



Impact reduction of heavy metals present in leachate discharges by stabilization-solidification using Portland cement and sodium silicates

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Abstract

The purpose of this study was to explore a clean and effective method to remediate the environmental risks of the Fe, Cd, Ni, Hg, Cr, Pb and Zn in ALZINC leachate discharges (Ghazaouet, west of Algeria). The process consists of a stabilization / solidification (S/S) treatment of these sludge using hydraulic binders, followed by hardening and compacting in order to limit the solubility and the mobility of the pollutants. Then the leachate discharges samples were kneaded with a Portland cement and sodium silicates (Na_2SiO_3). These processes were tested on autumn and winter and evaluated during 95 days of S/S for each sample.

Characterization of the leachate discharges samples were studied by scanning electron microscopy, energy dispersive spectroscopy, Fourier transformed infrared spectroscopy, and X-ray diffraction. The determination of elements was by Inductively Coupled Plasma-Atomic Emission Spectrometry, Cold Vapor-Atomic Absorption Spectrophotometry, and Atomic Absorption Spectrophotometry. The findings indicated significant stabilization of Cd, Ni, Zn, Pb, Hg, and Fe, with reductions exceeding 70%. Although the reduction ratio for Cr was comparatively lower, it remained within permissible limits, adhering to environmental regulations, which is an indicative of the potential S/S processes of sludge taken from the leachate discharges.

Keywords: leachate discharges, sludge, stabilization, solidification, zinc hydrometallurgy.

I Introduction

Heavy metals produced by industrial activities is one of the most important environmental problems at present [1]. Their ions are difficult to decompose and can enter the surface via rainwater, pollute the environment and cause many problems for the health of all organisms in the food chain [2]. Due to extremely high levels of heavy metals and their harm to the environment, these residues usually undergo treatment using adsorption, stabilization, and verification to reduce their toxicity [3-5]. Solidification/stabilization (S/S) technology is commonly applied to fix metal ions within a solid substrate. This method involves incorporating binding agents like lime, cement, chemically bonded phosphate binders, etc., to effectively immobilize and encapsulate the metal ions [6]. Hydraulic binders are commonly employed in the management of waste materials that contain high levels of moisture, which is absorbed through hydration processes. Cement is the primary example of a hydraulic binder. However, more cost-effective alternatives are extensively utilized, encompassing various ashes, pulverized blast furnace slag, dust from cement kilns, by-products from industrial processes, anhydrite, and additional substances with lesser utility [7].

Iron or rather steel is by far the most widely used metal accounting for about 95% of total metal production. Zinc is the fourth most widely used metal after iron, aluminum, and copper in terms of the quantity produced. The production of refined zinc in 2017 is up to 13 million tons [8]. Zinc is an important component of heavy metal pollutants, as it pollutes both the soil and water and it causes serious environmental pollution but negatively impacts the human body and is classified as a hazardous waste [9].

The ALZINC complex in Ghazouet (western Algeria) presents a significant environmental challenge, generating approximately 500,000 tons of hazardous waste annually in the form of industrial mud. This waste primarily contains heavy metals, including zinc, copper, and iron [10]. Zinc hydrometallurgy system is a highly interconnected system with many of the metals being derived from the zinc ores and as by products. Almost all the associated metals, such as Fe, Pb, Cu, Ag, Cd, Co and Ge, imported accompanied with the raw material (e.g. zinc calcine) were emitted by zinc hydrometallurgy system as metabolic by products [11].

The proposed method is considered as an environmentally friendly and efficient approach to the comprehensive solidification and stabilization of heavy metals from leachate discharges of zinc hydrometallurgy. For this, different methods for determining heavy metals ions have been employed, such as atomic absorption spectrometry (AAS), inductively coupled plasma (ICP), and cold vapor atomic fluorescence spectrophotometry (CVAFS). In addition, X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), and scanning electron microscopy (SEM) coupled with energy-dispersive spectrometry (EDS) (SEM/EDS) were performed to characterize the ALZINC leachate discharges samples to achieve the solidification stabilization mechanism.

II Materials and methods

II.I The study area

The Leachate discharges used in this study was obtained from ALZINC leachate discharges in Ghazouet, is located in northwestern Algeria region (34XM+9CG, N7AA). ALZINC leachate releases containing toxic elements such as heavy metals contribute to soil pollution; contamination may be present outside the individual grains and within the pore structure. Table 1 shows the average of chemical composition of leaching residues: percentage of various elements [12] and Figure 1 shows a map of the studied area (ALZINC, Ghazouet).

Table 1: Chemical composition of leaching residues: percentage of various elements

Elements %	Zn	S(SO ₄ ⁻)	Pb	Fe	Cu	Cd	SiO ₂	Mn	Mg	Ca
Leaching	34.69	6.16	1.83	28.24	0.92	0.071	5.46	0.35	0.94	1.2

residues										
Elements %	Ba	As	Cr	Na	K	Co	F	Ag	Ge	Ni
Leaching residues	0.8	0.039	0.0066	0.069	0.055	0.0086	0.6	1.37	0.0021	0.0027

