was selected as the best leaching time. Table 2 presents the XRF analysis results of the sulfuric leaching solid residue (SLSR) under the optimum leaching conditions (8% H<sub>2</sub>SO<sub>4</sub>, 85 °C, 1/15 S/L, 240 min), which demonstrates that the main elements in the final residue were Fe, Si, Ca and Mg.

**Table 2.** Overall chemical analysis of sulfuric acid solid residue (SASR).

| Compound<br>wt. %                                     | Fe <sub>2</sub> O <sub>3</sub> | NiO  | SiO <sub>2</sub> | ZnO  | V <sub>2</sub> O <sub>5</sub> | CaO  | Na <sub>2</sub> O | Al <sub>2</sub> O <sub>3</sub> | TiO <sub>2</sub> | MnO   | MgO  | K <sub>2</sub> O | P <sub>2</sub> O <sub>5</sub> | SO <sub>3</sub> | Pb   | L.O.I | Others |
|-------------------------------------------------------|--------------------------------|------|------------------|------|-------------------------------|------|-------------------|--------------------------------|------------------|-------|------|------------------|-------------------------------|-----------------|------|-------|--------|
| Final Residue<br>after H <sub>2</sub> SO <sub>4</sub> | 18.93                          | 0.89 | 26.57            | 0.64 | 0.072                         | 10.2 | <0.01             | 5.81                           | 0.377            | 0.101 | 6.83 | 0.052            | <0.01                         | 9.75            | 3.61 | 8.13  | 6.34   |

The sulfuric acid solid residue (SASR) was characterized by XRD analysis, as shown in Figure 1a,b. In comparison with the XRD analysis of the WLSR sample, it can be found that almost no peaks attributed to minerals bore nickel (e.g., Ni<sub>2</sub>SiO<sub>4</sub>, NiS<sub>2</sub> and NiSO<sub>4</sub>) or zinc. This confirms the thermodynamic analysis of the chemical reactions described above in Section 3.2.

However, after leaching, the intensities of peaks corresponding to CaSO<sub>4</sub> and PbSO<sub>4</sub> were increased. In addition, the intensity of SiO<sub>2</sub> peak increased after leaching, indicating the complete dissolution of these accompanying elements. For further explanation of the phase transformation, SASR samples were investigated using scanning electron microscopy (SEM), and the obtained results are shown in Figure 5. The results indicated that the residue contained a negligible concentration of heavy metals. However, this solid residue (SASR) is recommended to be used in the next study as thermally treated adsorbents to remove undesirable ions from industrial wastewater.



**Figure 5.** Backscattered electron image of SASR (a); distribution mapping of the different elements (b) and EDX element analysis (c).

### 3.4. Purification and Recovery of Ni and Zn from Leachate

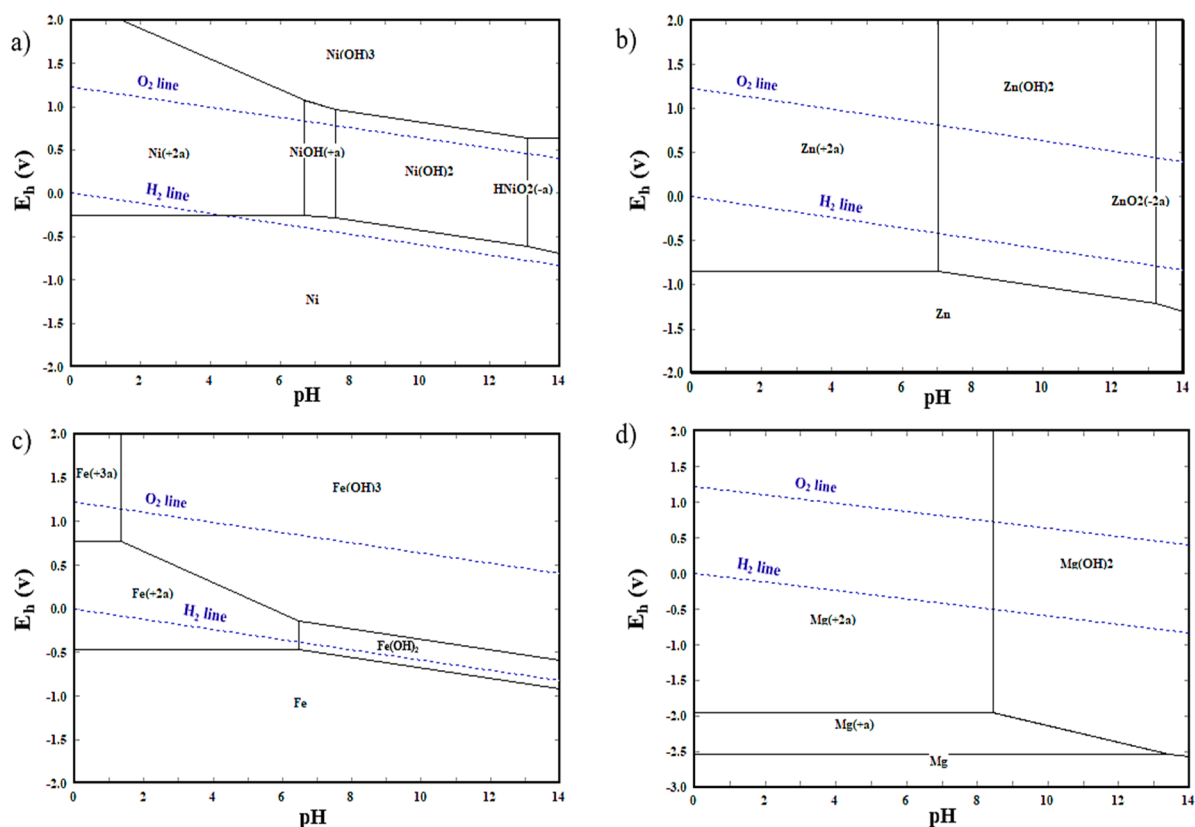
#### 3.4.1. Precipitation Behavior of Fe and Mg from the Leachate

Table 3 shows the complete chemical analysis of leachate using ICP-OES analysis, which contains Ni (11.417 g/L) and Zn (4.6462 g/L), as well as Fe (13.168 g/L) and Mg (9.783 g/L), which are the most inevitable dissolved impurities in solution that need to be removed to obtain a final Ni-Zn product of high purity.

**Table 3.** Chemical composition of the leachate (g·L<sup>−1</sup>).

| Components     | Ni    | Zn   | Fe    | Mg   | V    | Al   | Ca   | Ti   | K    | Na   | Mn   | Pb   | Si   | SO <sub>4</sub> <sup>2−</sup> |
|----------------|-------|------|-------|------|------|------|------|------|------|------|------|------|------|-------------------------------|
| Content, (g/L) | 11.42 | 4.65 | 13.17 | 9.79 | 1.17 | 0.96 | 0.13 | 0.31 | 0.06 | 1.31 | 0.46 | 0.02 | 0.88 | 150.25                        |

