

Article

Radiation Techniques for Tracking the Progress of the Hydrometallurgical Leaching Process: A Case Study of Mn and Zn

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Abstract: With advancements in hardware and software, non-destructive radiometric analytical methods have become popular in a wide range of applications. A typical case is the study of the leaching process of metals from mineral ores and mine tailings. The objective of the current study was to develop a radiometric method based on neutron activation analysis (NAA), in particular, delayed gamma neutron activation analysis (DGNAA), to monitor the process of Mn and Zn leaching from Ti ore, Cu mine tailings, and Zn-Pb mine tailings. The DGNAA method was performed using a neutron source: a deuterium-tritium (D-T) neutron generator for Mn and a MARIA research nuclear reactor for Zn. Laboratory-scale Mn leaching from Ti ores, Cu tailings, and Zn-Pb tailings was investigated using delayed gamma-rays of ⁵⁶Mn (half-life of 2.6 h). The dissolution efficiencies of Mn were found to increase with interaction time and HCl concentration (1 to 5 M) and to vary with the leaching temperature (22.5 to 110 °C). Such results were found to agree with those obtained by total reflection X-ray fluorescence (TXRF) spectrometry for the same samples. ⁶⁵Zn (half-life of 244 days) was chosen to investigate real-time/online leaching of Zn in Ti ore, Cu tailings, and Zn-Pb tailings. During online monitoring, Zn recovery was also reported to increase with increased leaching time. After approximately 300 min of leaching, 80%, 79%, and 53% recovery of Zn in Zn-Pb tailings, Ti ore, and Cu tailings, respectively, were reported. Theoretically, developed mathematical prediction models for ⁶⁵Zn radiotracer analysis showed that the spherical diffusion model requires much less time to attain saturation compared to the linear diffusion model. The results of NAA for Zn were compared with those obtained by handheld X-ray fluorescence (handheld-XRF) and TXRF analysis. The analyzed samples encompassed leached Ti ore, Cu tailings, and Zn-Pb tailings which were subjected to different conditions of leaching time, temperature, and HCl concentrations. The XRF analysis confirmed that the leaching efficiencies of Zn rise with the increase in leaching time and HCl concentration and fluctuate with leaching temperature. The developed approach is important and can be applied in laboratories and industrial setups for online monitoring of the recovery of any element whose isotopes can be activated using neutrons. The efficiency of the metal-recovery process has a direct impact on the normal operation and economic advantages of hydrometallurgy.



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1. Introduction

Hydrometallurgical Recovery of Mn and Zn Strategic Metals

Strategic metals refer to vital minerals used in renewable technologies and other rapidly emerging sectors [1–3]. Mn and Zn are strategic metals in a variety of industrial uses, including the production of steel, paint, carbon-zinc batteries, electronics, chemicals, foods, medicines, and nonferrous alloys [4–6]. Due to the potential environmental hazards and the growing demand for Zn and Mn metals for life, it is critical to extract them from ores and secondary sources (tailings/waste, etc.). Such metals are useful in today's circular and global economy [7–9]. Pyrometallurgy (thermal treatment of the material containing the metals) and hydrometallurgy are well-known techniques for processing Mn and Zn minerals [4,9]. In contrast to pyrometallurgy, hydrometallurgical methods involving the use of solutions for metal recovery are more ecologically friendly, efficient at recovery, use less energy, and are cost-effective [10]. These processes entail leaching, solvent extraction, and ion exchange, amongst other processes. Since MnO_2 and Zn ores such as ZnFe_2O_4 are resistant to various leaching conditions, their recovery must be carried out under reducing conditions. This transforms the insoluble form of the metal into a solvable form in an aqueous medium [5,11,12]. Ascorbic acid ($\text{C}_6\text{H}_8\text{O}_6$) occurs naturally (as vitamin C) and may be used as a leaching agent and reductant in the hydrometallurgical recovery of Mn and Zn [5,13].

The leaching process is a key non-selective hydrometallurgical process in which a liquid chemical agent interacts with a solid phase to dissolve the solid either completely or partially [2,14]. Such hydrometallurgical procedures are commonly associated with heterogeneous reactions. Although leaching frequently occurs at a solid/liquid boundary layer, it can also involve ongoing interactions between the leaching agent and ore/mineral host material. This might be viewed as a distinguishing characteristic of heterogeneous reactions as opposed to homogeneous reactions, in which the reaction takes place during any given phase [15]. It should be noted that the number of phases in the leaching process is mostly determined by the solid's chemical and physical characteristics, the kind of lixiviant used, and the experimental setup. It is worth mentioning that the ionic strength affects the dissolution kinetics of metal complexes produced following the leaching process. The competition for metal ions across the leaching medium and the solid material (ore) may change as the ionic strength rises. High ionic strength can have an impact on the leaching solution's density and viscosity, which can then have an impact on how reactants and products are transported to and from the solid phase [16].

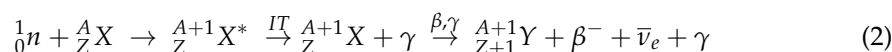
The various models that have been used to describe the leaching processes of different metals, include the shrinking-core, shrinking-particle, Noyes–Whitney Equation (NWE), and uniform-pore models, amongst others [15,17]. These models have become increasingly common in hydrometallurgy over the past 20 years for demonstrating the dissolution kinetics of Zn and Mn [17]. The leaching mechanism and the properties of the solid particles are taken into consideration when creating such models [15]. The three main mechanisms that regulate leaching are chemical reaction at the solid particle surface, diffusion across the product layer, and a combination of both [18,19]. NWE will consequently be followed if leaching is regulated by diffusion via the product layer shown in Formulae (1) [20], as follows:

$$\frac{dC}{dt} = K(c_s - c) \quad (1)$$

where c_s and c denote the solubility and concentration of the dissolved material at time t , respectively, K is the proportionality constant, and dC/dt represents the dissolution rate. Rapid chemical reactions at the interface cause the liquid film to instantly saturate; the

diffusion of liquid across the film to the liquid bulk medium is the limiting step. NWE continues to evolve, and that fact forms the basis of our novel model, which was developed in our NAA hydrometallurgical study of Zn.

The application of NAA can play a key role in the optimization of the metal-recovery processes. The innovation of NAA has been the crucial development of inorganic trace-analysis approaches with the lowest quantification and detection limits. The technique has majorly been applied in metal-ion-separation procedures such as precipitation, solvent extraction, and ion exchange but is rarely applied in studies of the leaching processes. Nuclear reactions in NAA are caused by irradiation of the material to be analyzed with neutrons. The most important reaction is the neutron radiative capture reaction (n, γ). The reaction products can be investigated using prompt gamma-radiation, emitted during irradiation from the created highly excited nucleus (prompt gamma neutron activation analysis—PGNAA), or delayed gamma-radiation, emitted during the radioactive decay of the unstable nucleus formed after its previous de-excitation (delayed gamma neutron activation analysis—DGNAA) [21,22]. DGNAA is the most commonly used approach. The emitted gamma radiation can then be analyzed for identification and quantification of the activated elements. Equation (2) shows the nuclear reactions that most commonly occur in DGNAA, as follows:



where A is the atomic mass, Z represents the atomic number, X is the target nuclide, n is the neutron, IT is the isomeric transition, β is the beta particle, γ is the gamma radiation, Y is the product nucleus, and $\bar{\nu}_e$ is the electron anti-neutrino.

DGNAA is especially appropriate for metals with large neutron-capture cross-sections, as it achieves extremely high sensitivity. However, one-third of the elements cannot be analyzed by this method because they cannot form radioactive products [23]. To analyze the induced radioactivity, different types of gamma-ray detectors can be used, such as high-purity germanium (HPGe) semiconductor detectors or NaI (Tl) scintillation detectors. By tracking the route that the radionuclide takes from reactants to products, investigators can use the decay characteristics to study the mechanism of chemical reactions [24]. Radiotracers possess advantages such as detectability in situ, excellent detection sensitivity and physicochemical compatibility, and a limited memory effect [25]. Because of the rapid response, radiotracers are dependable, resulting in accurate findings [26].

For years, DGNAA has been confined to expensive research nuclear reactor laboratories. This limitation restricts the applicability of the technique across various scientific fields and industrial settings. The increasing development of non-reactor neutron sources can make these techniques significantly more widely accessible. When deuterium-deuterium (D-D) or deuterium-tritium (D-T) nuclear fusion reactions are used, neutron generators produce fast neutrons with energy of 2.5 MeV or 14 MeV, respectively. Unlike isotopic sources, once the neutron generator is turned off, no neutron radiation is produced. Tritium leakage detectors are advised in addition to the internal accelerator tube carrying the tritium target that is hermetically sealed in the D-T neutron generator. This setup must be controlled by the interlock safety system to protect the operators [23]. Furthermore, for safe operation, as with any radiation generator, appropriate shielding and individual dosage-monitoring devices are required. With NAA based on both nuclear reactors and neutron generators, chemical reactions of elements such as Zn and Mn can be studied. The limits regarding the migration of radioactive isotopes from radioactive-waste repositories are not established, as such phenomena are not observed due to the safety measures undertaken. Nevertheless, certain findings from the research can be utilized to forecast migration in hypothetical scenarios and to strategize the construction of sorption barriers in surface repositories for radioactive materials. Regulatory bodies such as the International Atomic Energy Agency (IAEA) and the European Atomic Energy Community enforce stringent standards, stressing safe and responsible practices in industrial and scientific studies. These regulations

necessitate proper handling, comprehensive risk assessments, and disposal protocols. Also, they necessitate storage, continuous monitoring and reporting to lessen potential hazards inherent to the use of radionuclides.

This paper seeks to offer a novel offline approach using a D-T neutron generator and gamma spectroscopy to track Mn extraction from Ti ore, Cu tailings, and Zn-Pb tailings by leaching. The paper also attempts to provide a method for monitoring the dissolution of Zn from the same samples in real-time/online by using ^{65}Zn obtained by sample neutron activation in a nuclear research reactor. The development of a novel mathematical approach for studying the kinetics of real-time/online Zn leaching is also demonstrated in the research.

2. Materials and Methods

2.1. Materials

Three materials were selected for the study. Cu tailings and Zn-Pb tailings were collected from the landfill reservoir in Gilów, Poland by INCT. Ti ore was sourced from Rogaland, Norway by INCT. With a distinct identification code, date, and sample location, the samples were labelled appropriately. The samples used for the study were finely ground using a pestle and mortar to increase the surface area for the interaction between the leaching agents and the sample [27]. The quartering method was applied to homogenize the finely ground samples for further analysis [28]. Separation of the fractions of the bulk material was done manually using a sieve with a pore diameter of 75 μm for further analysis. A calibrated (Ohaus PioneerTM PX224/1 OHAUS Europe GmbH, Greifensee, Switzerland) analytical balance was used to determine the proper masses for each technique employed in the analysis.