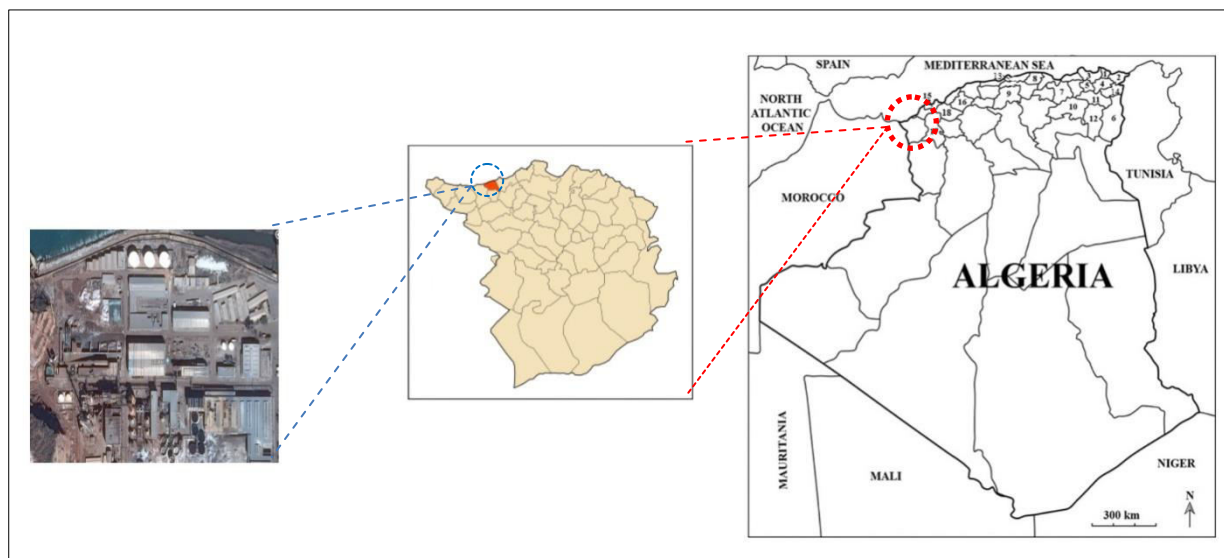


Fig. 1: Map of the studied area showing the ALZINC leachate discharges in Ghazouet area.

II.II Environmental Release Limits Set by European Committee

The limit values for releases to the environment are taken according to the orders of the following European committee:

- Decree of December, 30 2002 (Directive 1999/31/EC according to the Council Decision of 12/19/2002).
- Decree of 12/31/2004.
- Decree of 03/15/2006.
- Decree of 01/08/1998.

Table 2: European committee sets environmental release limits for compliance.

Components	Cadmium (Cd)	Total chromium (Cr)	Nickel (Ni)	Zinc (Zn)	Lead (Pb)	Mercury (Hg)	Chrome Hexavalent (Cr VI)	Iron (Fe)
Limit Values (mg/kg)	2	150	50	300	100	1	75	350

II.III Chemicals

All working solutions were prepared with ultrapure distilled water and all chemicals of analytical reagent grade was purchased from Sigma Aldrich India.

II.IV Cement

An ordinary type of cement (LAFARGE MATINE NA442 CEM II/B-L 42.5 N) certified, compliant with Algerian (NA442 - 2013) and European (EN 197-1) standards, selected for the experimental material, primarily consists of calcium oxide (CaO), aluminum oxide (Al₂O₃), silicon dioxide (SiO₂), and iron (III) oxide (Fe₂O₃) and less than 3%, 2.3% and 0.07% of SO₃, MgO and chlorides respectively[13].

II.V Stabilization and solidification process

The hydraulic binders utilized in this research are Portland Artificial Cement (CPA) and sodium silicate (Na₂SiO₃). The process of inerting 1 m³ (approximately 1000 kg) of sludge involves adding 162 kg of Portland cement and 3.5 kg of sodium silicates (Na₂SiO₃).

Transfer of sludge on the two-screw table: It is carried out by a mechanical shovel (TRAX) which deposits the mud on the table; the two screws are used to fragment it and to drive it to the following equipment:

Transverse screw: It serves as a conduit for the transfer of the sludge to the mixer by adding products (cement, silicate and water) via pipes connecting the cement silo, the water tank and the silicate tanks.

Mixer: This equipment is used to collect the sludge mixed with the additives products and transform it into pasty products; the latter after kneading are pushed outwards onto the ground.

After the treatment process, we obtain a pasty mixture transformed with time into a solid matrix which avoids its evaporation and its contamination by toxic products.