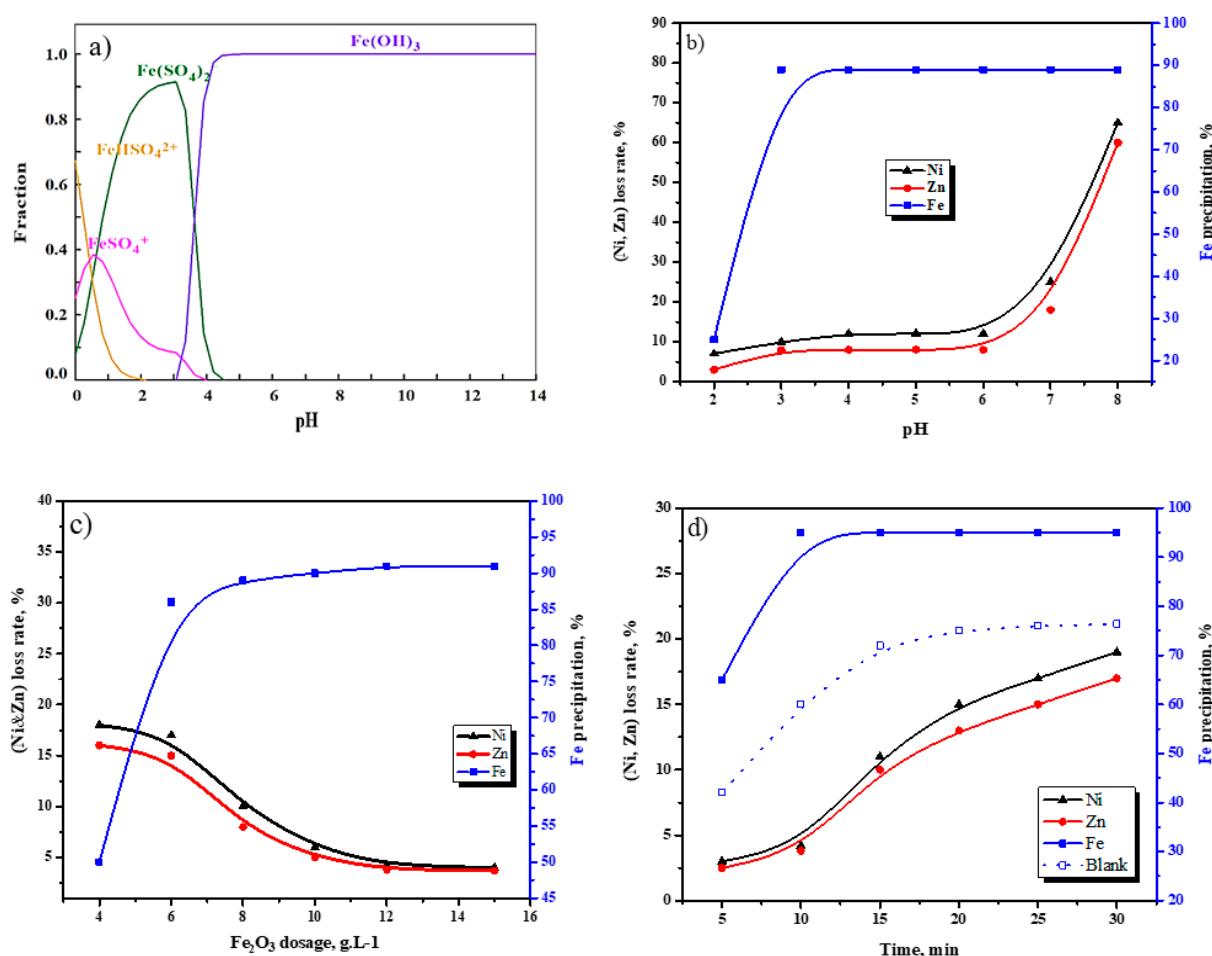
The Eh–pH graphs were obtained using the software HSC Chemistry 9.3 at 25 °C, and the obtained results are shown in Figure 6. The top and lower dotted lines in each graph depict the O<sub>2</sub>/H<sub>2</sub>O and H<sub>2</sub>O/H<sub>2</sub> stability limitations, respectively. In the water-stable zone, nickel may stably exist in the stable form of Ni<sup>2+</sup> when the solution pH value is less than 6, as illustrated in the Ni–H<sub>2</sub>O system in Figure 6a, and when the pH value rises above 8, Ni<sup>2+</sup> is transformed to Ni(OH)<sub>2</sub>. As demonstrated in Figure 6b, zinc can exist in the solution in the form of Zn<sup>2+</sup> at a pH lower than 7; in the stable region of water, as indicated by the Zn–H<sub>2</sub>O system, Zn<sup>2+</sup> will be transformed to Zn(OH)<sub>2</sub> when the pH value rises over 8. The Fe–H<sub>2</sub>O system is depicted in Figure 6c. It is shown that, in the water-stable region of the lower pH solution (<1.4), iron can exist in the form of Fe<sup>2+</sup> and Fe<sup>3+</sup>. The latter (Fe<sup>3+</sup>) will be transformed to Fe(OH)<sub>3</sub> precipitation when the pH value surpasses 1.4. Mg<sup>2+</sup> can stably exist in acidic solutions, whereas Mg(OH)<sub>2</sub> can stably exist in alkaline solutions, as shown in the Mg–H<sub>2</sub>O system in Figure 6d.



**Figure 6.** Eh–pH diagrams of Ni–H<sub>2</sub>O system (a), Zn–H<sub>2</sub>O system (b), Fe–H<sub>2</sub>O system (c) and Mg–H<sub>2</sub>O system (d) at 25 °C, where all the concentrations of Zn, Ni, Fe and Mg are 1 mol/L.

Figure 7a illustrates the species distribution of 13.168 g/L Fe in sulfuric acid solution (156.25 g/L  $SO_4^{2-}$ ) at various pH levels. It can be observed that  $Fe^{3+}$  ions react with  $SO_4^{2-}$  to create  $FeHSO_4^{2+}$ ,  $FeSO_4^+$ , and  $Fe(SO_4)_2^-$  complex ions at pH value below 3. When the pH rises over 3.5,  $Fe(OH)_3$  precipitates progressively, and beyond 4.8, virtually all iron complex ions are turned into  $Fe(OH)_3$ .

At different pH settings, the rate of Fe ion precipitation and the rate of Ni and Zn ion losses were studied. The precipitation time was set at 10 min, the  $Fe_2O_3$  nucleating agent was introduced at a concentration of 8 g/L, and the stirring speed was set at 500 rpm. Figure 7b shows the measured findings, which indicate that the precipitation rate of Fe ions was more than 89% in the pH range of 3 to 6 but only 25.7 percent when the pH was 2. With a rise in pH from 2 to 8, the rate of nickel and zinc loss increased dramatically from 7% and 3% to 65% and 60%, respectively. As a result, a pH of about  $4.8 \pm 0.2$  was confirmed to be the best value. The loss of nickel and zinc ions can be attributable to two factors. One is the precipitation of certain nickel and zinc ions due to the solution's high pH value, which may be avoided by lowering the pH as much as possible. The other is the adsorption loss due to iron ion precipitation, which is unavoidable but can be reduced by shortening the precipitation reaction time. Thus, in the next section, the appropriate precipitation time was determined.



**Figure 7.** Species distribution diagrams of Fe-H<sub>2</sub>SO<sub>4</sub> systems (a) containing 0.235 mol/L of Fe and 1.56 mol/L of SO<sub>4</sub><sup>2−</sup>, Effect of pH value (b), Fe<sub>2</sub>O<sub>3</sub> added amount (c) and precipitation time (d) on Fe precipitation rate and Ni, Zn loss rates.

The effect of Fe<sub>2</sub>O<sub>3</sub> addition dosage (4, 6, 8, 10, 12 and 15 g/L) as a crystallizing agent on the removal of Fe and loss of Ni, Zn was examined under the following conditions: a pH value of nearly 5, for 10 min precipitation time, 500 rpm stirring speed. Figure 7c presents the Fe precipitation rate as well as the Ni and Zn loss rates. It can be observed that, as the amount of Fe<sub>2</sub>O<sub>3</sub> addition rises, the Fe precipitation rate increases dramatically. At the same time, the adsorption loss of Ni and Zn is significantly reduced. As a result, the dose of 12 g/L Fe<sub>2</sub>O<sub>3</sub> was selected as the best value. This confirms that Fe<sub>2</sub>O<sub>3</sub> is an efficient crystallizing agent for eliminating Fe from leachate.

The effect of precipitation time on Fe ion precipitation rate and the rate of loss of Ni and Zn ions was investigated by varying the precipitation time in the range from 5 to 30 min with a 5 min interval. The precipitation was carried out using a dosage of 12 g/L Fe<sub>2</sub>O<sub>3</sub> as a crystallizing agent, at 5 pH and 500 rpm stirring speed. Figure 7d shows that, with the addition of a Fe<sub>2</sub>O<sub>3</sub> powder as a crystallizing agent, the iron precipitation rate can approach 95% after 10 min, while the iron precipitation rate does not exceed 60% without the addition of a Fe<sub>2</sub>O<sub>3</sub> powder as a crystallizing agent, as shown by the dotted line. On the other hand, the losing rate of Ni and Zn is noticeably increased after 10 min. As a result, the precipitation time of 10 min was selected as the best magnitude to precipitate the maximum available amount of Fe ions and, at the same time, reduce the losing rate of Ni and Zn ions to the minimum value.