2.2. Reagents and Instruments

The following reagents were used: nitric acid (HNO_3) 65% pure p.a. (POCH S.A., Gliwice, Poland), hydrochloric acid (HCl) 37% pure p.a. (POCH S.A., Gliwice, Poland), L-ascorbic acid pure p.a. (VWR Chemicals, Atlanta, GA, USA), and silicon oil (CarlRoth, Karlsruhe, Germany). For the cleaning apparatus and the preparation of all aqueous solutions, double-distilled water was utilized.

The instruments applied in the characterization of the samples included the following: S1 TITAN Handheld X-ray fluorescence analyzer (Bruker, Berlin, Germany) from the Faculty of Chemistry University of Warsaw (Poland) for elemental analysis; ELAN DRC II inductively coupled plasma quadrupole spectrometer (PerkinElmer, Waltham, MA, USA) from the Institute of Nuclear Chemistry and Technology (INCT), Warsaw (Poland) for elemental measurements; D8 Advance X-ray Diffractometer (Bruker, Billerica, MA, USA) equipped with a Cu X-ray tube, Bragg-Brentano optics with fixed slits, Ni filter, and Lynx SSD160-2 position sensitive detector from the National Medicines Institute (Warsaw, Poland) for phase-composition analysis; DSM 942 scanning electron microscope (LEO-Zeiss, Oberkochen, Germany) from INCT for analysis of morphological changes in the leached and undigested samples; Zeiss optical microscope and Nikon inverted microscope Eclipse Ti-S from INCT for analysis of specific surface area of the powdered samples; Nanohunter II TXRF spectrometer with Mo X-ray tube (Rigaku, Japan) from AGH University of Science and Technology, Kraków (Poland) for elemental analysis of the leached Mn and Zn. NAA of ^{56}Mn was accomplished using a 320 MP D-T neutron generator (Thermo Fisher Scientific, Waltham, Massachusetts, USA) from the Central Laboratory of Radiological Protection (CLRP), Warsaw (Poland), and High Purity Germanium (HPGe) gamma-ray detector GX1018 with data acquisition software Genie 2000 v3.2 (Canberra, Meriden, CT, USA) from INCT. For NAA of ^{65}Zn , the MARIA Research Reactor from Świerk (Poland) and the 3" $\times$ 3" NaI (Tl) scintillation detector (from INCT) with TDR v2.8.0.0 data acquisition software, both manufactured by TD Electronics (Warsaw, Poland), were used.

2.3. Sample Preparation for Further Analysis

2.3.1. D-T Neutron-Generator Analysis for Offline NAA of Mn Leaching

The application and use of the D-T neutron generator presented in this paper is a new approach to DGNA. Most of the effort was devoted to building the test stand and demonstrating that neutron activation of Mn with the D-T neutron generator can be performed. In this case, Mn was selected to illustrate the concept due to its short half-life of 2.6 h. The research focused on tracking the ^{56}Mn changes in the activated samples using HPGe. The amount of leached Mn was determined by comparing the obtained results with results from the prepared reference Mn source.

All the samples prepared from Ti ore, Cu tailings, and Zn-Pb tailings were activated and measured under the same conditions. The number of counts collected during gamma-spectrometry was recalculated to the number of counts at $t = 0$ (the time at which the neutron activation was completed). The recalculation was necessary due to the differences in times between the end of irradiation and the start of measurements (the gap varied from 10 to 30 min). For all experimental dependencies, three independent runs were performed. That is because the lifetime for the D-T neutron generator is approximately 1000 h, which limits the number of samples that could be analyzed [23]. The results obtained in the study were presented as the average value from the runs and the spread of the experimental values obtained. The spread in this case represented the repeatability of the determination of experimental points.

The experiments were conducted by the application of HCl as a leaching agent and 10% ascorbic acid as a reducing agent. A double-walled glass leaching reactor (batch reactor) with a volume of 3 L was used for the tests conducted under different conditions of leaching temperature (22.5, 50, 70, 90, and 110 °C), leaching time (1 to 10 h at 70 °C) and concentration (1 to 5 M HCl at 70 °C). The temperature of the system was conditioned throughout the study by the application of a thermostat fitted with a peristaltic pump to heat and inject the silicon oil continuously in a closed loop into the leaching vessel. With respect to the selected solid-to-liquid (S/L) ratio of 1:7, the reagents were transferred into the reactor. The suspensions were continuously mixed by the stirrer mounted on the leaching reactor. After every hour, a 100 mL aliquot of the leached solutions was filtered using 0.45 µm filters into three labelled 50 mL sample containers. The labelled samples leached under different conditions were then taken to the D-T neutron generator for activation (Figure 1). The irradiation of the 50 mL sample was conducted for 1 h under a neutron yield of 1.2×10^8 n/s. The hourly-activated leached samples were then measured for ^{56}Mn radioactivity using the HPGe detector. During the NAA, a dosimeter was used to measure the radiation of each activated sample before handling it to determine the radiation dose rate to which personnel would be exposed. The radiation dose rate on the surface of the container for all samples was below 1 µSv/h (the dose rate of natural radiation in Poland is approximately 0.1 µSv/h [29]). Therefore, all samples could be safely handled by personnel.

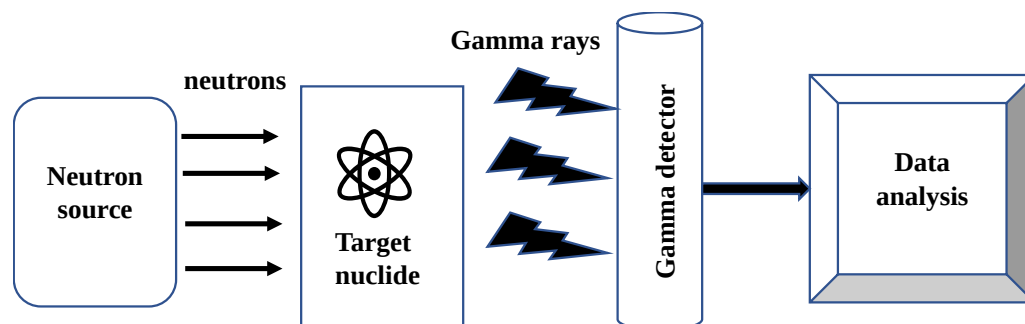


Figure 1. Schematic presentation of the neutron activation analysis methodology. It illustrates the procedures involved in irradiating a sample with neutrons and detecting the emitted radiation to identify and quantify elements.

2.3.2. TXRF Analysis of the Mn in the Leached Samples

For comparison purposes, TXRF was used to measure the same samples analyzed by NAA using a neutron generator. With 50 kV, 12 mA, and a 500 s analysis duration, a TXRF spectrometer with Mo X-ray tube with a silicon drift detector was employed to measure the samples. Triplicate measurements were taken using 10 µL of each sample while using Ga as the internal standard. Each sample was dried using a hot plate and placed onto the reflector (sample carrier) for TXRF analysis. The obtained results were thereafter compared with those acquired from NAA. The final results were presented as 95% confidence intervals in the following form:

$$\text{Concentration}(\text{mg/kg}) = \bar{x} \pm \frac{t \times SD}{\sqrt{n}} \quad (3)$$

where $\bar{x}$ and SD denotes the arithmetic mean and the sample standard deviation, t represents the critical value from the two-tailed t-distribution at a 95% confidence level with $(n - 1)$ degrees of freedom, and n indicates the number of replicates ($n = 3$).

2.3.3. Preparation of ^{65}Zn Using MARIA Research Reactor

For the online analysis, ^{65}Zn radiotracer was used to monitor the kinetics of Zn leaching. The preparation of the ^{65}Zn radiotracer was done by measuring 400 mg of Ti ore using a calibrated analytical balance. The same procedure was repeated for the Cu tailings and the Zn-Pb tailings. Triplicate materials were then packaged separately in labelled 1 mL plastic containers, sealed, and covered with aluminum foil. The samples were then placed in a metallic tube for transportation to the MARIA nuclear research reactor for neutron activation. The activation conditions were a thermal neutron flux of $2.5 \times 10^{14} \text{ n}/(\text{cm}^2\text{s})$ and a 20 min activation time; other parameters are shown in Table 1 [30]. The samples were kept to ‘cool’ (radioactivity reduction) for three weeks at the nuclear research reactor facility and a further 1.5 months at the INCT in a Pb shield due to high initial activity. The activity of a specific radioisotope was determined by Equation (4), as follows:

$$A = \frac{6.023 \times 10^{23} \times \Phi \times m \times G \times \sigma_{at} \times 10^{-24}}{100M} \times \left\{ 1 - e^{\frac{-0.693\tau}{T_{1/2}}} \right\} \times e^{\frac{-0.693t}{T_{1/2}}} \quad (4)$$

whereas A denotes activity (Bq), Φ is the thermal neutron flux ($\text{n}/(\text{cm}^2\text{s})$), G denotes abundance (%), M signifies the molar mass of the sample (g), σ_{at} indicates the cross-section for the thermal neutrons (barns), τ is the irradiation time (h), m denotes elemental mass (g), $T_{1/2}$ symbolizes half-life (h), and t represents the time of activity decay (h).

Table 1. Neutron-activation parameters computed for 400 mg of the sample under a neutron flux of $2.5 \times 10^{14} \text{ n}/(\text{cm}^2\text{s})$ (for all the samples).

Samples	Target Nuclide	m (g)	G [%]	Φ [$\text{n}/(\text{cm}^2\text{s})$]	σ_{at} [barns]	τ [h]	Activated Radioisotope	$T_{1/2}$ [h]	M [g]	Cooling Time [h]	A [Bq]
Ti ore	^{64}Zn	0.0001652	49.17	2.5×10^{14}	0.731	0.66	^{65}Zn	5856.24	65.38	1354	3639
Zn-Pb tailings	^{64}Zn	0.00512	49.17	2.5×10^{14}	0.731	0.66	^{65}Zn	5856.24	65.38	1354	112,800
Cu tailings	^{64}Zn	0.00002	49.17	2.5×10^{14}	0.731	0.66	^{65}Zn	5856.24	65.38	1354	440

Method Validation for Zn Analysis

Fly ash and Soil 5 Certified Reference Materials (CRM) were used to verify the precision of the analytical technique, ensuring that the acquired results from the DGNAA agree with the actual or standard value. The reference samples were prepared in the same way as the examined materials, and the experimental quantities of Fe, Sc, and Zn were compared to the certified values, as shown in Table 2. A t -test revealed that there were no significant discrepancies between the certified and experimental values ($p > 0.05$). That indicated that the use of the DGNAA method was accurate and dependable in the study.

To ensure the reliability and accuracy of the detection system, the NaI(Tl) scintillation detector was calibrated for energy and efficiency using the gamma energy lines of the standard reference materials of ^{60}Co (1332 and 1172 keV) and ^{137}Cs (661.67 keV). The background impulses/minute were recorded using a NaI (Tl) scintillation detector and subtracted from the sample spectrum.

Table 2. Validation of the DGNAA method (mg/kg).