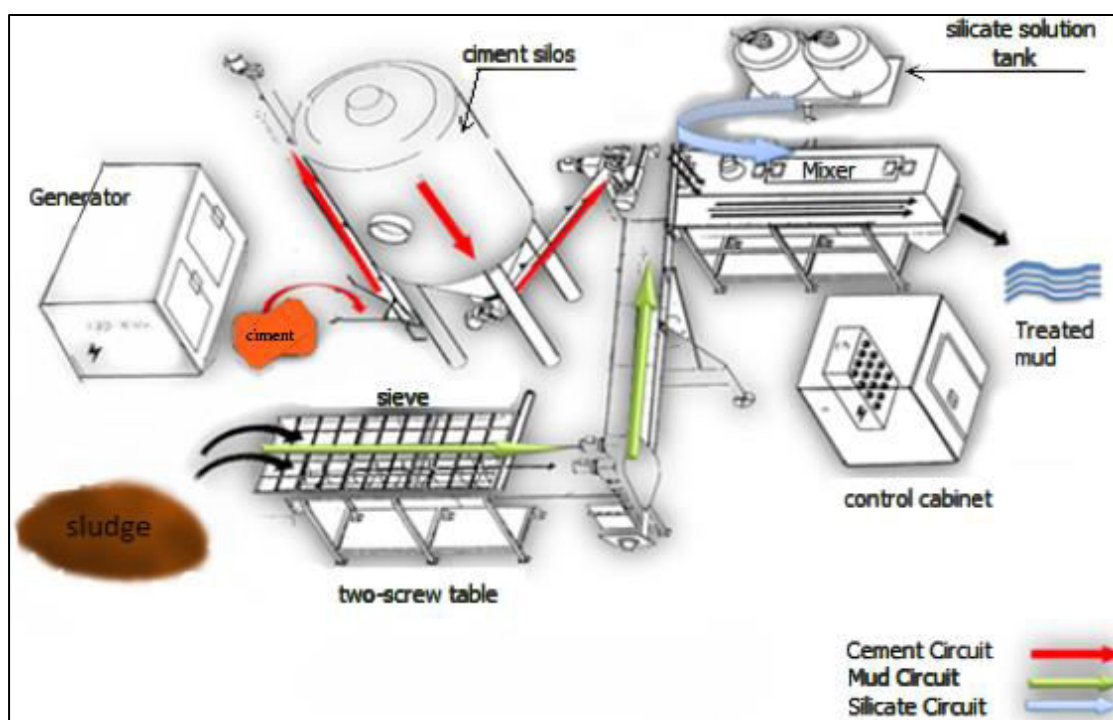


Fig. 2: Inerting method for ALZINC leachate releases treatment.

II.VI Sampling

Sampling was carried out at the site of ALZINC in the leachate recovery area by core sampling in cylindrical specimens in accordance with the French standard X31-210 (diameter = 4 cm, height = 8 cm). Two samples (A) and (B) were taken from the ALZINC sludge before the inerting and hardening treatment, and two comparative samples (A1) and (B1) were taken from the same sludge After treatment. The samples were conveyed to the testing laboratory in refrigerated containers and subsequently stored at 4°C until the analysis was conducted. Following the same proportions of inerting process, we take 10 kg of ALZINC sludge and add 1.62 kg of cement along with 35 g of silicates in a water solution. After one month of hardening, two samples (A1 and B1) are collected for analysis.

The leaching consists in bringing into contact and with permanent agitation for 24 hours, (100 g) of each test sample with one liter of distilled water. After filtering with 0.45 µm filters, 200 ml of each solution (A), (B), (A1) and (B1) are taken for analysis to determine the values of heavy metals and alkali metals before and after treatment and curing.

II.VII Analysis methods

II.VII.1 X-ray diffraction:

X-ray diffraction was used for determination of chemical and mineralogical compositions of the sludge that extracted from the leachate discharges. Phase analysis was carried out using a PHILIPS Xpert powder diffractometer (X-ray) coupled to a computer operating system with Cu K α radiation ($\lambda = 1.54051 \text{ \AA}$) at a scan rate of $2^\circ/\text{min}$, an operating voltage of 40 kV, and a current of 40 mA.

II.VII.1 Scanning Electron Microscope (SEM) and Energy-Dispersive X-ray Spectroscopy (EDS or EDAX).

The morphology and nanostructures of ALZINC leachate discharge samples were analyzed using a Scanning Electron Microscope (SEM) and characterized with Energy-Dispersive X-ray Spectroscopy (EDX) utilizing the ZEISS SmartEDX system.

II.VII.2 Fourier Transform Infrared Spectroscopy (FTIR)

Fourier Transform Infrared (FTIR) spectroscopy analysis was performed on the ALZINC leachate discharge samples using the Shimadzu-8300 IRTF system. This method was employed to identify and characterize the principal functional groups within the samples.

II.VII.3 Atomic Absorption Spectrometer:

The analysis of Chrome Hexavalent (Cr VI) and Iron (Fe) is carried out through Atomic Absorption Spectrometry (AAS), providing comprehensive insights into the heavy metal composition of ALZINC samples.

The apparatus used is Perkin Elmer type 1100 B, this model is atomic absorption spectrometer controlled by a microprocessor, equipped with a cathode-ray display.

II.VII.4 Inductively coupled plasma:

Inductively Coupled Plasma (ICP) analysis is employed for the determination of Cadmium (Cd), Total chromium (Cr), Nickel (Ni), and Zinc (Zn), ensuring precise measurement of these elements. Furthermore, the presence of Lead (Pb) is assessed using ICP analysis. The Inductively coupled plasma used in this study was Perkin Elmer 5300 DV optical emission ICP, it can detect all metals and even some metalloids and non-metals, it is consisting in ionizing the sample by a kind of extremely hot flame: up to 8000 K by injecting it into argon or helium plasma. The sample enters the plasma in liquid or solid form undergoing the following state changes: fusion (for solids), vaporization, ionization[14, 15].

II.VII.5 Cold Vapor Atomic Absorption Spectrometry:

Mercury (Hg) is detected using Cold Vapor Atomic Absorption Spectrometry (CVAAS) using Agilent VGA 77, it was implemented to analyze heavy metals, it is consisting in determining the mercury vapor content and the particulate mercury inorganic compounds according to ISO 17733/2004. The mercury vapor is removed from a solid absorbent by means of a diffusion badge or by pumping on an absorption tube; the particulate mercury inorganic compounds are removed by means of a quartz fiber filter. The lower limit of the working range of the method is between 0.01 g and 0.04 g of mercury and the upper limit is at least 30 g of mercury [16].