The obtained Fe precipitate was then separated from the leachate, calcined at 600 °C for 2 h and characterized using XRD and SEM-EDX. The XRD pattern of the calcined precipitate is shown in Figure 8, demonstrating that the calcined product was Fe<sub>2</sub>O<sub>3</sub>. Figure 9 displays

a micrograph of the precipitate, with EDX analysis and distribution mapping of Ni, Zn and Fe elements. The obtained Fe precipitate was composed mainly of iron, with very small amounts of Ni and Zn ions.

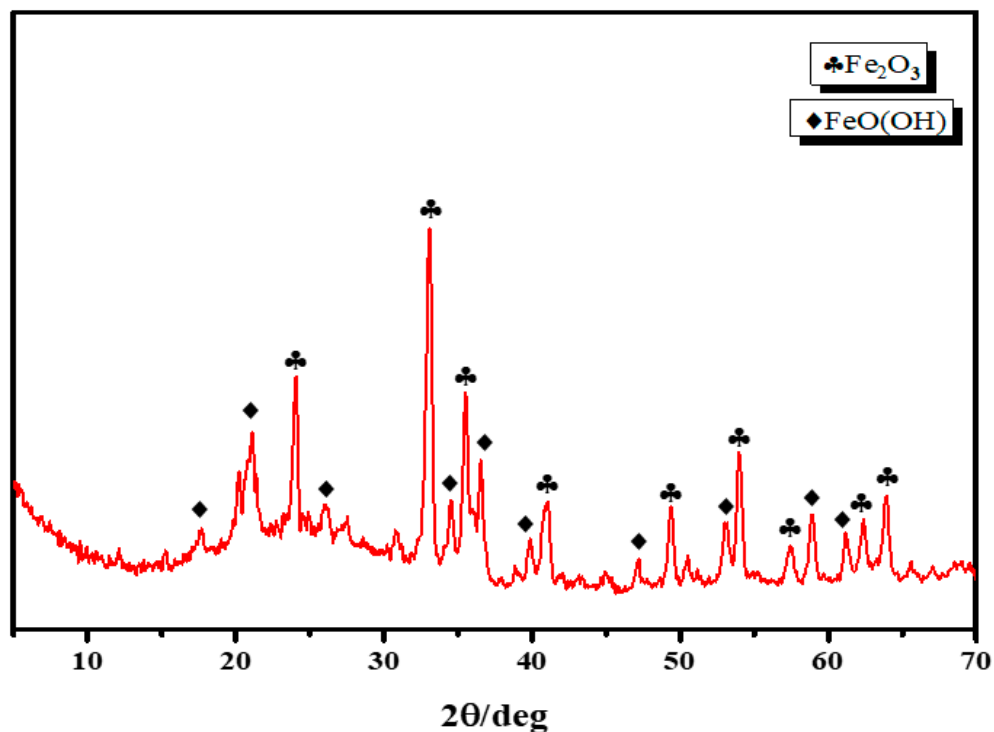


Figure 8. XRD patterns of  $\text{Fe}_2\text{O}_3$  calcined precipitate.

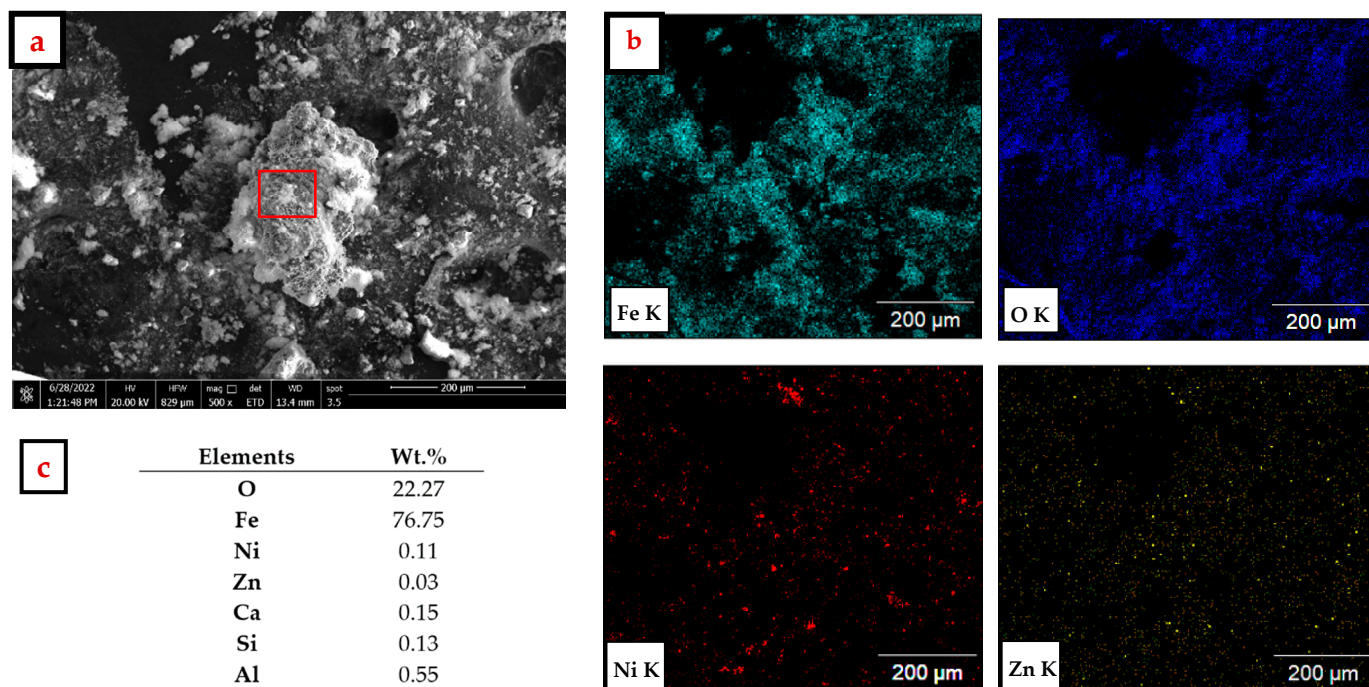


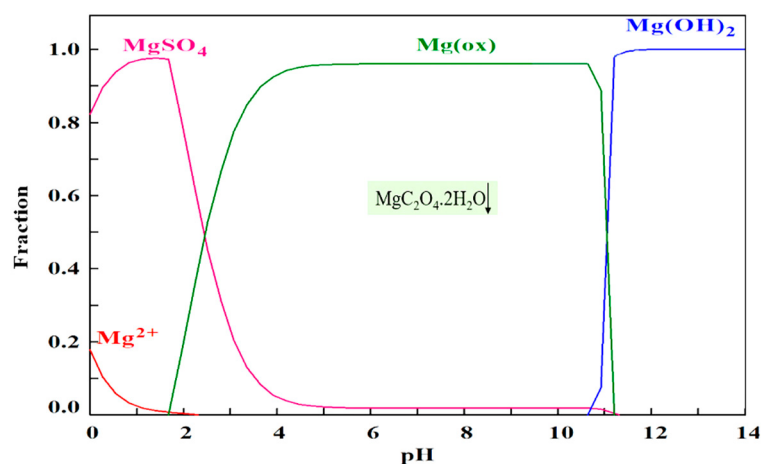
Figure 9. The backscattered electron image of the iron precipitate (a); distribution mapping of the different elements (b) and EDX element analysis of the red rectangle area (c).

According to the above-mentioned results, at 5 pH, 12 g/L added  $\text{Fe}_2\text{O}_3$  dosage and 10 min precipitation time, the rate of iron precipitation reaches 95.5%, whereas Ni and Zn ions loss are around 4.2% and 3.8%, respectively. The purification steps of the Ni/Zn-bearing leachate are listed in Table 4. It was found that the predominant constituent in the purified solution after Fe precipitation was Ni and Zn ions, which have impurity components presented in an undesirable amount (e.g., Mg) and hence need extra purification.