	Experimental Values	Fly Ash-Certified Values
Fe	$49,511 \pm 5867$	$48,900 \pm 1400$
Zn	627 ± 36	569 ± 58
	Experimental Values	Soil 5 Certified Values
Fe	$49,837 \pm 5672$	$44,500 \pm 1000$
Zn	402 ± 16	368 ± 8.2
Sc	15.5 ± 0.7	14.8 ± 0.66

Online Measurements for Hydrometallurgical Leaching of Zn

The concentration of metals in the liquid medium is the primary factor in tracking the effectiveness of the leaching process. To monitor the effects of changing one (or more) parameters on the efficiency of the leaching process in real-time, a suitable radiotracer was employed. In this case, ^{65}Zn was used. The counts were measured and recorded before the start of the leaching process. Thereafter, leaching test was done using 5 M HCl and 10% ascorbic acid under the following conditions: 70 °C, a stirrer with 400 rotations per minute (rpm), a peristaltic pump at 35 rev/min (revolutions per minute), and a flow rate of 64 mL/min, a leaching time of around 300 min, and a solid-to-liquid (S/L) ratio of 1:7. Next, 400 mg of the activated sample, reagents, and non-activated samples were then transferred at once into the double-walled glass leaching reactor, as shown in Figure 2. The variation of the activity of the ^{65}Zn (with gamma energy of 1116 keV) radiotracer with time was monitored after every minute using a Pb-shielded NaI(Tl) scintillation detector. The Pb-shield was used to minimize the effect of the background counts on the analytical signal from ^{65}Zn . The spectrum was recorded using TDR v.2.8.0.0 data-acquisition software.

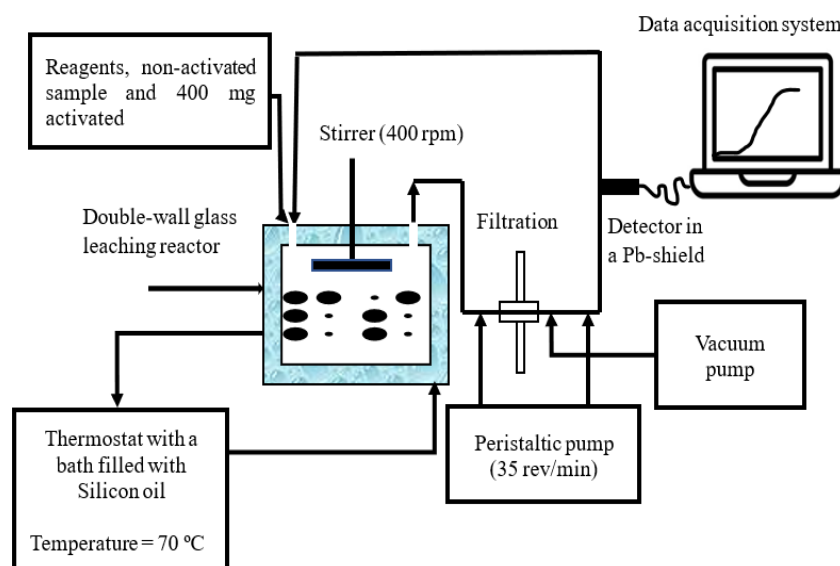


Figure 2. Scheme for investigation of leaching time using gamma radiotracer methodology.

The procedure was repeated three times to minimize the generation of radioactive waste, as ^{65}Zn has a relatively long half-life (244 days). The results from the study were showcased by presenting the mean value obtained from the runs alongside the variability

among the experimental values. In this context, the variability signified the repeatability of the measurements.

Mathematical Modelling for the Leaching Process

The leaching process of solids in the solutions can be theoretically described by the model based on the Noyes–Whitney equation modified by Nernst and Brunner, in which they introduced saturation at the solid-liquid interface before the diffusion takes place. The resulting expression can be represented by the following equation:

$$\frac{dc}{dt} = \frac{A \times D}{V \times \delta} (c_s - c) \quad (5)$$

where dc/dt represents the dissolution rate of a given substance and c_s and c are the concentrations of that substance at equilibrium (solute's solubility) and at time t , respectively. D is the diffusion coefficient of the substance through the unstirred liquid layer (a value that depends, among other factors, on the type of solute and solvent, its viscosity, and temperature), A represents the interfacial surface (specific surface area), V denotes the solution volume, and δ is the thickness of the diffusion layer. The specific area was estimated by using a novel approach based on the optical microscope technique. A total of 15.2 mg of the sample was dissolved in 2 mL of H_2O . The solution was then diluted 20 times, and 1 mL of the solution was transferred to the Bürker cell-counting chamber (Paul Marienfeld GmbH & Co. KG, Lauda-Königshofen, Germany) from INCT. Using the Zeiss optical microscope, the particles were counted using a counting device and were found to number 19,120,000 in 15.2 mg of the sample. Next, 76 particles were then selected. Their average diameter was estimated using a Nikon Inverted Microscope Eclipse Ti-S which was found to be 18 μm . Assuming the spherical nature of the particles, the specific surface area (A) was computed by applying $A = 4 \pi r^2$.

If the chemical reaction at the solid-solution interface is fast, the layer with the saturated solution of the dissolved substance is formed immediately and its diffusion to the solution bulk becomes the limiting step in the dissolution process. The thickness of that layer increases as the diffusion progresses (Figure 3).

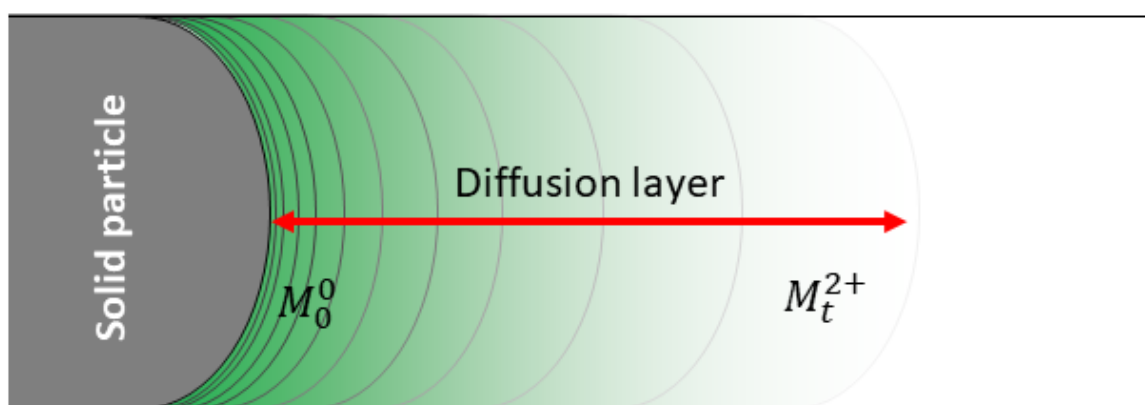


Figure 3. Schematic representation of the diffusion model for the metallic (M) particle-dissolution process.

The thickness of the diffusion layer (δ) is therefore a time-dependent factor. The form of that relationship depends on the geometry of the diffusion field. When the formalism developed for the description of mass-transport behavior at the electrode-solution interface during the electro-dissolution process is adopted, the relevant expressions take the following form [31]:

$$\delta = \sqrt{\pi D t} \quad (6)$$

for the linear geometry of the diffusion field (dissolution of macroparticles).

And

$$\delta = \frac{r_0 \times \sqrt{\pi D t}}{r_0 + \sqrt{\pi D t}} \quad (7)$$

for the spherical geometry of the diffusion field (dissolution of microparticles), where r_0 is the radius of the microparticle of the solid.

By taking the above equations for δ into account and assuming that the surface area term remains constant throughout the dissolution process, the concentration of a dissolved substance at a given time can be obtained by integrating Equation (7) at $t = 0$ and $c = 0$. The results are as follows:

$$c = c_s \left(1 - e^{-\frac{A}{V} \sqrt{\frac{D}{\pi}} \times \sqrt{t}} \right) \quad (8)$$

And

$$c = c_s \left(1 - e^{-\frac{A}{V} \left[\sqrt{\frac{D}{\pi}} \times \sqrt{t} + \frac{D}{r_0} \times t \right]} \right) \quad (9)$$

for the linear and spherical geometries of the diffusion field, respectively.

The magnitude of a solute's diffusion coefficient has a direct effect on the dissolution rate. It can be either increased under the influence of temperature or decreased as a result of an increase in the solution viscosity caused by increased ionic strength. When the concentration of the ionic species increases, the mean distance between ions or molecules will decrease and the short-range interactions will start to influence the transport of the species. Under such conditions, the system cannot be treated as ideal, and, in consequence, the variation of activity coefficients must be taken into account according to the Debye–Hückel theory [32]. This leads to some changes in the species diffusivities, which are no longer constant parameters, but concentration-dependent functions expressed in the general form as follows:

$$D = D^0 \left(1 + \frac{d \ln f}{d \ln c} \right) \quad (10)$$

where D^0 is the diffusion coefficient of infinitely diluted species and f denotes the activity coefficient of that species.

The predictions based on the derived model may be limited by several factors. For example, not all grain surfaces are covered with dissolvable material, and there is a chemical reaction between the metal-bearing mineral and the leaching agent (acid, in our case) [20]. Nevertheless, given a set of experimental data, the functional dependence of the process rate can be evaluated and radiotracers can be used to provide data to evaluate process kinetics.

XRF and TXRF Analysis of the Zn Leached from the Samples

To confirm the trend of time dependence obtained from the online analysis of the Zn, a handheld XRF and TXRF study was conducted on the leached samples. It was also possible to analyze the influences of temperature and HCl concentration on Zn recovery. Leaching time varied from 1 to 10 h, while the HCl concentration ranged from 1 to 5 M and the leaching temperatures studied were 22.5, 50, 70, 90, and 110 °C. For handheld XRF, a 100 mL aliquot of leached was collected for assessments for each type of material under the same experimental conditions. Using a 4 W Rh target, 50 kV, and 80 μ A, five replicate measurements were conducted under a signal-acquisition time of 1 min. The final results were presented as a 95% confidence interval (CI), as shown in Equation (3), but with $n = 5$, representing the five replicates.

With 50 kV, 12 mA, and a 500 s duration for analysis, a TXRF spectrometer with Mo X-ray tube with a silicon drift detector was employed to test the same specimens. First, 10 μ L of each sample was used for each measurement, which was done in triplicate on the reflector. Next, Ga was employed as the internal standard. The samples were then dried using a hot plate before measurements. The outcome was presented as a 95% CI using Equation (3) with $n = 3$ for the triplicates.

The leaching efficiencies of both Mn and Zn in the leaching studies were determined using Equation (11), as follows:

$$\text{Leaching efficiency (\%)} = \frac{\text{Amount of metal ion in the leachate (mg)}}{\text{Amount of the metal ion in the feedstock (mg)}} \times 100 \quad (11)$$

3. Discussion of the Results

3.1. Characterization of the Solid Samples

3.1.1. Handheld XRF Analysis of the Chemical Composition of the Solid Samples

Table 3 shows the results acquired through the analysis of the solid samples. Of importance in the study was the availability of Mn and Zn oxides in all the samples considered for the assessment. Additionally, the technique revealed the presence of other compounds in varying amounts.