III RESULTS AND DISCUSSION

III.1 Characterization of ALZINC leachate discharges before and after S/S processes

III.1.1 X-ray diffraction (XRD)

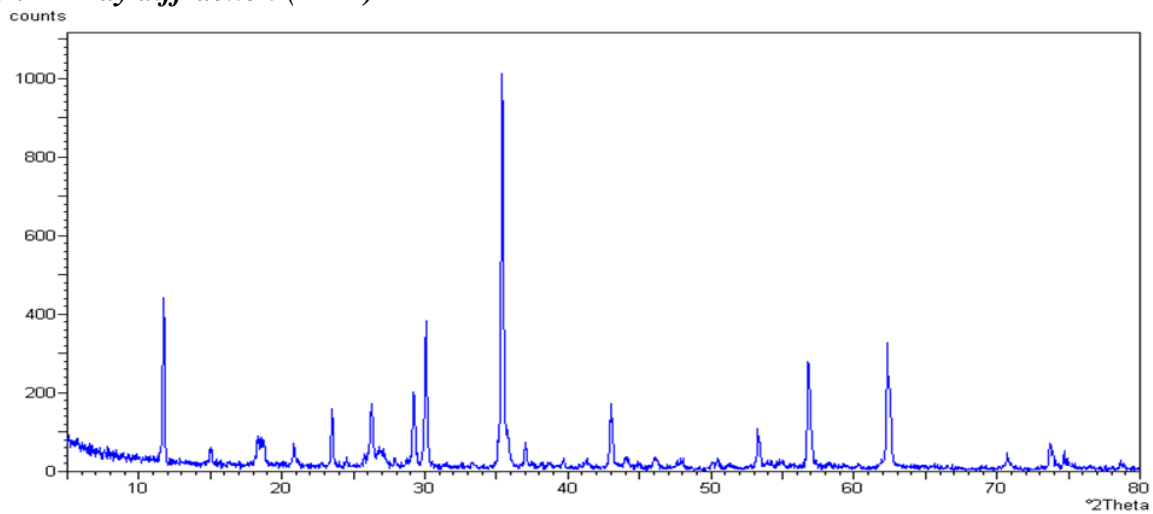


Fig. 3: XRD patterns of ALZINC leachate discharges before treatment.

The X-ray diffraction (XRD) patterns of ALZINC leachate discharges exhibit distinct peaks at various 2θ angles, providing valuable insights into the composition and the crystalline structure of the sample. The observations revealed that the majority of the mineral phases initially present in the mineral sludge sample remained intact prior to the leaching process[17]. Peaks at 11.5° corresponding to plan (001), 15° (003), and 18.5° (111) suggest the presence of crystalline phases with specific lattice arrangements. The peak at 21° (101) indicates the possible existence of another crystalline component. Peaks at 23.5° (002), 26.5° (111), and 29.5° (101) further contribute to the characterization of the sample's crystallographic nature.

The identified peaks correspond to various crystalline phases, including zinc vanadium oxide (ZnVOH), zinc iron oxide (ZnFe_2O_4), zinc oxide (ZnO), Iron (II, III) oxide (FeO, Fe_2O_3 , Fe_3O_4), Coulsonite (FeV_2O_4), Titanium oxide (TiO_2), Magnesium oxide (MgO), Copper oxide (CuO), Lead Silicate (Pb_3SiO_5) and potentially more. Notably, the sample exhibits a complex composition of oxidized metals, with zinc ferrite emerging as the predominant element. Zinc is observed in diverse forms, often in combination with iron or other metallic elements (M) like Copper, Nickel, vanadium, titanium, forming a general formula MOFe_2O_3 . Peaks at 30° (220), 35.5° (311), and 37° (222) each correspond to distinct 2θ angles and further support the diverse nature of metal compounds within the ALZINC leachate discharges. The prominent peaks at 43° (012), 53.5° (422), and 57° (230) provide additional evidence of specific crystal orientations. The peaks at 62.5° (440), 71° (611), 74° (622), and 75° (041) contribute to the comprehensive understanding of the sample's crystallographic composition. Overall, the XRD patterns reveal a diverse array of crystalline phases, laying the foundation for detailed analyses and potential implications in the context of leaching processes and the characterization of industrial waste products.

III.I.2 Fourier Transform Infrared Spectroscopy (FTIR)