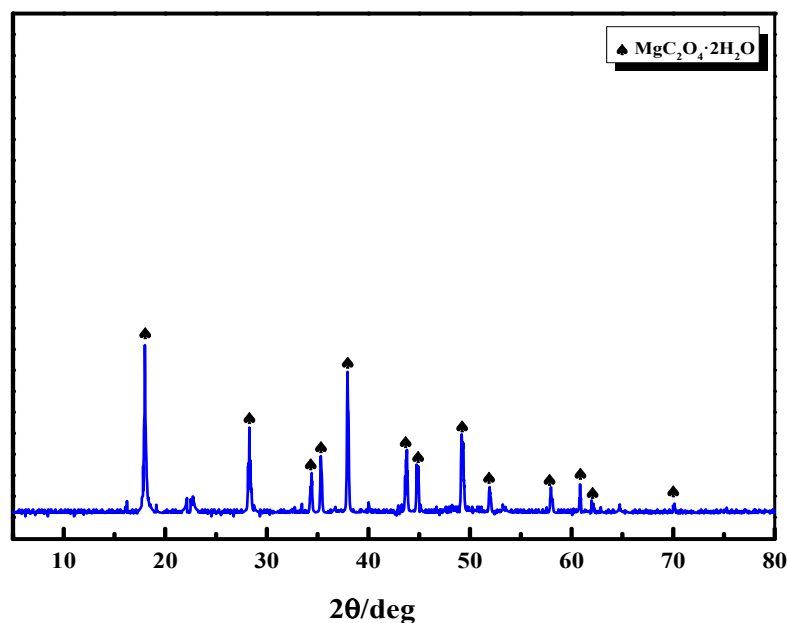
**Table 4.** Overall composition of the purified leachate before and after Fe and Mg precipitation (g/L).

| Components                                                 | Ni     | Zn     | Fe     | Mg    | V     | Al    | Ca     | Ti     | K      | Na     | Mn    | Pb     | Si    | $\text{SO}_4^{2-}$ |
|------------------------------------------------------------|--------|--------|--------|-------|-------|-------|--------|--------|--------|--------|-------|--------|-------|--------------------|
| Before purification                                        | 11.417 | 4.6462 | 13.168 | 9.783 | 0.981 | 1.016 | 0.1283 | 0.3142 | 0.060  | 1.3087 | 0.461 | 0.0228 | 0.883 |                    |
| After purification (Fe precipitation)                      | 10.901 | 4.397  | 0.305  | 9.564 | 0.875 | 0.862 | 0.1323 | 0.298  | 0.0596 | 1.288  | 0.062 | 0.0513 | 0.747 |                    |
| After purification (Mg precipitation)                      | 10.78  | 4.355  | 0.182  | 0.254 | 0.564 | 0.314 | 0.0216 | 0.215  | 0.0544 | 0.991  | 0.035 | 0.0489 | 0.605 | 150.25             |
| Composition of the residual solution (Ni–Zn precipitation) | 0.051  | 0.046  | 0.082  | 0.098 | 0.235 | 0.076 | 0.032  | 0.209  | 0.0383 | 0.087  | 0.062 | 0.0416 | 0.327 |                    |

As previously stated in Section 3.4.1, the magnesium content in the sulfuric acid solution can be converted to magnesium hydroxide precipitate by elevating the pH over 9.0. This procedure uses a lot of NaOH; in addition, the alkaline solution that results is harmful to the environment. Magnesium may be converted into magnesium oxalate by oxalic acid, which is an ecologically beneficial organic acid. Therefore, in our study, oxalic acid was employed as a precipitant to remove magnesium from the leachate. Figure 10 illustrates the species distribution of 9.564 g/L Mg and 40 g/L  $\text{C}_2\text{O}_4^{2-}$  (equal 1.5 molar ratio ( $\text{H}_2\text{C}_2\text{O}_4$ )/(Mg)) in a sulfuric acid solution (150.25 g/L  $\text{SO}_4^{2-}$ ) at various pH levels. It can be observed that magnesium mostly occurs in the form of a  $\text{MgSO}_4$  complex or  $\text{Mg}^{2+}$  in a highly acid solution (pH < 2). On the other hand, the soluble magnesium ions are progressively converted into a precipitate of magnesium oxalate as the pH of the solution rises, and under a pH range of 4 to 10, magnesium oxalate is the most common form of magnesium. Magnesium oxalate is gradually transformed into magnesium hydroxide precipitation when the pH of the solution is raised. Anyway, adopting the relevant process conditions as follows—0.45 mol/L oxalic acid, 6 pH solution, 2 h precipitation time and 25 °C precipitation temperature—and according to the findings, nearly all magnesium (96.97%) existed as  $\text{MgC}_2\text{O}_4$  precipitate. Then, the slurry was filtered to separate the precipitate and then dried in a drying oven at 90 °C. The dried Mg containing precipitate was then characterized using XRD to detect the phases of the precipitate as shown in Figure 11. The chemical composition of the Zn and Ni containing solution after Mg precipitation is presented in Table 3, which indicates that the Mg concentration was reduced to 0.254 g/L.



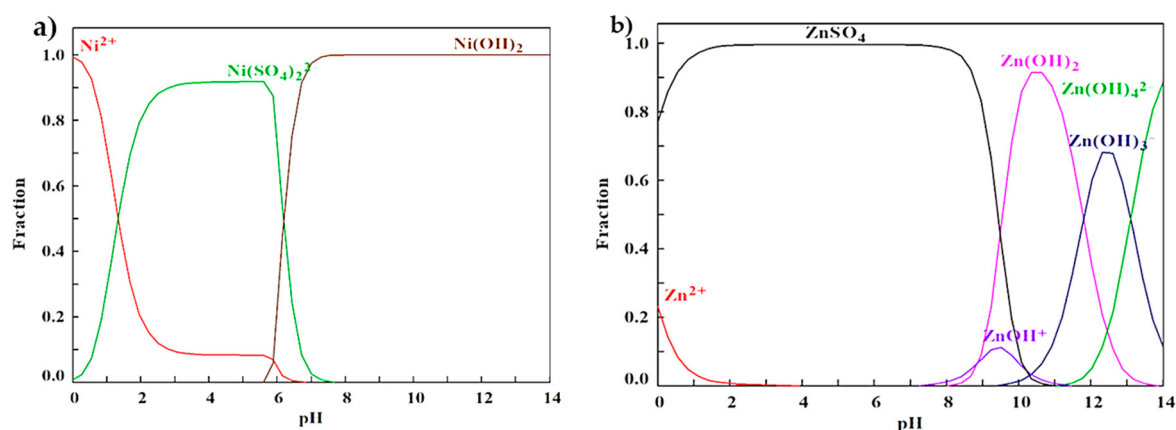
**Figure 10.** Species distribution diagrams of  $\text{C}_2\text{O}_4^{2-}/\text{Mg-H}_2\text{SO}_4$  systems containing 0.393 mol/L  $\text{Mg}^{2+}$ , 0.45 mol/L  $\text{C}_2\text{O}_4^{2-}$  and 1.5625 mol/L  $\text{SO}_4^{2-}$ .