Table 3. Elemental analysis of the solid materials (%wt).

	Ti Ore	Cu Tailings	Zn-Pb Tailings
Al ₂ O ₃	6 ± 1	29 ± 5	20 ± 0.05
SiO ₂	1.3 ± 0.01	25 ± 3	23 ± 2
K ₂ O	0.03 ± 0.001	2 ± 0.01	3.2 ± 0.05
CaO	4 ± 0.1	2.5 ± 0.04	2.2 ± 0.021
TiO ₂	38 ± 10	0.124 ± 0.037	0.28 ± 0.09
V ₂ O ₃	0.12 ± 0.02	0.052 ± 0.003	-
MnO	0.13 ± 0.02	0.0857 ± 0.0275	0.102 ± 0.02
Fe ₂ O ₃	33 ± 1.1	0.818 ± 0.06	1.02 ± 0.1
Na ₂ O	0.8 ± 0.03	1 ± 0.005	1.3 ± 0.0033
ZrO ₂	0.02 ± 0.001	0.351 ± 0.03	0.094 ± 0.005
ZnO	0.02 ± 0.001	0.0154 ± 0.0016	1.023 ± 0.019
PbO	0.28 ± 0.002	0.027 ± 0.0041	0.2 ± 0.015
CuO	0.01 ± 0.0001	0.22 ± 0.008	0.0102 ± 0.0015
LOI	13 ± 0.7	17.8 ± 0.6	18 ± 0.4
Others	3.29	21.01	29.57

3.1.2. ICP-MS Chemical Analysis of the Solid Samples

The method was used in this study as a control technique. The obtained results for different elements are presented in Table 4. The technique confirmed the presence of Mn and Zn, alongside other elements.

Table 4. ICP-MS analysis of the solid samples (mg/kg).

	Ti Ore	Cu Tailings	Zn-Pb Tailings
Co	119 ± 4	19 ± 2	14 ± 2
Cu	130 ± 50	3210 ± 196	64 ± 5
Cr	515 ± 19	312 ± 12	12 ± 2
Mn	2299 ± 122	2797 ± 128	1312 ± 38
Zn	413 ± 15	50 ± 5	13,000 ± 1000
V	1188 ± 34	100 ± 5	18 ± 2
Mo	2 ± 0.1	11 ± 1	5 ± 1
Ni	174 ± 66	235 ± 16	33 ± 3
Sb	-	1 ± 0.1	9 ± 1
Fe	350,000 ± 20,000	10,000 ± 1000	10 ± 1
Cd	0.4 ± 0.02	1 ± 0.01	83 ± 3
Pb	3 ± 1	480 ± 22	8099 ± 722
La	1.1 ± 0.01	14 ± 1	2 ± 1

Table 4. Cont.

	Ti Ore	Cu Tailings	Zn-Pb Tailings
Ce	3 ± 0.2	26 ± 1	4 ± 1
Pr	0.4 ± 0.01	4 ± 1	1 ± 0.1
Nd	2 ± 0.2	16 ± 1	2 ± 0.1
Sm	0.5 ± 0.01	4 ± 1	1 ± 0.1
Eu	0.2 ± 0.01	2 ± 0.1	1 ± 0.1
Gd	0.5 ± 0.01	4 ± 0.01	1 ± 0.1
Tb	0.1 ± 0.01	1 ± 0.01	1 ± 0.1
Dy	0.4 ± 0.01	3 ± 0.1	1 ± 0.1
Ho	0.1 ± 0.01	1 ± 0.01	1 ± 0.1
Er	0.3 ± 0.01	2 ± 0.1	1 ± 0.1
Tm	0.1 ± 0.01	1 ± 0.1	1 ± 0.1
Yb	0.3 ± 0.01	2 ± 0.1	1 ± 0.1
Lu	0.1 ± 0.01	1 ± 0.1	1 ± 0.1

3.1.3. XRD Analysis of the Solid Samples

Figure 4 displays the primary phases identified by XRD examination of Cu tailings, Zn-Pb tailings, and Ti ore. Manganese dioxide (MnO_2), manganese (II) oxide (MnO), zinc sulfide/sphalerite (ZnS), and zinc oxide (ZnO) were the main phases of our elements of interest. Besides, high amounts of SiO_2 (silica) and $\text{CaMg}(\text{CO}_3)_2$ (dolomite) were revealed in Cu tailings, while significant amounts of FeTiO_3 (ilmenite) were reported in Ti ore. The results are in agreement with the handheld XRF and ICP-MS results, which showed the presence of Mn and Zn in Tables 3 and 4, respectively. MnO_2 is known to be a stable compound, and it was necessary to employ a reducing agent to transform it into the easily leachable mineral phase by reducing the high oxidation states to low, solvable states [5,11,12,33].

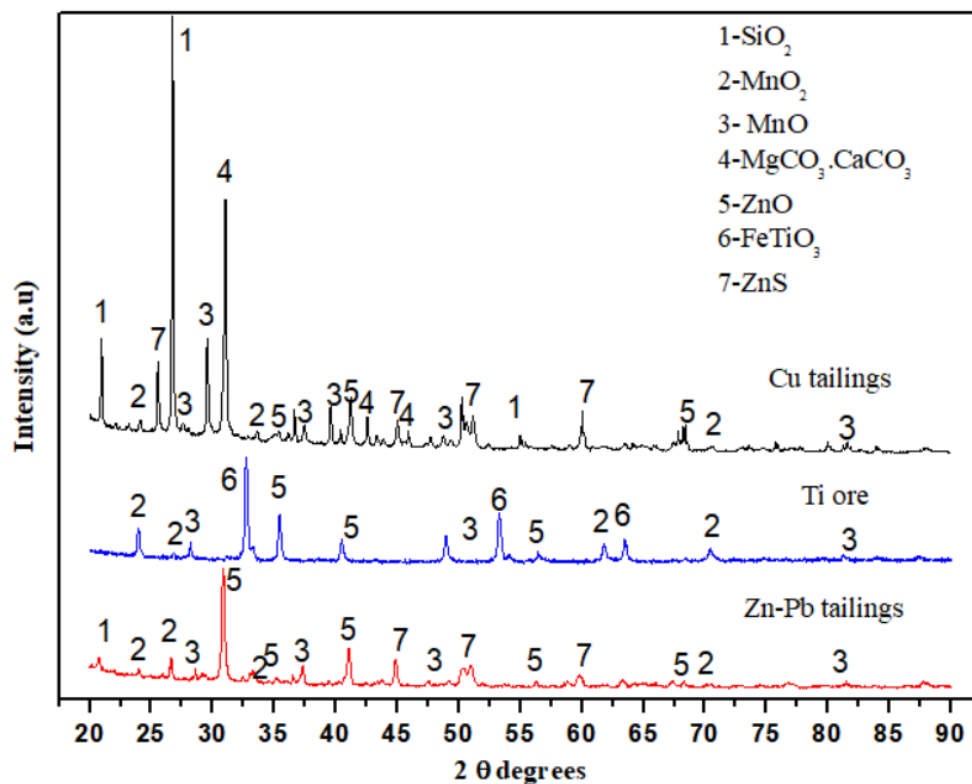


Figure 4. XRD spectrum of the Cu tailings, Zn-Pb tailings, and Ti ore solid samples. The analysis gives insights into the crystalline structures available in the samples, which aids in the identification of minerals and primary phases.

3.1.4. Scanning Electron Microscopy (SEM) Analysis

SEM analysis indicated that after 6 h of interaction between the leaching agents and the sample, cracks/holes were seen in the particles (Figure 5). That could be linked to the enhanced reaction surface at the interface of beneficial minerals. Additionally, faster diffusion accompanies the formation of cracks, which contributes to improved dissolution of the metals [6]. That means the regions with cracks contained minerals, hence offering the surface for interaction between the reagents and the metals. Such reactions result in the alteration of the crystal lattice of the metals both on the exterior and within the particles. The reactions involved anion adsorption from ionized HCl and ascorbic acid to the surface and within the particulate. The small particle diameter ($\leq 75 \mu\text{m}$) and easy accessibility of the reagents to the reacting surfaces (both exterior and internal) of the molecule can be attributed to the quick leaching rate [34]. That result emphasizes the importance of surface morphology in determining leaching kinetics [35].

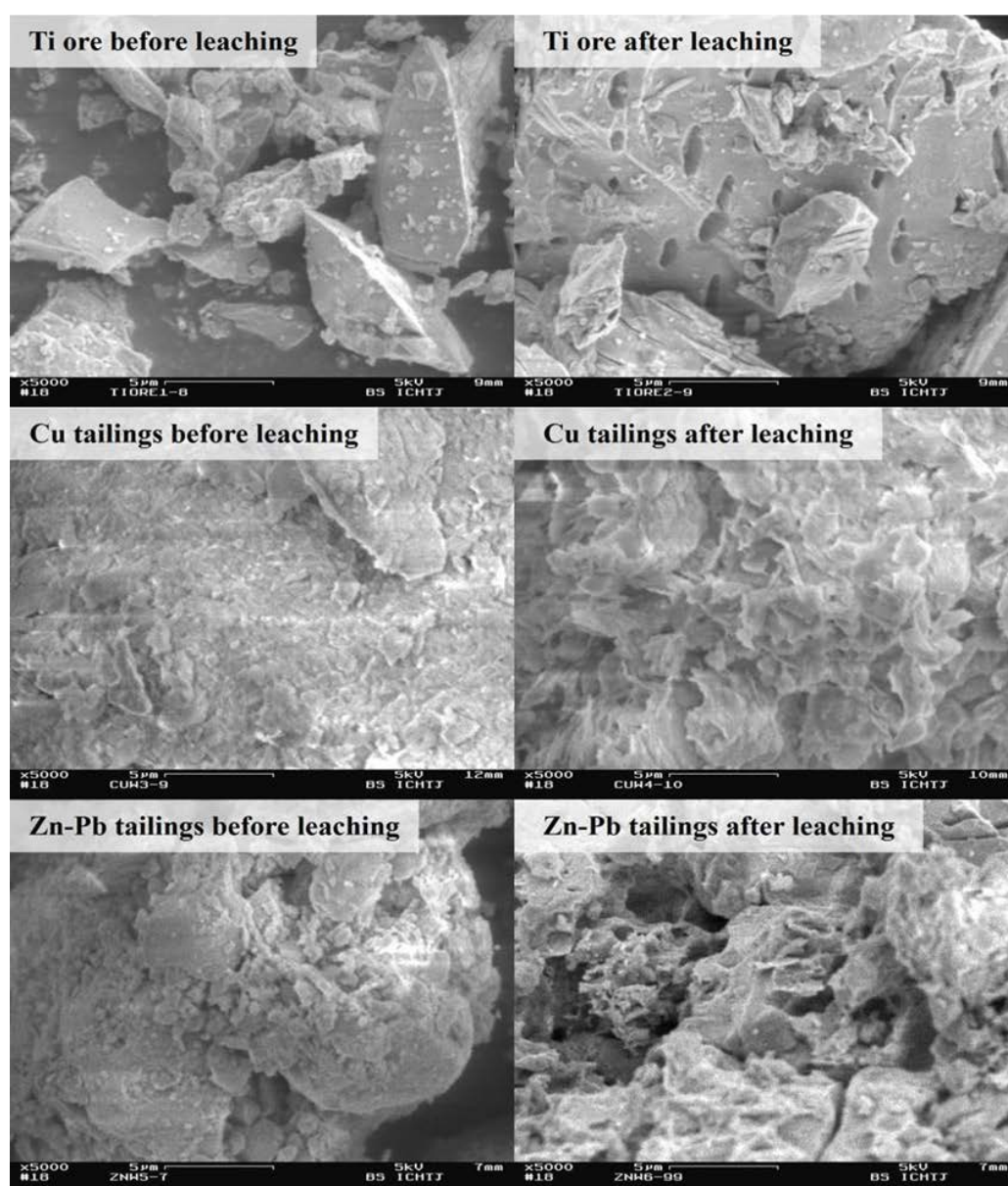


Figure 5. SEM analysis of the morphological changes of Cu tailings, Zn-Pb tailings, and Ti ore before and after 6 h of leaching. The measurements provide a visual understanding of the changes taking place at the microscale level during the interaction of leaching agents with the sample.