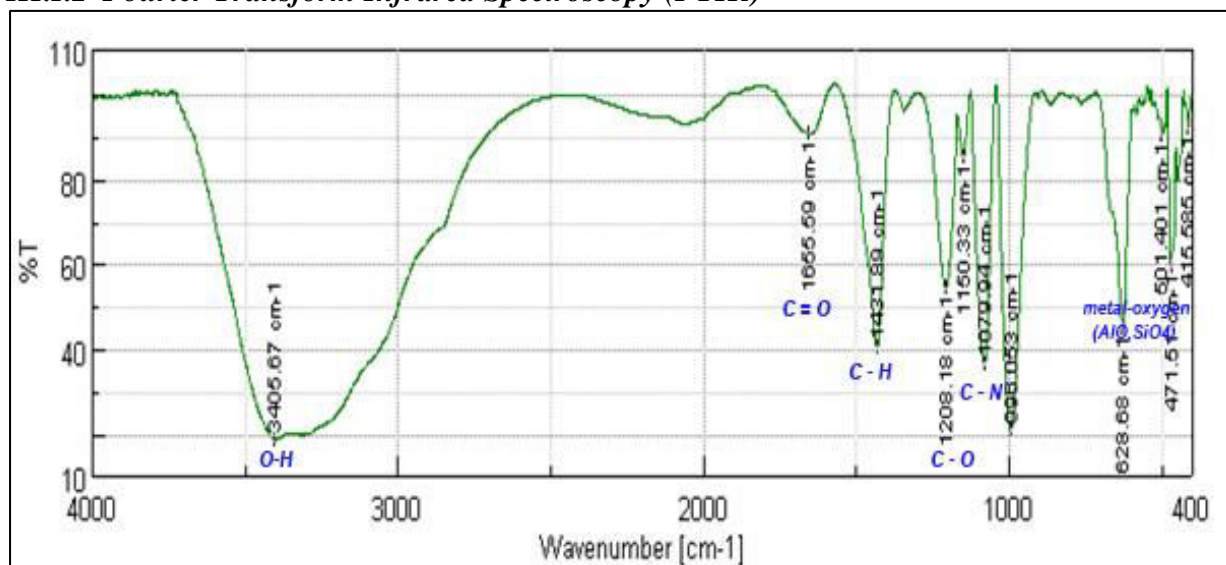


Fig. 4: Fourier Transform Infrared Spectroscopy spectrum of prepared ALZINC leachate discharges.

The Fourier Transform Infrared Spectroscopy (FTIR) spectrum of the prepared ALZINC leachate discharges reveals distinctive peaks at various wavenumbers, providing insights into the chemical composition of the sample. The peak at 3406 cm^{-1} indicates O-H stretching vibrations, suggesting the presence of water or hydroxyl groups. A notable peak at 1656 cm^{-1} corresponds to C=O stretching vibrations, indicative of carbonyl groups in organic compounds. Additionally, the presence of alkanes or aliphatic compounds is suggested by the peak at 1432 cm^{-1} , representing C-H bending vibrations. Peaks at 1208 cm^{-1} and 1150 cm^{-1} point to C-O stretching vibrations, commonly found in alcohols, ethers, and esters. The peak at 1080 cm^{-1} signifies C-N stretching vibrations, suggesting the presence of amines or amides. Furthermore, vibrations related to metal compounds are evident, with peaks at 629 cm^{-1} , 501 cm^{-1} , 471 cm^{-1} , and 416 cm^{-1} indicating metal-oxygen (AlO, SiO₄) stretching and bending vibrations. These findings collectively highlight the diverse chemical composition of the ALZINC leachate discharges, with potential implications for understanding the leaching process and optimizing waste treatment procedures[18].

III.I.3 Scanning Electron Microscope (SEM) and Energy-Dispersive X-ray Spectroscopy (EDS or EDAX).

The provided scanning electron microscope (SEM) image showcases the textural characteristics of a leachate sample from ALZINC leaching process. The image, captured under high-vacuum conditions at an accelerating voltage of 10.00 kilovolts (kV), reveals a complex topography with varied electron density.