**Figure 11.** XRD patterns of  $\text{MgC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$  precipitate.

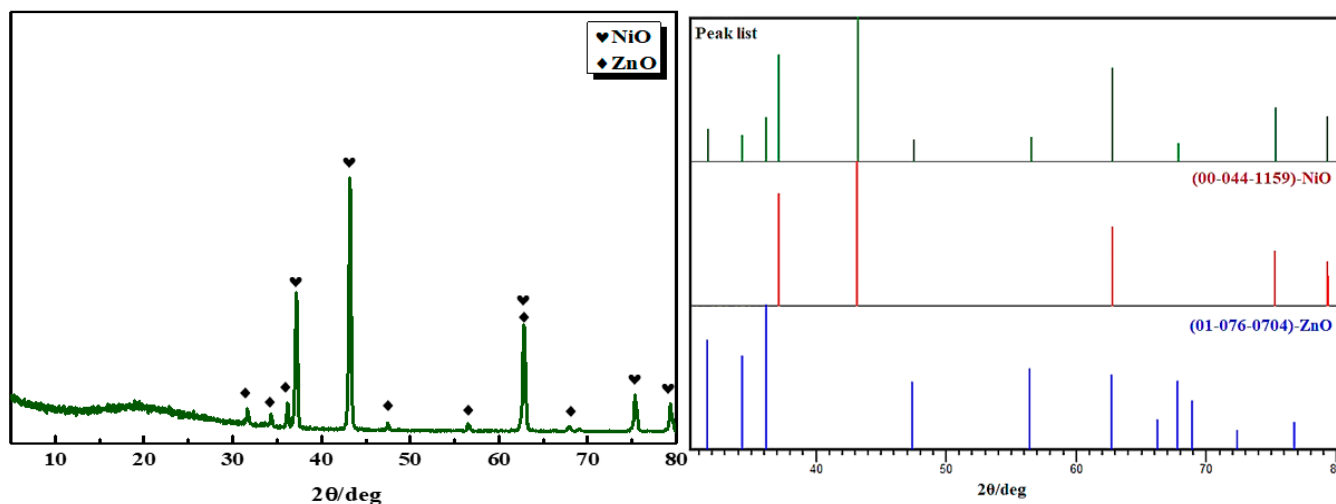
#### 3.4.2. Recovery of Nickel and Zinc from Raffinate

Once Fe and Mg have been removed from the solution, Ni and Zn can then be precipitated by raising the solution's pH to approximately 8.0 by adding NaOH. Figure 12a,b illustrates the species distribution of 10.78 g/L Ni and 4.335 g/L Zn in sulfuric acid solution (150.25 g/L  $\text{SO}_4^{2-}$ ) at various pH levels. It can be observed that nickel mostly occurs in the form of  $\text{Ni}(\text{SO}_4)_2^{2-}$  complex in a weak acid solution ( $\text{pH} < 5$ ). When the pH rises over 6.0,  $\text{Ni}(\text{OH})_2$  precipitates progressively, and beyond 8.0, almost all nickel complex ions are turned into  $\text{Ni}(\text{OH})_2$ , as shown in Figure 12a.



**Figure 12.** Species distribution diagrams of Ni-Zn/H<sub>2</sub>SO<sub>4</sub> systems containing 0.1836 mol/L Ni (a), 0.0662 mol/L Zn (b) at 1.5625 mol/L SO<sub>4</sub><sup>2−</sup>.

On the other hand, Figure 12b demonstrates that zinc ion mainly exists in the form of ZnSO<sub>4</sub> at the pH value of the solution less than 7, and as the pH value increases above 8.0, the soluble Zn ions are progressively converted into ZnOH<sup>+</sup> and Zn(OH)<sub>2</sub> precipitate. With the further increase in the pH value to above 10, the Zn(OH)<sub>2</sub> precipitate is re-dissolved as Zn(OH)<sub>3</sub><sup>−</sup> and Zn(OH)<sub>4</sub><sup>2−</sup>. In any case, the recovery of Ni and Zn from purified solution was conducted by a direct precipitation method at pH 9, allowing it to stand for 1 h at 25 °C, and the precipitation efficiency was over 92.25% and 85.51% for Ni and Zn, respectively. The precipitates were then calcined at 450 °C for 2 h before being characterized using chemical analysis and SEM-EDX. The XRD pattern of the calcined precipitate is shown in Figure 13, demonstrating that the calcined product consists mainly of mixed Ni-Zn oxide.