3.2. DGNAA of Mn Using a D-T Neutron Generator and TXRF Spectrometry

The success of activating specific nuclides using neutrons depends on the amounts of the target nuclide in the sample. ICP-MS analysis revealed that the concentrations of Mn in Ti ore, Zn-Pb tailings, and Cu tailings were 2299 ± 122 mg/kg, 1312 ± 38 mg/kg, and 2797 ± 128 mg/kg, respectively, Table 4. However, handheld XRF analysis indicated Mn at 0.1300 ± 0.02 %wt in Ti ore, 0.0857 ± 0.0275 %wt in Cu tailings, and 0.1020 ± 0.02 %wt mg/kg in Zn-Pb tailings, respectively, Table 3. There was a significant difference between the values reported from ICP-MS compared to those obtained from handheld XRF on Ti ore and Cu tailings ($p < 0.05$). That is because the handheld XRF spectrometer suffers from background and matrix effects, unlike ICP-MS [3,36].

Using neutrons from the D-T neutron generator, it was feasible to activate short-lived radioisotopes with low radioactivities in the leached samples. That allowed the analysis of the samples a few minutes after the activation without the need to ‘cool’ them (no need for radioactivity reduction). The activation of ^{55}Mn to ^{56}Mn (n,γ) was possible because ^{55}Mn has a sufficient neutron capture cross-section (σ_{ct}) of 13.3 barns for thermal neutron capture. However, for the fast neutrons, it is about 3.1 millibarns [37]. The neutron cross-section represents the probability of the interactions between the neutrons and the target nuclide (here: ^{55}Mn) [38]. Apart from ^{56}Mn , other radioisotopes resulting from $^{50}\text{Ti}(n,\gamma)^{51}\text{Ti}$ ($\sigma_{\text{ct}} = 0.179$ barns) and $^{51}\text{V}(n,\gamma)^{52}\text{V}$ ($\sigma_{\text{ct}} = 4.9$ barns) were detected using the HPGe detector. The detector was chosen for the offline analysis of the specimens owing to its superior photon-detection efficiency and resolving power [39]. However, we could not do the gamma spectrometry analysis of ^{51}Ti and ^{52}V with satisfactory results due to their short $T_{1/2}$ values of 5.76 and 3.75 min, respectively.

TXRF analysis served as a quality-control method for NAA. Figure 6 shows a typical spectrum for samples considered in the study. In TXRF, the sample was excited by both the primary and reflected beams meant to improve the fluorescence signal. The detector is close to the sample because of the small incidence angle, which results in a high detection efficiency. Each of these characteristics results in detection limits within the $\mu\text{g/kg}$ range [40].

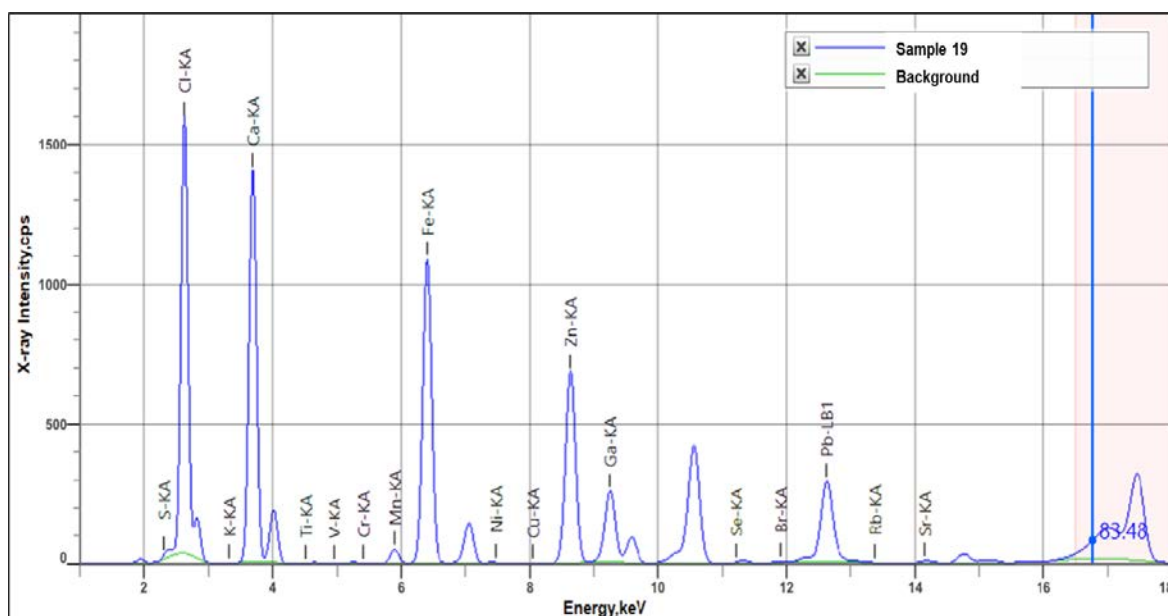
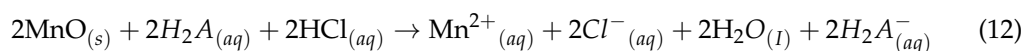


Figure 6. The TXRF spectrum for sample 19. The areas under the peaks indicated the amounts of the elements in the material.

3.2.1. NAA and TXRF Analysis for the Time Dependence of Leaching Mn

Leaching of the Mn was carried out using a solution of HCl and a low amount of the organic reducing agent (H_2A). This is because the minimal use of reducing agents provides an approach to reduction reactions that also considers resource conservation and environmental protection [4]. The chemical reaction that was considered to be feasible under all examined conditions is shown in Equation (12).



Different leaching efficiencies for Mn were reported depending on the material, method, and conditions under which the samples were leached. High leaching efficiencies were reported from the NAA method compared to TXRF, Figure 7. After 10 h of leaching, NAA resulted in 87, 72, and 38% Mn-leaching efficiencies from Ti ore, Cu tailings, and Zn-Pb tailings, respectively. Contrariwise, 57, 48, and 42% dissolution efficiencies of Mn were recorded by TXRF analysis on Ti ore, Cu tailings, and Zn-Pb tailings, respectively. The disparity in the results demonstrates how the NAA and TXRF approaches differ in terms of sensitivity and measurement capabilities. NAA is more sensitive and accurate at quantifying trace elements. The higher sensitivity of NAA may result in higher reported leaching efficiency than TXRF, which may underestimate the amount of leached Mn. In both cases, Mn leaching was found to increase with time in all the samples. Ti ore and Cu tailings presented improved dissolution efficiencies of Mn compared to Zn-Pb tailings. The increased leaching rate with time in general is attributable to sufficient time for the interaction between the leaching agents and the samples [41]. Similar observations were reported by scientists while leaching Mn under different conditions [12,13,41].

It is worth mentioning that, for NAA, the first two and four hours of leaching Mn did not produce adequate Mn from Zn-Pb and Cu tailings, respectively. The quantity of a particular neutron-activation product created during neutron irradiation is proportional to the concentration of its parent isotope and thus to the associated elemental quantity. The method relies on the neutron radiative capture reaction (n,γ), which causes the specimen to emit gamma rays, which are then analyzed, allowing the user to detect, identify, and assess the existence of radioactivity in the sample [42]. Therefore, the lower the amount of the element in the sample, the lower the likelihood of activating and detecting the radioisotope.

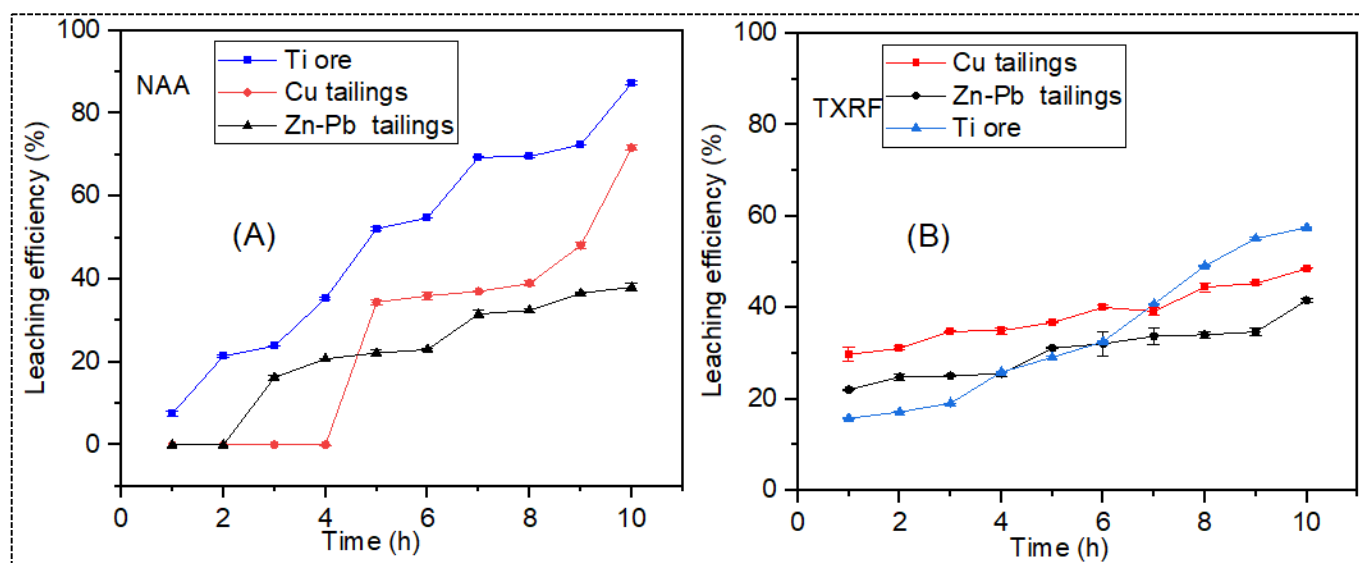


Figure 7. Graphs of the NAA (A) and TXRF analyses (B) represent the time dependence of Mn leaching from Ti ore, Zn-Pb tailings, and Cu tailings. Error bars represent 95% confidence intervals.