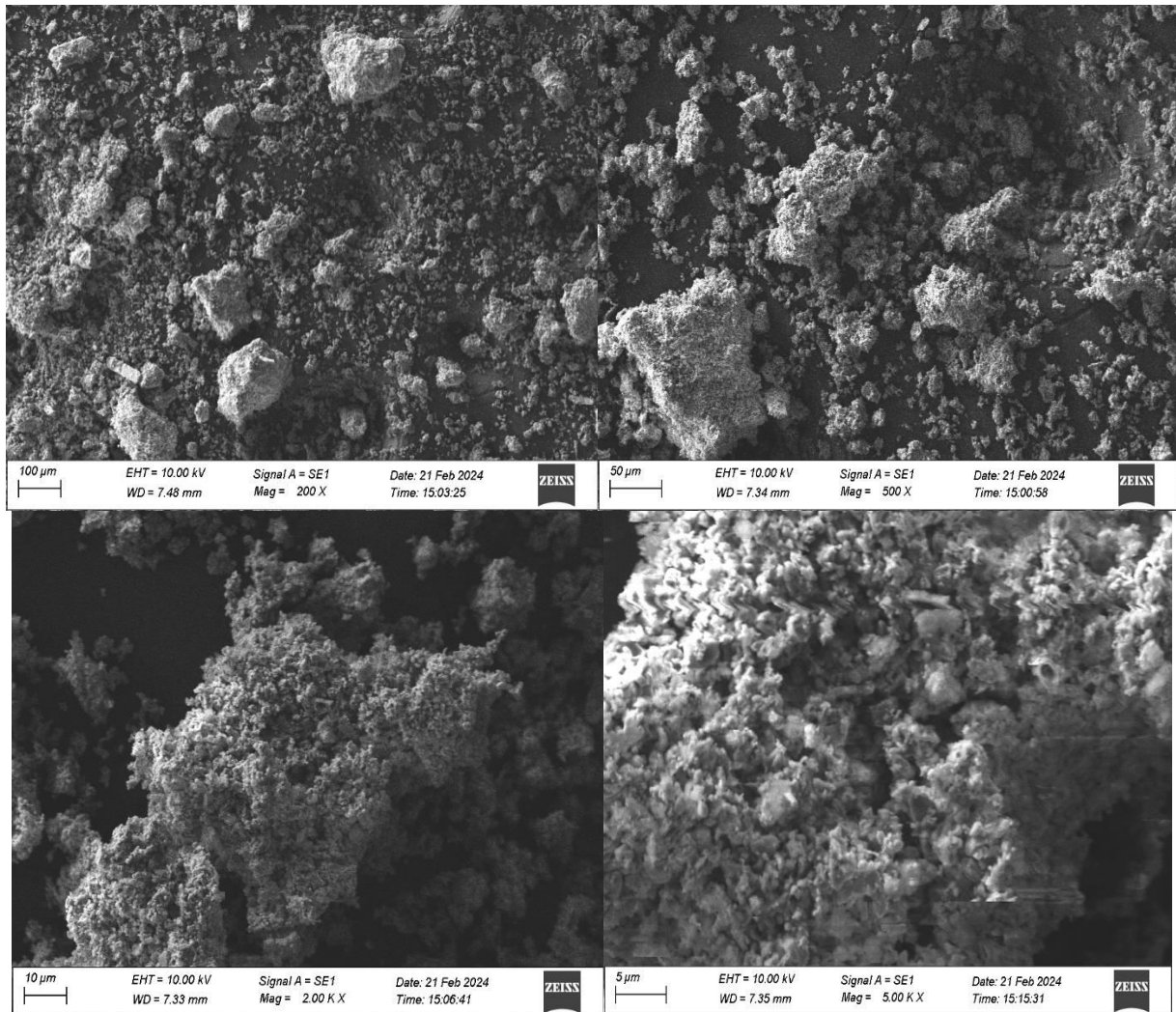


Fig. 5: Scanning Electron Microscopy (SEM) micrographs of ALZINC leachate discharge particles at various magnifications ranging from 100 to 5 micrometers.

The set of SEM micrographs (Fig. 5) presents a multi-scale view of an ALZINC leachate discharge, revealing a textured landscape of aggregated particles. Magnifications ranging from 200x to 5000x provide a hierarchical perspective on the material's morphology, with the finer details becoming increasingly apparent at higher zoom levels. The consistent roughness across varying magnifications suggests a complex composition, likely a result of industrial processing. These images serve as a visual metric for analyzing particle size, distribution, and the potential for trace element mapping in environmental studies.

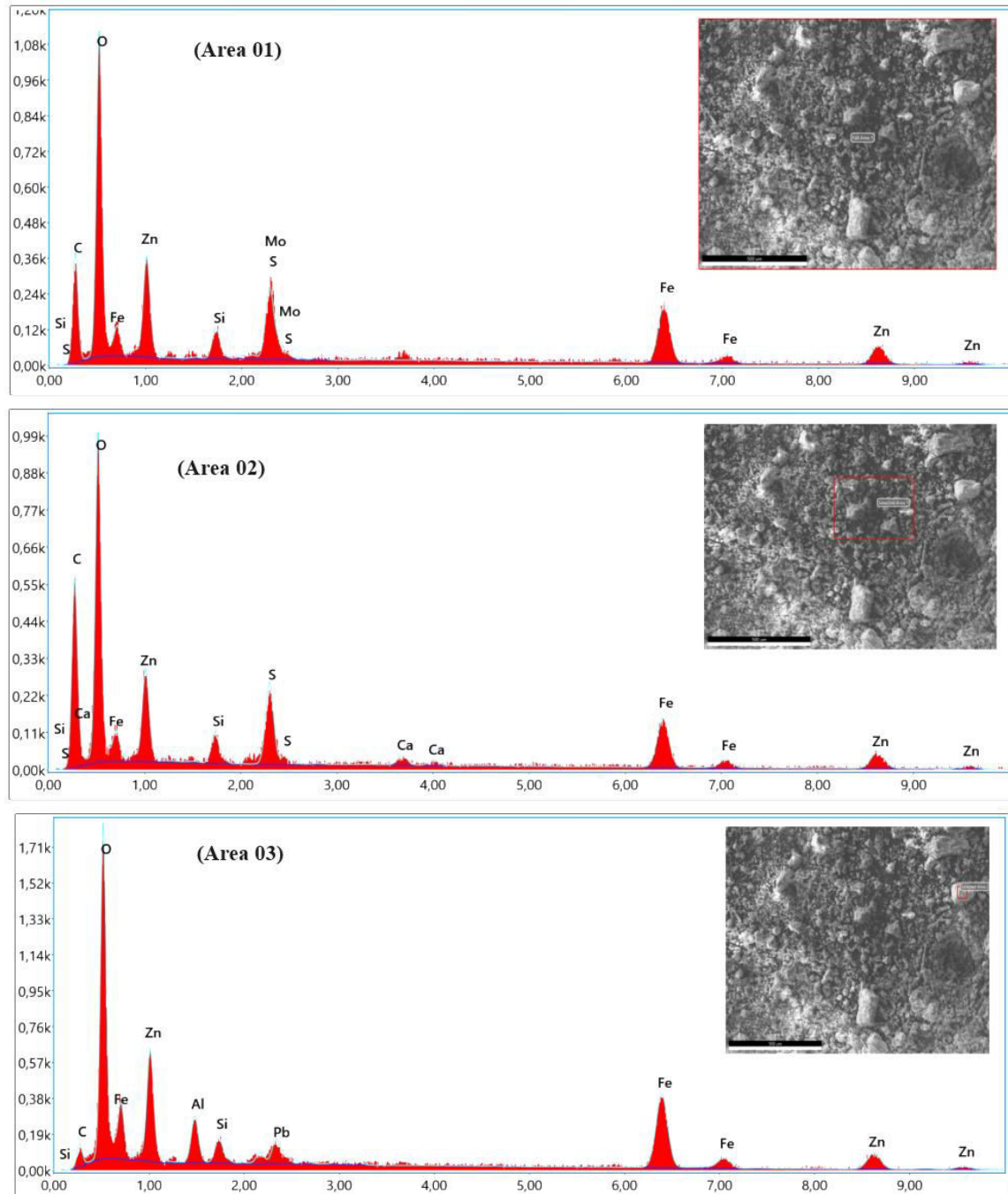


Fig. 6: Elemental Analysis of ALZINC Leachate Particulates via Energy-Dispersive X-ray Spectroscopy.