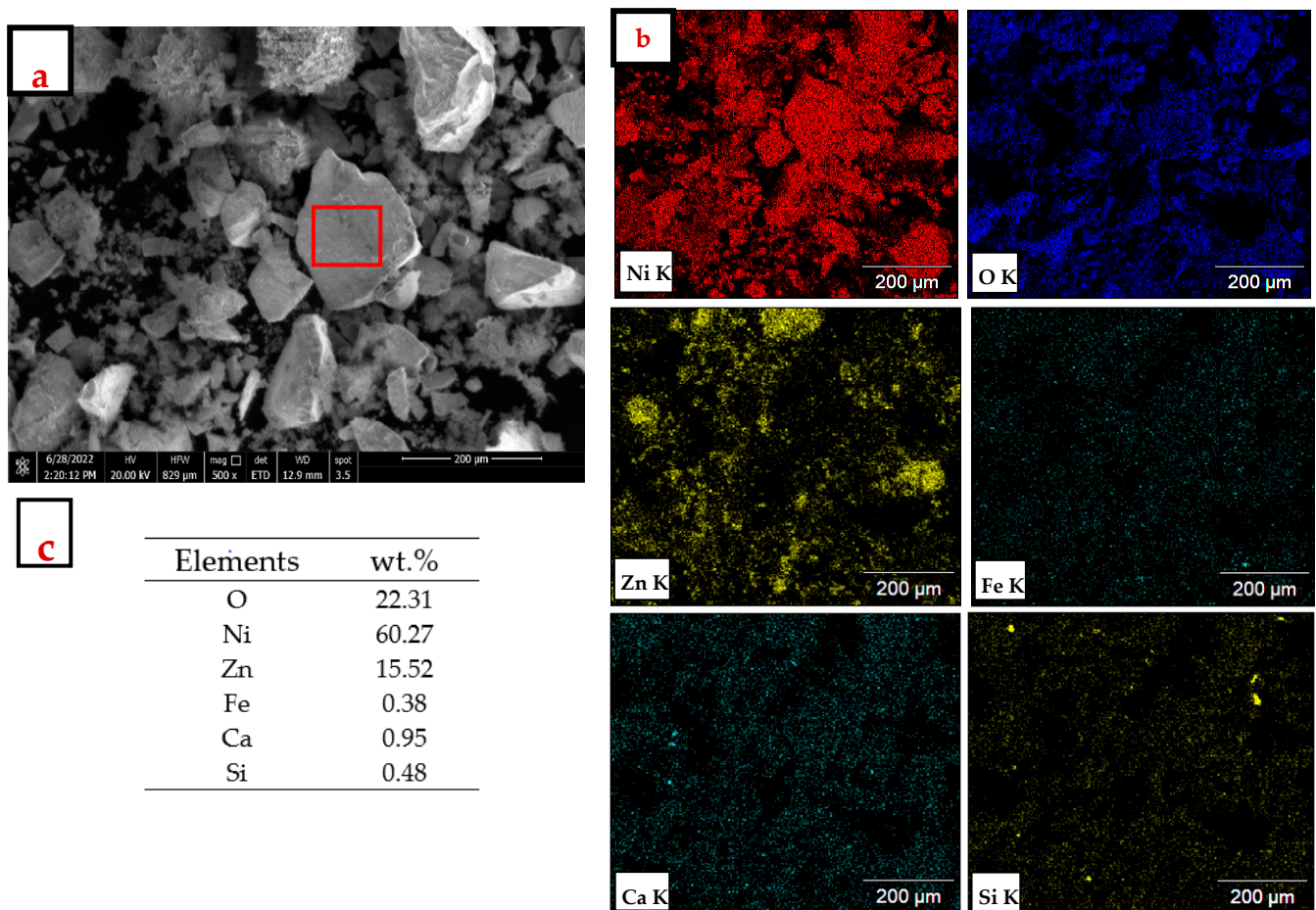


**Figure 13.** XRD patterns of NiO-ZnO precipitate.

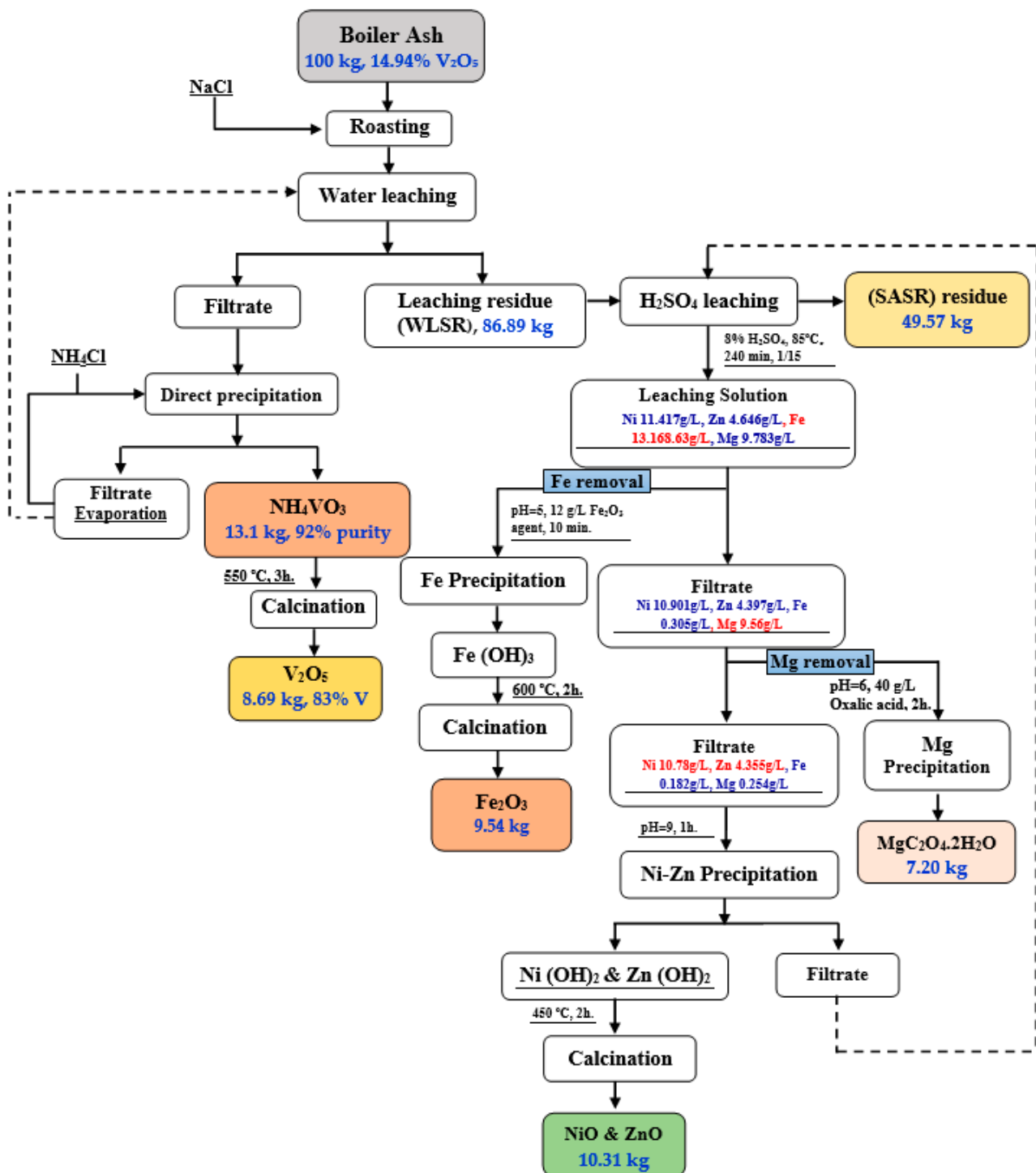
According to the chemical analysis presented in Table 5 and EDX of Ni/Zn hydroxide precipitate shown in Figure 14, the product composed mainly of Ni (37%) and Zn (23%) would require additional processing steps (i.e., re-leaching and/or solvent extraction/electrowinning) to recover the containing metals' values. While this is a saleable product and easily integrated into any existing Ni and Zn extraction flowsheets, it would command a considerably lower price than the pure metal, and thus, this would affect the economics of any plant using this process.

**Table 5.** Overall composition of the Ni/Zn product (wt.%).

| Elements | NiO   | ZnO   | Fe   | Al    | Mn    | Ca    | Mg    | K     | pb    | Na    | Si    | V     | Ti    |
|----------|-------|-------|------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|
| (wt.%)   | 57.75 | 36.86 | 0.85 | 0.195 | 0.068 | 1.883 | 0.132 | 0.016 | 0.043 | 0.985 | 1.138 | 0.016 | 0.062 |

**Figure 14.** Scanning electron micrographs for Ni-Zn precipitation powder (a), distribution mapping of the different elements analysis (b) and EDX element analysis of the red rectangle area (c).

According to the obtained results of the current study mentioned above, the proposed and recommended flowsheet for the extraction of Ni, Zn, Fe and Mg from water leaching solid residue is shown in Figure 15.



**Figure 15.** The proposed scheme for the recovery of Ni, Zn, Fe and Mg from water leaching solid residue obtained from the salt roasting of Egyptian boiler ash.

### 3.5. Kinetics Analysis

#### 3.5.1. Leaching Kinetics of Nickel

Heterogeneous fluid–solid reaction may be used in leaching processes. The reaction progress can be controlled by the following steps: (1) the mass transfer of reactants and products between the fluid molecules and the external surface of the solid particle, (2) the diffusion of reactants and products within the pores of the solid, (3) chemical reaction between the reactants in the fluid and in the solid [60,61]. One or more of these factors might

control the rate of the reaction according to the slowest link step. The un-reacted shrinking core model (SCM) is the most used mathematical model to describe the heterogeneous reactions in leaching mineralogical ores. In discussing the following kinetic properties, the controlling steps in the SCM were checked for the whole reaction time.

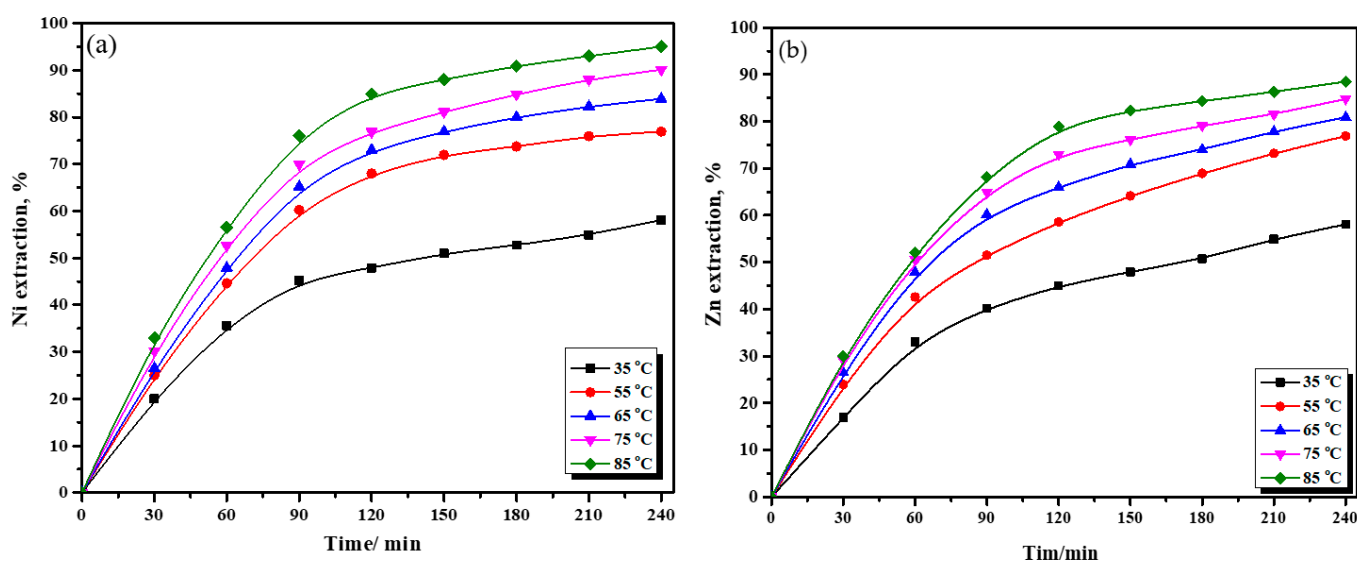
$$1 - (1 - x)^{2/3} = K_1 t \quad (15)$$

$$1 - (1 - x)^{1/3} = K_c t \quad (16)$$

$$1 - 3 \times (1 - x)^{2/3} + 2 \times (1 - x) = K_d t \quad (17)$$

where  $x$  is the conversion fraction of Ni or Zn particles,  $K_1$  is the apparent rate constant ( $\text{min}^{-1}$ ) for the fluid film diffusion,  $t$  is the reaction time,  $K_c$  is the rate constant for the chemical reaction, and  $K_d$  is the rate constant for diffusion through product layer.