3.2.2. Dependence of Mn Leaching on the Temperature of the Solution

For both techniques, the leaching efficacy of Mn was shown to increase as the temperature increased from 22.5 to 70 °C in all the samples (Figure 8). Further elevation of the temperature resulted in a decline in Mn leaching in Zn-Pb tailings. Specifically, NAA showed a drop in the leaching efficiency from 37% at 70 °C to 19% at 110 °C. TXRF followed the same trend: a decline in dissolution efficacy was observed from 36% at 70 °C to 23% at 110 °C. That implies Mn exists as stable MnO_2 or in other forms that are difficult to dissolve in Zn-Pb tailings, which might need a reducing agent to reduce Mn^{4+} to soluble Mn^{2+} [5,11,12]. However, ascorbic acid, which was used as a reducing agent in this study, becomes unstable at temperatures above 80 °C. That decreases Mn leaching at high temperatures [5,13]. Additionally, the boiling point of HCl is 100 °C, and an increase in temperature beyond its boiling point leads to the evaporation of Cl^- ions in the form of HCl gas [43]. That can lower the leaching performance of HCl due to the reduction of its overall concentrations in the solution [43].

Both techniques showed that the ideal temperature for leaching Mn in Ti ore and Cu tailings was above 110 °C. Particularly, NAA yielded 86 and 85% leaching efficiencies of Mn from Cu tailings and Ti ore, respectively. Under the same conditions, 59 and 52% Mn dissolution efficiencies from Cu tailings and Ti ore, respectively, were acquired by the TXRF method. The trend for both approaches could be attributed to the availability of Mn in the form of MnO which does not need the reducing agent. High temperatures are also known to play a key role in the leaching process of Mn [44].

The improvement in Mn leaching with an increase in temperature might be attributed to a rise in the number of activated particles and more robust collisions, resulting in improved contacts and thus higher liquid-solid mass transfer [7]. The viscosity of the mixture also tended to decrease as the temperature rose. That is known to accelerate the migration of ions, solid particles, and solvent molecules, increasing the number of collisions between molecules. This facilitates the diffusion of the leaching agent to the ore surface, thereby enhancing the leaching rate of Mn ions [5]. That demonstrates that the method of dissolution varies as the leaching temperature changes [10,27].

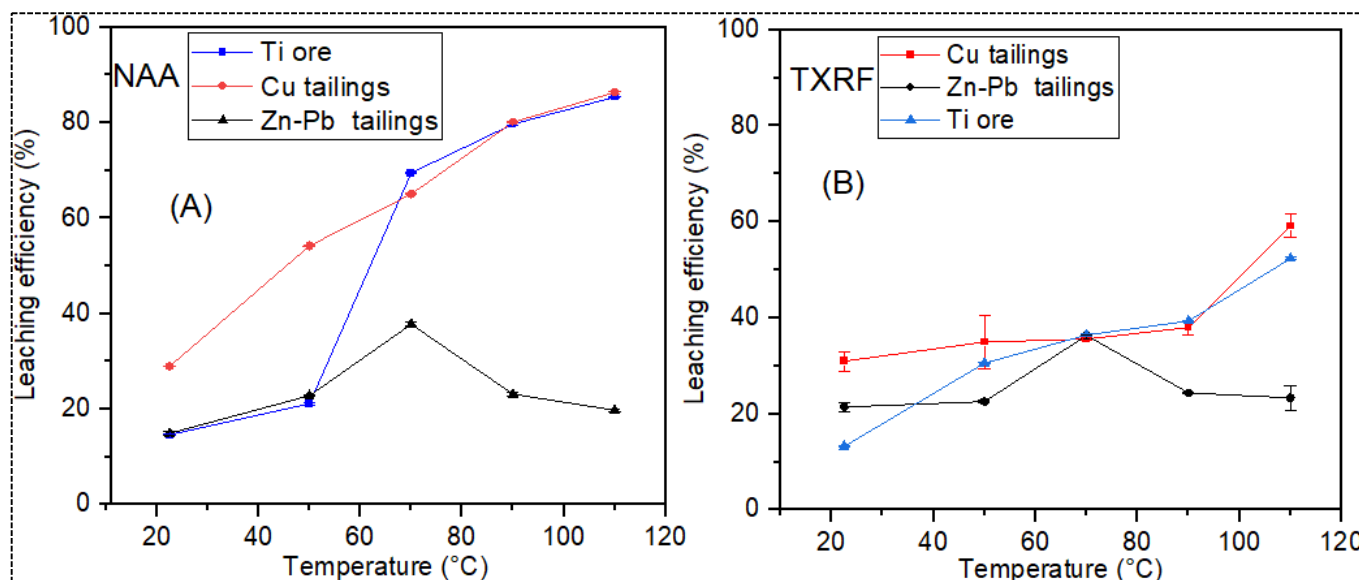


Figure 8. The findings from NAA (A) and TXRF analysis (B) showing the variation in the efficiency of Mn leaching with temperature in Ti ore, Zn-Pb, and Cu tailings. Error bars represent 95% confidence intervals.

3.2.3. Dependence of Mn Leaching on HCl Concentration

The influence of HCl concentration on the degree of leaching Mn from Ti ore, Zn-Pb tailing, and Cu tailings was studied for 6 h. The findings are given in Figure 9. According to NAA, the dissolution of Mn was 70% when 5 M HCl was used in Cu tailings, compared to 54% in Ti ore and 23% in Zn-Pb tailings. The TXRF analysis revealed that the leaching efficiencies of Mn were 47% in Cu tailings, 52% in Ti ore, and 36% in Zn-Pb tailings. The trend observed by both methods is likely related to the chemical composition and mineralogy of the materials. Cu tailings appeared to contain Mn in more readily leachable forms compared to Ti ore and Zn-Pb tailings. The presence of interfering compounds in Zn-Pb tailings might have contributed to their reduced leaching effectiveness. Generally, the leaching capacity of Mn was greatly boosted when the HCl concentration was raised from 1 to 5 M in all the samples. That is because, at high acid concentrations, there are sufficient Cl^- ions for displacement reactions and subsequent formation of more soluble chloro-complexes of Mn [45,46]. This suggests that product diffusion across the surface to the bulk of the mixture also plays a significant role, possibly at a later stage of extraction.

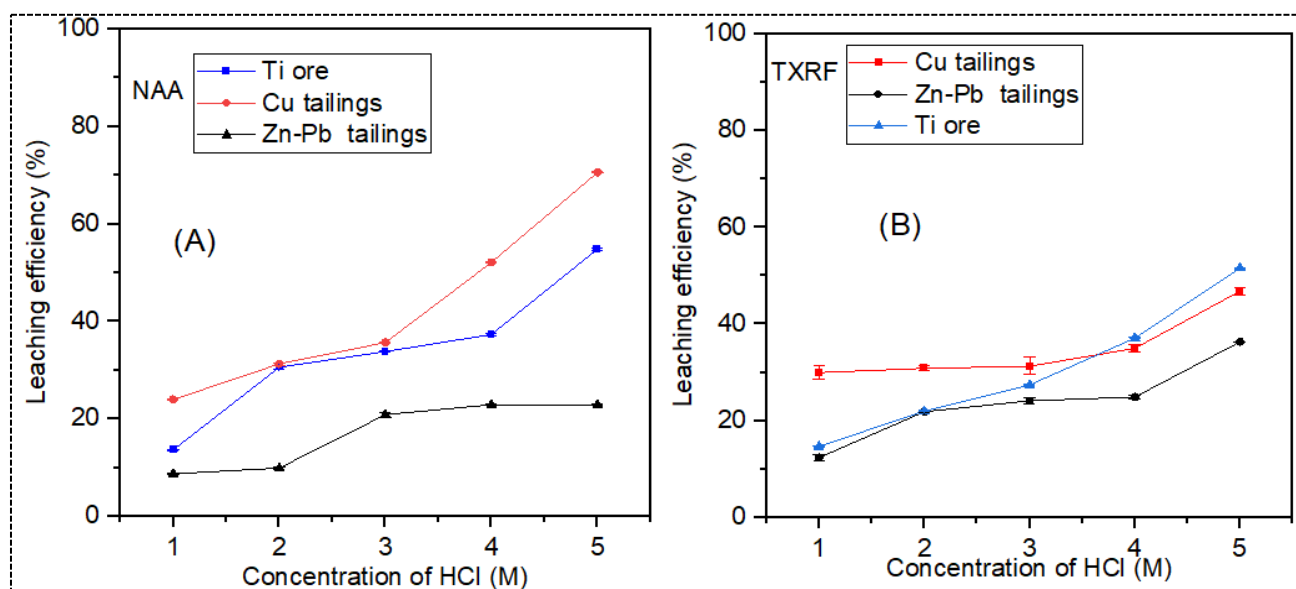
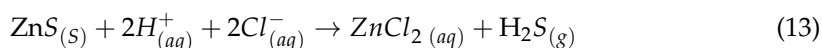


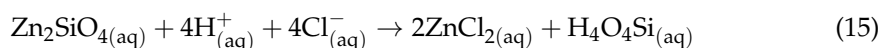
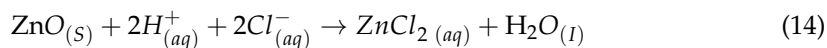
Figure 9. The outcomes obtained by NAA (A) and TXRF analysis (B) for Mn leaching in Ti ore, Zn-Pb, and Cu tailings, showing dependence on the HCl concentration. Error bars represent 95% confidence intervals.