Energy-Dispersive X-ray Spectroscopy (EDS) analysis of industrial leachate discharges has elucidated a variable elemental composition, indicative of complex industrial processes. The EDS spectrum (Fig. 6) revealed the presence of elements such as carbon, oxygen, silicon, sulfur, molybdenum, iron, and zinc (table 3). In particular, iron and zinc were found in significant quantities, reflecting their common occurrence in zinc processing waste. Variations across different sample areas suggest heterogeneity in the waste material, with some regions showing elevated levels of sulfur and molybdenum, potentially from sulfide minerals or industrial additives. The analysis underscores the need for targeted waste management

strategies to mitigate environmental impacts and recover valuable resources from industrial discharges.

Table 3:Comparative Elemental Composition of ALZINC Leachate Discharge Across Different Sample Areas.

Area 01			Area 02			Area 03		
Element	Weight %	atomic %	Element	Weight %	atomic %	Element	Weight %	atomic %
CK	17.77	35.88	CK	28.65	47.94	CK	4.51	11.75
OK	27.44	41.59	OK	28.13	35.34	OK	25.28	49.48
SiK	1.76	1.52	SiK	1.53	1.09	SiK	1.87	2.09
SK	1.83	1.39	SK	5.27	3.31	AlK	4.04	4.68
MoL	6.67	1.69	CaK	1.13	0.57	PbM	5.22	0.79
FeK	22.55	9.79	FeK	17.38	6.26	FeK	35.73	20.03
ZnK	21.97	8.15	ZnK	17.91	5.51	ZnK	23.35	11.18

III.1.4 Hardening of treated cuttings over time

The graph presented in Figure 5, obtained using dilatometric measurements, demonstrates a continuous improvement in the hardening of stabilized sludges over time. Sludges treated by stabilization-solidification using sodium silicate and artificial cement result in a hardening rate of 100% after 30 days, and the final residue will be more stable with very effective fixation of contaminants (Encapsulation). According to this result, as revealed by the dilatometer, the final discharge reaches a state of inertness, highlighting the success of the stabilization process in fortifying the structural integrity of the cuttings.

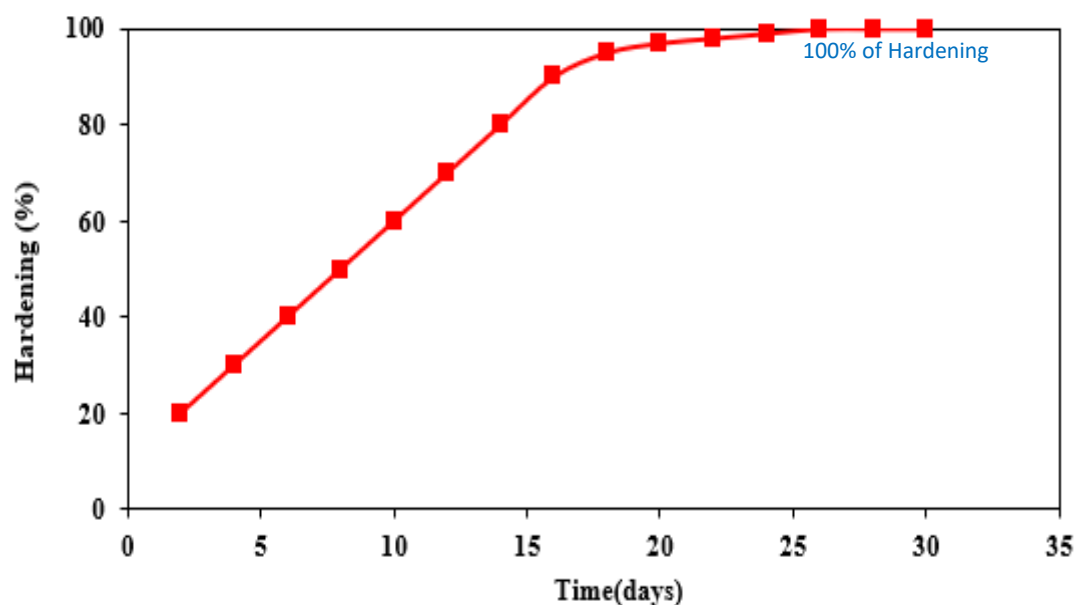


Figure 8: Curing curve of hardening of treated cuttings over time.

III.1.5 Chemical Speciation of Heavy Metals

III.1.5.1 Cadmium (Cd)

Initially, on June 20th, the Cd concentration was recorded at 5.89 mg/kg, which, following the S/S treatment by September 22nd, was reduced to 1.50 mg/kg. Similarly, a sample from October 14th showed an initial concentration of 2.09 mg/kg, which was also reduced to 1.36 mg/kg post-treatment by the same date in September. The observed reduction in cadmium (Cd) concentrations in ALZINC leachate discharges following S/S processes using Portland cement

and sodium silicates can be explained by the immobilization mechanisms of Cd within the cement matrix. The process involves the formation of insoluble hydroxides and the encapsulation of Cd particles by calcium silicate hydrate (C-S-H) gel and calcium hydroxide, which results in a highly impervious barrier around the Cd, significantly reducing its leachability.