The relationships of nickel extraction versus leaching time at different temperatures are plotted in Figure 16a, which presents that the dissolution of nickel increases gradually by increasing time and temperature. However, to understand the type of leaching mechanism prevalent of nickel leaching in sulfuric acid process, the leaching experiment during the whole reaction time was investigated to find which kinetic Equations (15)–(17) model can fit the reaction isotherms. Amongst the three controlling mechanisms, the liquid–film diffusion resistance is eliminated or minimized by effective stirring.



**Figure 16.** Effect of leaching time on the nickel (a) and zinc (b) dissolution at different temperature.

The obtained results are presented in Table 5 and Figure 17a,b. The left sides of Equations (15)–(17) were plotted as a function of time at different leaching temperatures and according to the obtained data from the optimal operating conditions. The values of the reaction rate constants ( $K$ ) were determined from the slope of the straight line of the relation between kinetic model and time. It was found that the correlation coefficient value for internal diffusion ( $k_d$ ) was 0.9990, while for chemical reaction ( $k_c$ ), it was 0.9763 and 0.9363 for liquid film diffusion. Based on the  $R^2$  values, it can be inferred that the predominant dissolution mechanism of nickel from WLSR is diffusion-controlled only. This due to production of a solid layer that appears to be a hindrance to the progression of the reactions and cannot be dissolved quickly [9]. Hence, the mass transfer efficiency in the generated layer was lower, which made the diffusion of reactants through it the control step.

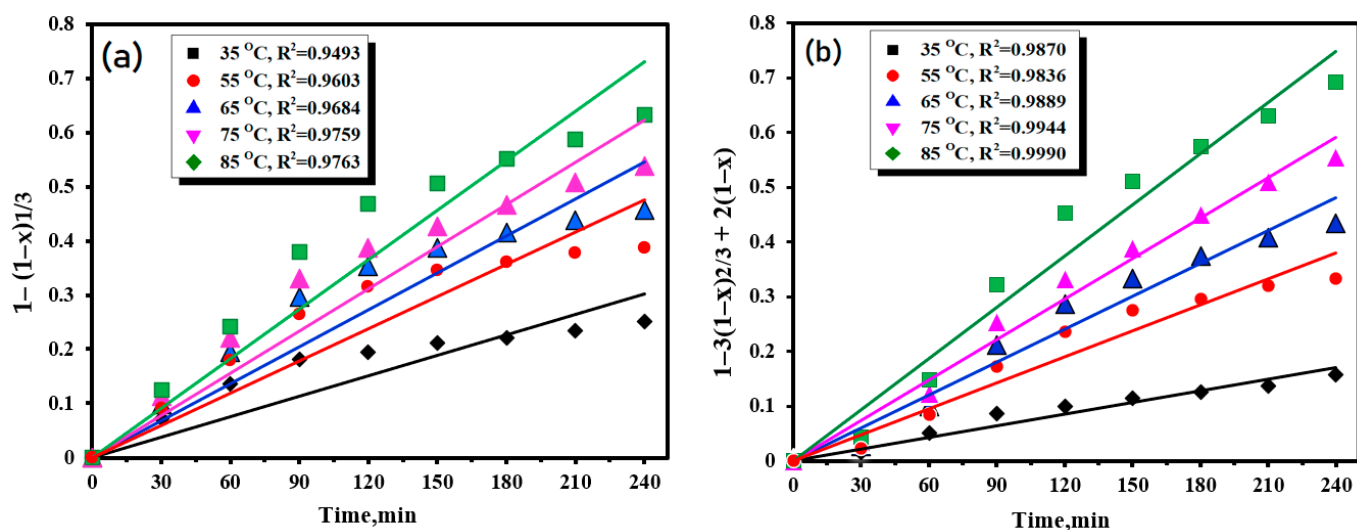


Figure 17. Plot of  $1 - (1-x)^{1/3}$  (a) and  $1 - 3(1-x)^{2/3} + 2(1-x)$  (b) vs. time at different temperature.

The apparent activation energy can be calculated by the Arrhenius Equation (18):

$$\ln k = \ln A - \frac{E_a}{RT} \quad (18)$$

where A is the frequency factor,  $E_a$  is the apparent activation energy of the reaction, R is the universal gas constant, and T is the reaction temperature in kelvin.

The logarithmic values of the reaction rate constants (K) of WLSR in sulfuric acid leaching were plotted against the reciprocal of the absolute reduction temperature (T), with obtained the  $K_d$  value in Table 6, and the result is displayed in Figure 18. Using the Arrhenius Equation (18), apparent activation energy ( $E_a$ ) in the whole Ni leaching process was calculated from the slope of straight line to be 20.26 kJ/mol ( $R^2 = 0.9917$ ); this value is lower than the apparent activation energy compared to other studies [14,36]. The diffusion-controlled process has an activation energy of around <12 kJ/mol, while chemical reaction-controlled process often has an activation energy of >40 kJ/mol; when activation energy is between 12 and 40 kJ/mol, the process is controlled by both diffusion and chemical reaction [62].

Table 6. Nickel leaching kinetics parameters of different models during the reaction time.

| Temperature | Liquid Film Diffusion Control |        | Surface Chemical Reaction Control |        | Solid Product Diffusion Control     |        |
|-------------|-------------------------------|--------|-----------------------------------|--------|-------------------------------------|--------|
|             | $1 - (1-x)^{2/3} = k_1 t$     |        | $1 - (1-x)^{1/3} = k_c t$         |        | $1 - 3(1-x)^{2/3} + 2(1-x) = k_d t$ |        |
|             | $k_1$                         | $R^2$  | $K_c$                             | $R^2$  | $K_d$                               | $R^2$  |
| 35 °C       | 0.0022                        | 0.9201 | 0.0013                            | 0.9493 | 0.001                               | 0.9870 |
| 55 °C       | 0.0033                        | 0.9282 | 0.0020                            | 0.9603 | 0.0016                              | 0.9836 |
| 65 °C       | 0.0036                        | 0.9336 | 0.0023                            | 0.9684 | 0.0020                              | 0.9889 |
| 75 °C       | 0.0040                        | 0.9369 | 0.0026                            | 0.9759 | 0.0025                              | 0.9944 |
| 85 °C       | 0.0044                        | 0.9363 | 0.0030                            | 0.9763 | 0.0030                              | 0.9990 |

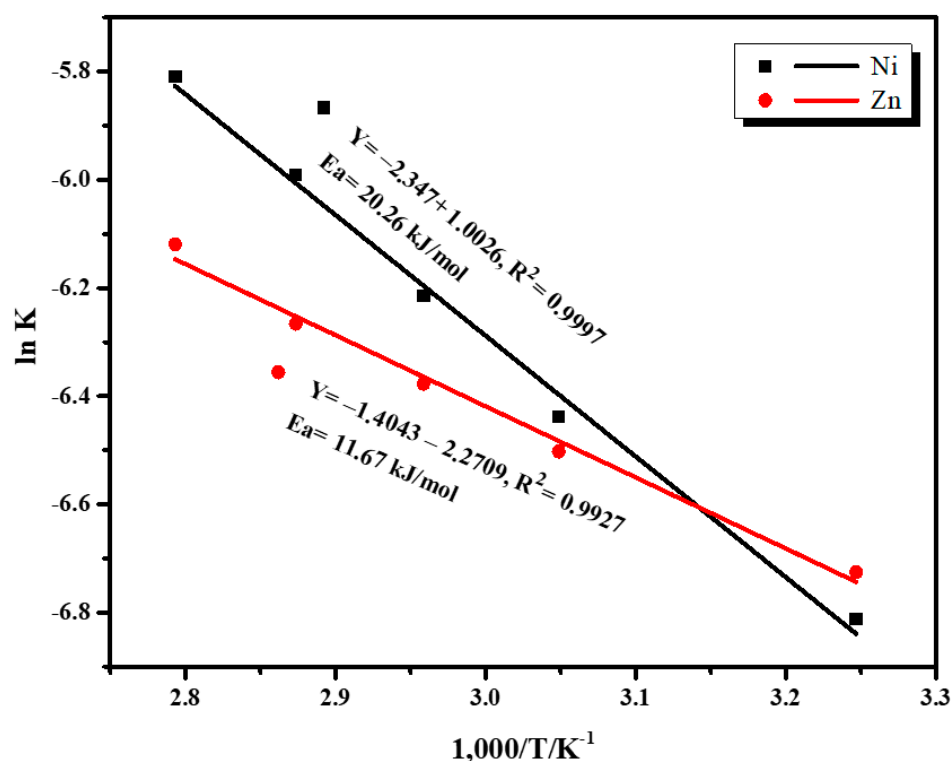


Figure 18. Arrhenius plot for nickel and zinc leaching from WLSR residue.