3.3. NAA Analysis Based on MARIA Nuclear Research Reactor

3.3.1. Online/Real-Time Tracking of Zn Leaching Using a ^{65}Zn Radiotracer

Several radioisotopes were detected in samples activated at the MARIA nuclear research reactor. After around two months of cooling, ^{65}Zn remained the main radioisotope used as a radiotracer. From DGNA analysis of the Zn in the solid samples received from the nuclear research reactor, concentrations of 50 ± 6 mg/kg in Cu tailings, $12,383 \pm 1000$ mg/kg in Zn-Pb tailings, and 182 ± 13 mg/kg in Ti ore were reported. The available ^{65}Zn radiotracer in the samples formed the basis of the radiometric approach used to monitor the leaching time of Zn. Tracking of the ^{65}Zn was done using the $3'' \times 3''$ NaI(Tl) scintillation detector. The detector was chosen for online analysis because it has high efficiency for gamma detection with a good performance at temperatures of 22.5 to 80 °C [47,48]. The study revealed that the Zn recovery in all the samples under the same leaching conditions increased with time (Figure 10). The expected main reactions were as follows:





From the study, 80, 79, and 53% of the initial Zn was leached from Zn-Pb tailings, Ti ore, and Cu tailings, respectively, Table 5. The percentage of leached ^{65}Zn was approximated using the impulses given in Figure 10 according to Equation (16), as follows:

$$\% \text{ of leached Zn} = \frac{FC}{TC} \times 100\% \quad (16)$$

where:

FC represents the last counts recorded in the liquid phase after 300 min of leaching following the background correction. On the other hand, TC signifies the counts recorded in the batch leaching reactor containing the activated sample and the non-activated sample before the leaching process. The target counts were obtained by subtracting the background impulses/min from the overall value recorded by the detector before the dissolution process started. The differences in rates of leaching could be attributed to the differences in the structures and concentrations of Zn in the samples, as shown by handheld XRF and ICP-MS analysis in Tables 3 and 4. Increased leaching time can be linked to improved interaction between the reagents and the elements of interest in the material containing the metals [41]. In general, there was a strong correlation between the counts recorded in the three samples ($R = 0.5$ to ≤ 1). That shows that the existence of Zn in the samples is affected by the same depletion and geological-formation factors. However, there was a significant difference in results acquired from Zn-Pb tailings compared to the ones recorded in Ti ore and Cu tailings ($p < 0.05$). That is because there was a high concentration of Zn in Zn-Pb tailings compared to Ti ore and Cu tailings, respectively (as per Tables 3 and 4 and NAA of the solid samples from the nuclear research reactor).

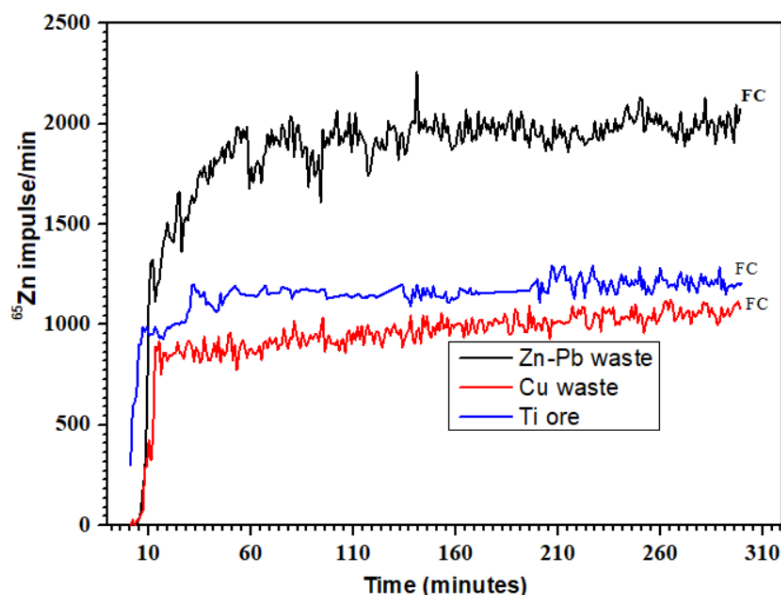


Figure 10. Online monitoring of Zn leaching using the ^{65}Zn radiotracer. Throughout the leaching process, the kinetics of Zn leaching can be monitored continuously.

Table 5. Leaching of Zn from the samples.

Sample	Target Counts (TC) (Impulse/min)	Final Counts (FC) (Impulse/min)	% of Zn Leached
Zn-Pb tailings	2603	2081	80
Ti ore	1532	1204	79
Cu tailings	2023	1080	53

3.3.2. Mathematical Modelling for the Online Radiotracer Leaching Studies for Zn

The kinetic mathematical model that represents the online leaching process of Zn^{2+} from the materials was developed using the findings of the experimental testing. The goal was to determine whether diffusion of Zn^{2+} from the core of the solid particle is the rate-limiting step during the leaching process. Based on the previously discussed NWE equation, two potential novel models that take the geometry of the diffusion zone into account were selected to study the chemical reaction: the linear diffusion model and the spherical diffusion model. The NWE equation was first rewritten to suit our study as follows:

$$\frac{d\text{Zn}_t^{2+}}{dt} = K \left(\text{Zn}_0^0 - \text{Zn}_t^{2+} \right) \quad (17)$$

where K is the proportionality factor, Zn_t^{2+} is the concentration of Zn at time t , and Zn_0^0 is the equilibrium concentration of Zn.

Some of the assumptions for the models were as follows:

The diffusion coefficient (D) of Zn^{2+} in the leaching medium remains constant for both the linear and spherical models. The D value was estimated based on the Stokes-Einstein equation through the application of the hydrodynamic radius of Zn^{2+} in the leaching medium with the empirically determined viscosity of 0.00132 Pa/s.

The hydrodynamic radius r of Zn^{2+} is constant and was calculated by employing the Stokes-Einstein equation through the application of the known diffusion coefficient of Zn^{2+} at infinite dilution in water ($7.5 \times 10^{-10} \text{ m}^2/\text{s}$) [49].

The specific surface area of the sample is constant. The average specific surface area for the sample (based on Nikon inverted microscope Eclipse Ti-S) used in modelling was found to be $1.3 \text{ m}^2/\text{g}$. The value is comparable to those found for ilmenite's particle analysis, as determined by other scientists: a specific area of $3.6 \text{ m}^2/\text{g}$ using vibratory ball-mill ESM 656-0.5 ks (Siebtechnik, Mülheim, Germany) and a specific area of $9.2 \text{ m}^2/\text{g}$ by the BET method [50,51]. That means the developed approach is reliable in estimating the specific surface area of the particles. The radius (r_0) of the sample's particle was treated as constant for the spherical model, and it was assumed that the volume of the solution did not change during the leaching process.

Figure 11 shows the mathematical models predicting the time dependence of leaching of Zn^{2+} from the samples considered in the study. By analyzing the linear and spherical diffusion models, one may easily notice that the time needed to reach the saturation level is significantly shorter for the spherical diffusion model. That is consistent with the experimental observation that the leaching process involving a solid in the form of fine powder (particle size in the μm range) is much more efficient compared to the dissolution process of a solid system consisting of grains with sizes in the cm range. That is more evident in the leaching of Zn^{2+} from Cu tailings compared to Zn-Pb tailings and Ti ore. The linear diffusion model seemed to describe the leaching process of Zn^{2+} from Zn-Pb tailings and Ti ore. The linear model implies that the leaching of Zn^{2+} from the materials is more effective for large particles, for which the chemical process reaches the steady state slowly compared to the spherical diffusion model. An increase in the dissolution rate may also occur as a result of a change in D under the influence of temperature and convection induced by mixing the system [15].

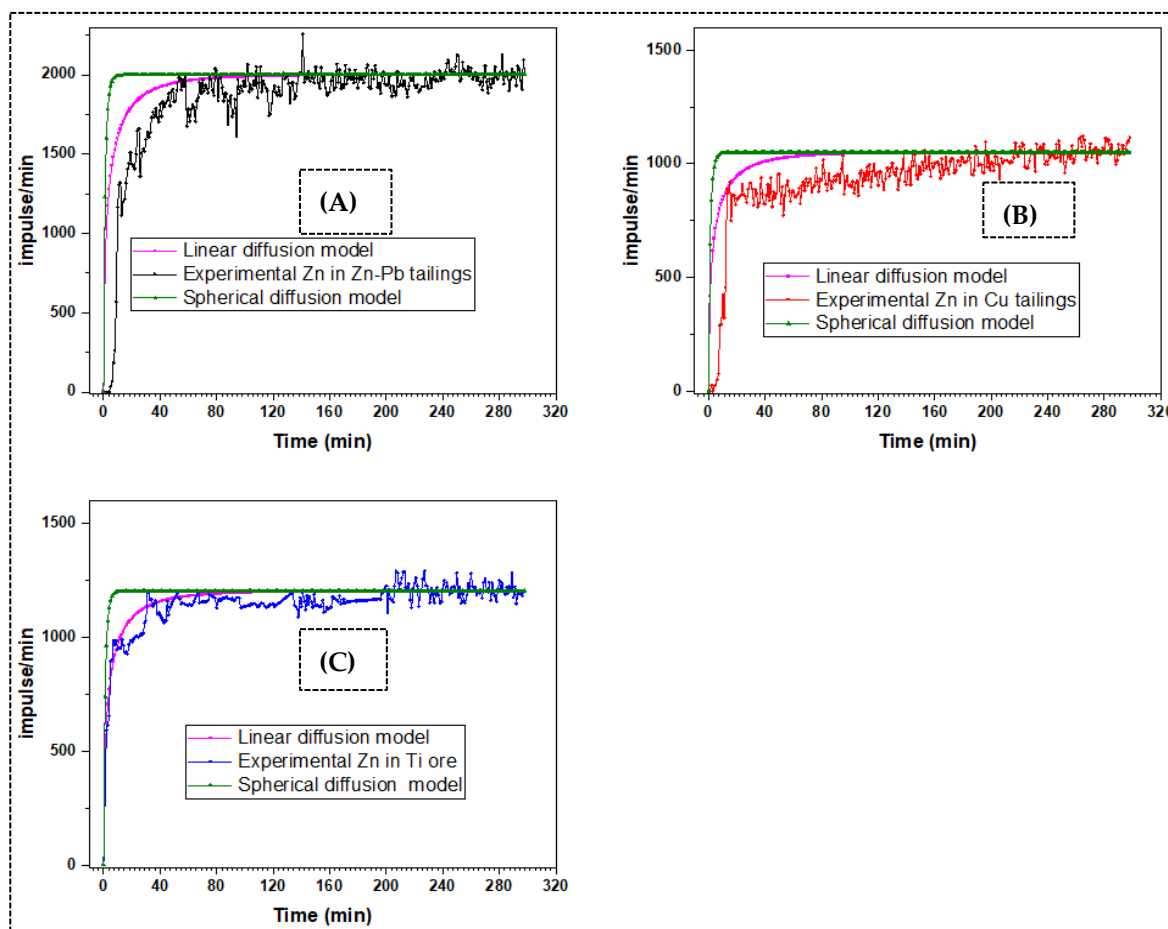


Figure 11. Experimental and computed counts for Zn by the linear and spherical diffusion models for Zn-Pb tailings (A), Cu tailings (B), and Ti ore (C).

3.3.3. Handheld-XRF and TXRF Analysis of the Zn Leached in the Samples

XRF and TXRF analysis of the leached sample under the same conditions was done to confirm the variation in Zn leaching with time shown by NAA of ^{65}Zn . For both XRF analyses, Zn leaching efficiencies were also found to rise with the increase in the reaction time (Figures 12 and 13). According to the handheld XRF, the optimum leaching time for Zn in Zn-Pb tailings was reported to be around 10 h. A 95% leaching efficiency was recorded at that time. However, under similar leaching conditions for the Cu tailings and Ti ore, the Zn leaching efficiencies were reported to be 72 and 60%, respectively, (Figure 12A).

However, after 10 h of leaching, TXRF analysis indicated leaching efficiencies of 99, 92, and 81% for Zn in Ti ore, Zn-Pb, and Cu tailings, respectively (Figure 13A). The differences could be linked to the variations in the sensitivities and detection limits between the two techniques. TXRF is more sensitive and hence can offer reliable measurements for trace elements. Generally, an increase in leaching time is known to enhance the reaction between the Zn mineral phases in the samples and the reagents [52].

Apart from the time variation, it was possible with both techniques to analyze the influence of HCl concentration (1 to 5 M) on the leaching of Zn (Figures 12 and 13, respectively). The dissolution of Zn was found to increase as the HCl concentration increased from 1 to 5 M. For example, handheld XRF indicated improved leaching efficiencies from 39 to 92%, 37 to 70%, and 30 to 70% for Zn-Pb tailings, Ti ore, and Cu tailings, respectively (Figure 12B). On the other hand, TXRF measurements showed changes in leaching efficiencies from 35 to 76%, 5 to 63%, and 41 to 90% for Zn in Zn-Pb tailings, Ti ore, and Cu tailings, respectively (Figure 13B). The general trends for both techniques can be attributed to a rise in Cl^- ions

at high acid concentrations, which react with ZnS and ZnO plus other Zn minerals in the sample [43].

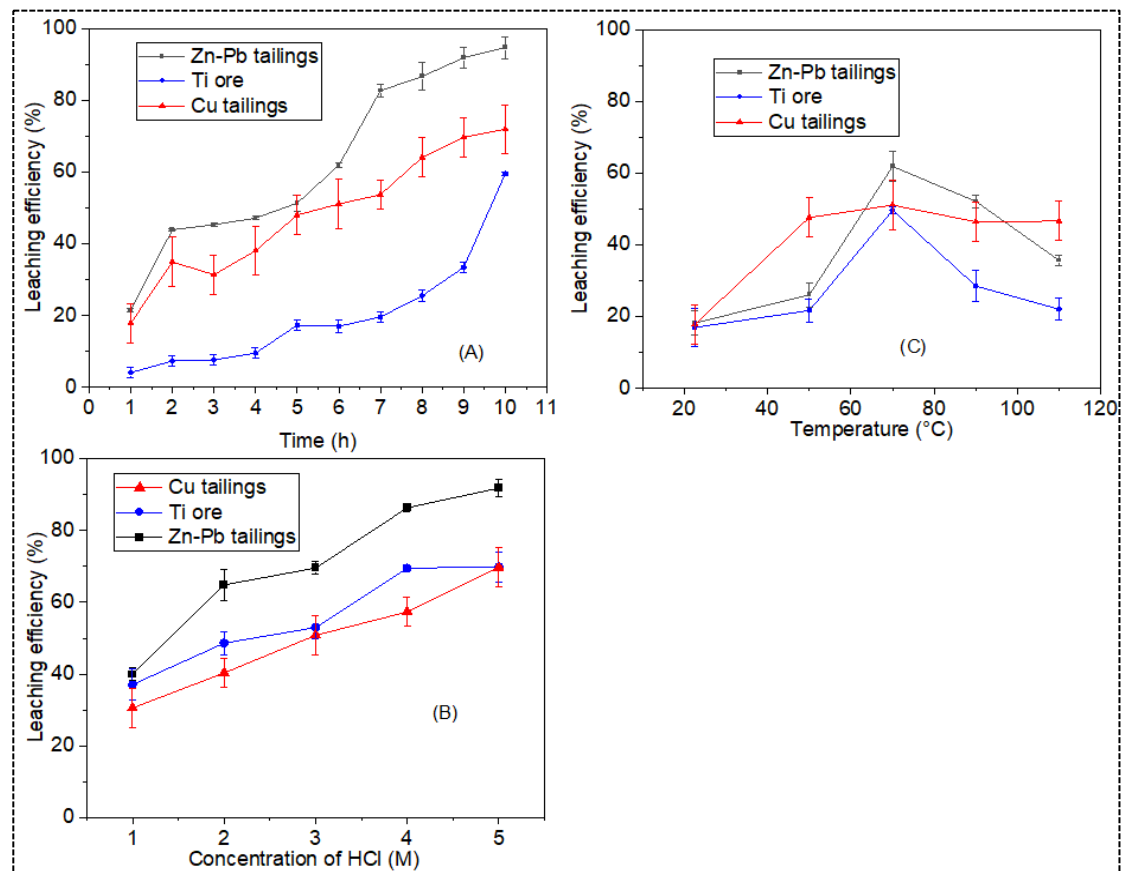


Figure 12. Handheld XRF analysis of Zn leaching from Ti ore, Zn-Pb tailings, and Cu tailings under different conditions of leaching time (A), HCl concentration (B), and leaching temperature (C). Error bars represent 95% confidence intervals.

Also, when the leaching temperature is raised, so is the proportion of Zn leaching, as shown in Figures 12C and 13C. This might be due to the high leaching temperature (temperature > 22.5 °C), which accelerates the interaction between the HCl and Ti ore, Zn-Pb tailings, and Cu tailings. However, the leaching efficiency decreased for Zn in Ti ore and Zn tailings at temperatures above 70 °C. That is because ascorbic acid, which was applied as a reducing agent, is sensitive to heat and degrades at higher temperatures. At temperatures beyond 70 °C, the breakdown rate increases dramatically, decreasing its usefulness as a reducing agent in the leaching process. HCl is also volatile, and as the temperature rises, the rate of evaporation increases. This can cause a drop in the concentration of HCl in the solution, limiting its effectiveness as a leaching agent [43]. Generally, the mineral dissolution kinetics improve with increasing temperature, leaching time, and HCl acid concentration [53].

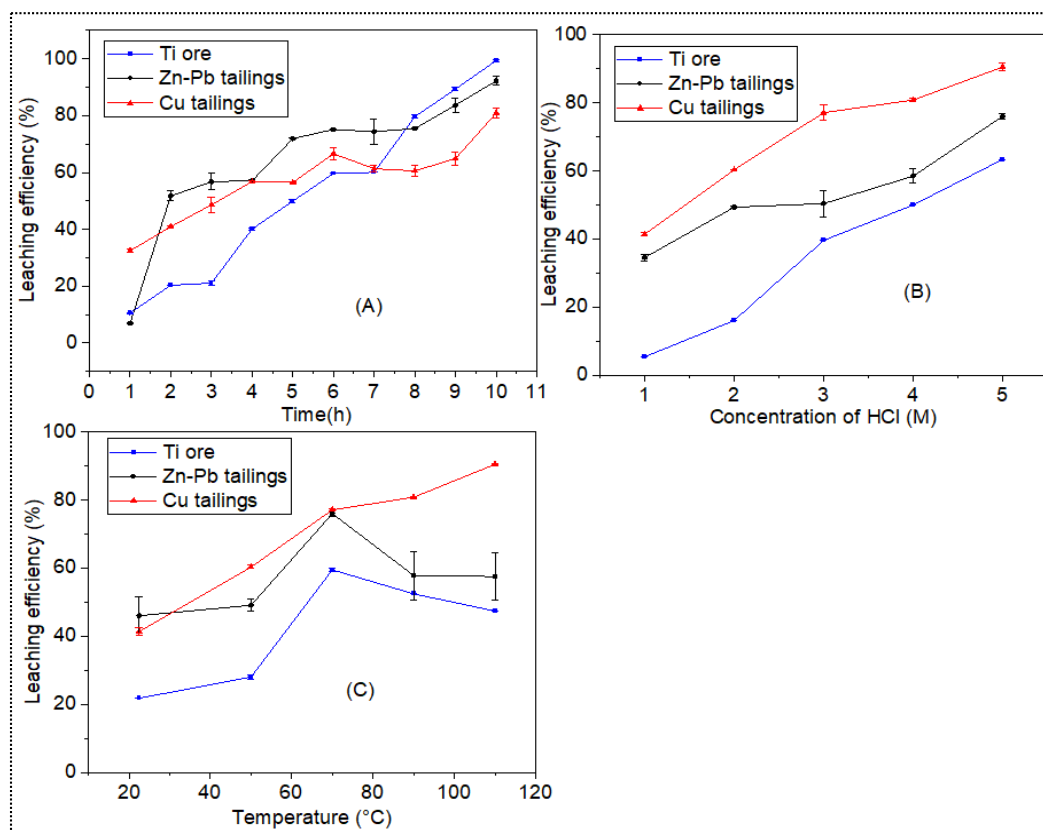


Figure 13. TXRF analysis of Zn leaching from Ti ore, Zn-Pb tailings, and Cu tailings under different conditions of leaching time (A), HCl concentration (B), and leaching temperature (C). Error bars represent 95% confidence intervals.

3.3.4. Future Applications

Moving forward, integrating radiation-based methods with recycling technologies will provide exciting opportunities for long-term metal extraction and environmental management. The next step in this research is metal recovery using solvent extraction, which allows the aqueous phase containing leached metals to be recycled for numerous leaching cycles [54]. This novel strategy not only saves resources but also reduces chemical waste, highlighting the significance of recycling in environmental stewardship. This approach improves efficiency while lowering overall environmental impact by optimizing metal content in the aqueous phase via multiple leaching cycles. These developments pave the path for more widespread uses of techniques such as NAA and XRF approaches in metal recovery, environmental remediation, and sustainable resource management.

4. Conclusions

The use of NAA based on a nuclear research reactor offered the possibility of developing a novel method of online tracking of Zn leaching in the materials. Zn leaching was found to increase with the increase in leaching time: after 300 min, 80, 79, and 53% of Zn was leached from Zn-Pb tailings, Ti ore, and Cu tailings, respectively. The D-T neutron generator made it feasible to design a novel approach appropriate for DGNAAs of short-lived radioisotopes with low radioactivity in liquid samples. Mn leaching was found to increase with time, HCl concentration, and temperature, according to the D-T neutron generator analysis (TXRF method confirmed the results). Because of the growing availability of D-T neutron generators, their usage will be increasing as well. The ease of use and underlying safety of this approach render it an appealing alternative to the high-thermal-flux reactor-based instrumental-DGNAAs for those practical situations where it is suitable. However, the lifetime for the D-T neutron generator, and thus the number of

samples that can be analyzed, is limited due to tritium decay. Handheld XRF was reported to be appropriate for analyzing the solid samples and the elements present in high amounts in the liquid sample. The handheld XRF and TXRF analyses of Zn were able to confirm that the leaching of Zn increased with the increase in leaching time, as indicated by the online radiotracer method. From the mathematical models, it was discovered that the spherical diffusion model requires substantially less time to attain saturation during the Zn leaching process as compared to the linear diffusion model. Handheld XRF and TXRF were found to be promising for offline analysis of metals, while DGNAA is ideal for online monitoring of mineral leaching. The techniques can therefore be applied in research and improved for applications in mining industries.

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