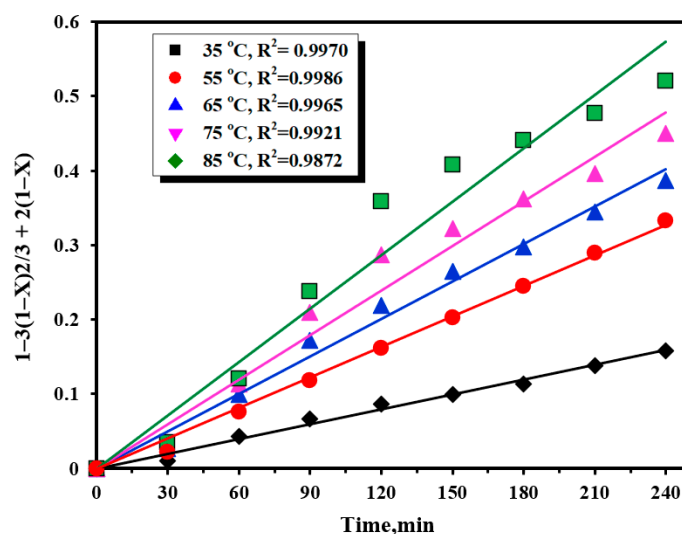
The current study shows that the apparent activation energy was between those of a typical diffusion-controlled process and a chemical reaction-controlled process, providing more evidence to prove that the sulfuric acid leaching process was controlled by both internal diffusion and interface chemical reactions. This can be attributed to the fact that the sulfuric acid concentration decreased as the leaching process proceeds, and thus the chemical reaction rate decreased, resulting in the chemical reaction becoming part of the rate-controlling step. Since the calculated value of 20.26 KJ/mol is near to the value of 12 kJ/mol significantly, the diffusion of the solid product layer contributed more than the chemical reaction to control the rate of leaching process [36]. Hence, the leaching rate improved with the increase in the leaching temperature and H<sub>2</sub>SO<sub>4</sub> concentration and decreased the particle size of WLSR.

### 3.5.2. Leaching Kinetics of Zinc

The leaching kinetics of zinc were studied by investigating the leaching experiments at 35 °C, 55 °C, 65 °C, 75 °C and 100 °C; the obtained results were plotted in Figure 16b, applying the left sides of Equations (15)–(17) vs. time at different leaching temperatures and based on data acquired from optimization studies of each condition. Table 7 and Figure 19 summarize the results. It was found that Equation (17) presented a better fit of the leaching experimental result, and the correlation coefficient value for (internal diffusion)  $k_d$  was 0.9566. This proved that the predominant dissolution kinetic mechanism of zinc from WLSR was controlled by the diffusion of reactants through a solid generated layer [9]. This might be because leaching occurs on the thin layer around the surface rather than on the surface itself, as the SCM suggests.

**Table 7.** Zinc leaching kinetics parameters of different models during the reaction time.

| Temperature/°C | Liquid Film Diffusion Control |        | Surface Chemical Reaction Control |        | Solid Product Diffusion Control         |        |
|----------------|-------------------------------|--------|-----------------------------------|--------|-----------------------------------------|--------|
|                | $1 - (1 - x)^{2/3} = k_1 t$   |        | $1 - (1 - x)^{1/3} = k_c t$       |        | $1 - 3(1 - x)^{2/3} + 2(1 - x) = k_d t$ |        |
|                | $k_1$                         | $R^2$  | $K_c$                             | $R^2$  | $K_d$                                   | $R^2$  |
| 35 °C          | 0.0022                        | 0.9010 | 0.0012                            | 0.9564 | 0.0011                                  | 0.9970 |
| 55 °C          | 0.0030                        | 0.9382 | 0.0018                            | 0.9613 | 0.0014                                  | 0.9986 |
| 65 °C          | 0.0033                        | 0.9214 | 0.0020                            | 0.9766 | 0.0016                                  | 0.9965 |
| 75 °C          | 0.0036                        | 0.9352 | 0.0023                            | 0.9677 | 0.0018                                  | 0.9921 |
| 85 °C          | 0.0039                        | 0.9344 | 0.0025                            | 0.9688 | 0.0021                                  | 0.9872 |

**Figure 19.** Plot of  $1 - 3(1 - x)^{2/3} + 2(1 - x)$  vs. time at different temperature.

The Arrhenius Equation (18) was plotted as  $\ln k$  vs.  $1/T$  for different temperatures, as shown in Figure 18. Arrhenius Equation is used to calculate the apparent activation energy ( $E_a$ ) of the zinc acid leaching process from the slope of the straight line, which is 11.67 kJ/mol ( $R^2 = 0.9927$ ). Both nickel and zinc have a lower apparent activation energy, implying that they are easy to leach, which agrees with the thermodynamic results in Section 3.2.

#### 4. Conclusions

In the current study, the hydrometallurgical processing of the water leaching solid residue obtained from salt-roasting of the Egyptian boiler ash for high purity and cost-effective extraction of valuable metals including Ni, Zn, Fe and Mg has been investigated. The obtained results can be concluded as follows:

1. The maximum extraction of Ni, Zn, Fe and Mg from water leaching solid residue after vanadium extraction from salt-roasting of the Egyptian boiler ash was 95.02%, 90.13%, 66.29%, and 75.73%, respectively, under the optimum leaching conditions of 8% (vol%)  $H_2SO_4$  concentration, 85 °C leaching temperature and 1/15 S/L ratio for 240 min leaching time.
2. The precipitation approach using  $Fe_2O_3$  as a nucleating agent was effective in removing the iron ions from the pregnant solution. The removal rate of iron ions increases to its maximum value of 95% by modifying the pH of the solution and the precipitation duration, with a minimal loss rate of Ni (4.2%) and Zn (3.8%).
3. An effective Mg precipitation efficiency of 96.9% was obtained after Fe removal, using 0.45 mol/L oxalic acid dose, 6 pH and 2 h precipitation time at ambient temperature.

Then, nickel and zinc in the purified solution was precipitated at pH of 9 as Ni-Zn hydroxide, which was subsequently transformed into  $\text{Ni}(\text{OH})_2$ ,  $\text{Zn}(\text{OH})_2$ , and  $\text{NiO-ZnO}$  by its calcining at (450 °C). The precipitation efficiency of Ni and Zn was 92.25% and 85.51%, respectively, and the final calcined product was composed mainly of 37% Ni and 23% Zn.

4. A kinetics analysis revealed that the nickel leaching process is controlled by both diffusion through solid product layer and chemical reaction, where diffusion through solid product layer contributes more, with an activation energy of 20.26 kJ mol<sup>-1</sup>. The kinetics of zinc dissolution are controlled by diffusion through solid product layer with an activation energy of 11.67 kJ mol<sup>-1</sup>.
5. The chemical and physical composition and properties of the obtained sulfuric acid solid residue (SASR) enhance and recommend its utilization as adsorbent to eliminate undesirable ions from industrial effluent.

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