These results indicate the effectiveness of the S/S treatment in immobilizing Cd, lowering its concentration to below the Limit Value of 2 mg/kg, which is the threshold for safe cadmium levels in treated waste. **Bin et al. [19]** reported a study on the solidification/stabilization of cadmium-contaminated soil by red mud-assisted blast furnace slag under excitation conditions, they showed that a low-carbon curing agent binder significantly enhanced the compressive strength and Cd chemical stability of the Cd-contaminated soil, thereby reducing Cd²⁺ leaching amounts and soil porosity. Same results found by **Song et al. [20]** when they used a novel binder incorporating bone meal and fly ash for sustainable stabilization/solidification of Cd and Pb in industrially heavy metal-contaminated site soils.

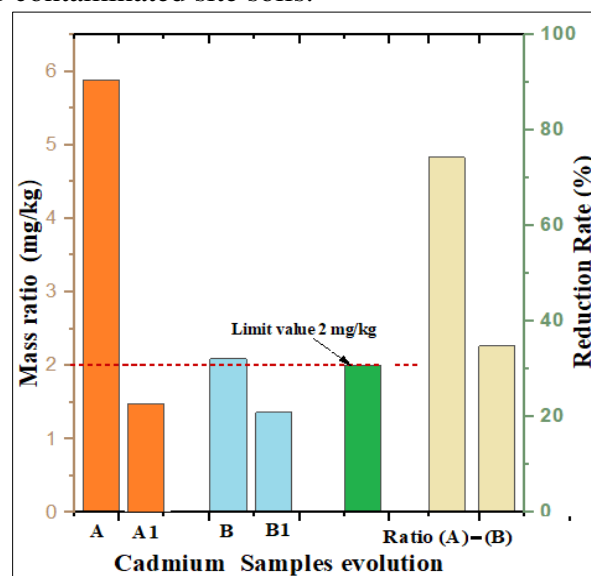


Fig. 3: Cd concentration before and after S/S processes

III.1.5.2 Nickel (Ni)

The observed reduction in Nickel (Ni) concentrations following the S/S treatment of ALZINC leachate discharges using Portland cement and sodium silicates reflects the effectiveness of this approach in immobilizing nickel contaminants. Initially, Nickel concentrations were significantly above the acceptable limit of 50 mg/kg, with values of 236.45 mg/kg and 82.45 mg/kg reported before treatment. After the S/S process, concentrations were reduced to 20.66 mg/kg and 39.15 mg/kg, respectively, both of which are below the regulatory limit. The process likely involves similar mechanisms to those for cadmium, where hydration reactions within the cement matrix and the formation of insoluble compounds significantly reduce the leachability of nickel, ensuring concentrations fall below regulatory limit values. This demonstrates the S/S process's capability to significantly lower the mobility and bioavailability of Nickel in treated wastes, thus mitigating environmental risks.

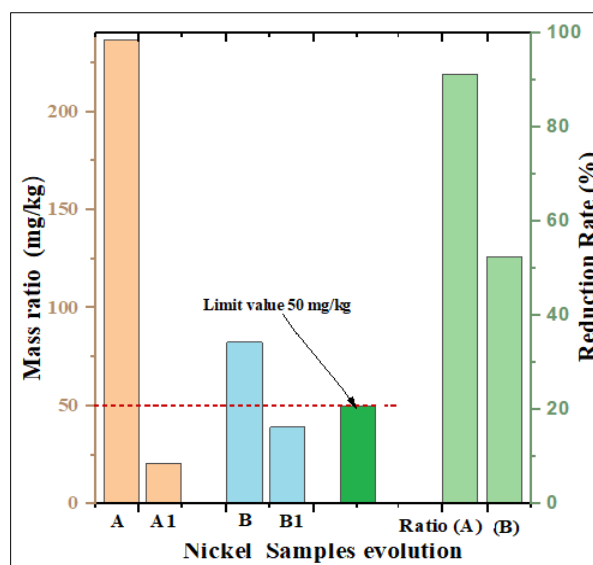


Fig. 3: Ni concentration before and after S/S processes

III.1.5.3 Chromium $Cr(VI)$ and Total Chromium

The results reveal a reduction in chromium ($Cr(VI)$) and total chromium concentrations, with $Cr(VI)$ concentrations before and after S/S showing minimal reduction in one instance and a more significant reduction in another. The total chromium concentrations showed a more substantial decrease after S/S, indicating the effectiveness of the S/S process in reducing chromium levels, albeit with variations in the effectiveness against $Cr(VI)$ specifically.

Recent studies relevant to the effectiveness of S/S treatments in reducing chromium concentrations include research on the mechanisms affecting the delayed efficiency of cement-based S/S processes and the utilization of various binders for contaminated soil treatment. For instance, a study by **Senneca et al. [21]** investigates the efficiency of a cement-based S/S treatment on chromium-contaminated soil, emphasizing the importance of understanding the main mechanisms responsible for metal immobilization and the potential decrease in process efficiency due to delayed reactions. Another pertinent study by **He et al. [22]** focuses on the evolution of freeze-thaw properties of cement-lime solidified contaminated soil, specifically addressing the treatment of hexavalent chromium contaminated soil and exploring the engineering characteristics of the solidified soil under different cycles of freezing and thawing. These studies suggest that while S/S processes, including those utilizing Portland cement and sodium silicates, can effectively reduce total chromium concentrations, the specific reduction of $Cr(VI)$ may require careful consideration of the treatment conditions and potential long-term changes in contaminant mobility and bioavailability. The research underscores the complexity of chromium stabilization and the need for tailored S/S strategies to ensure long-term immobilization and compliance with regulatory limits.

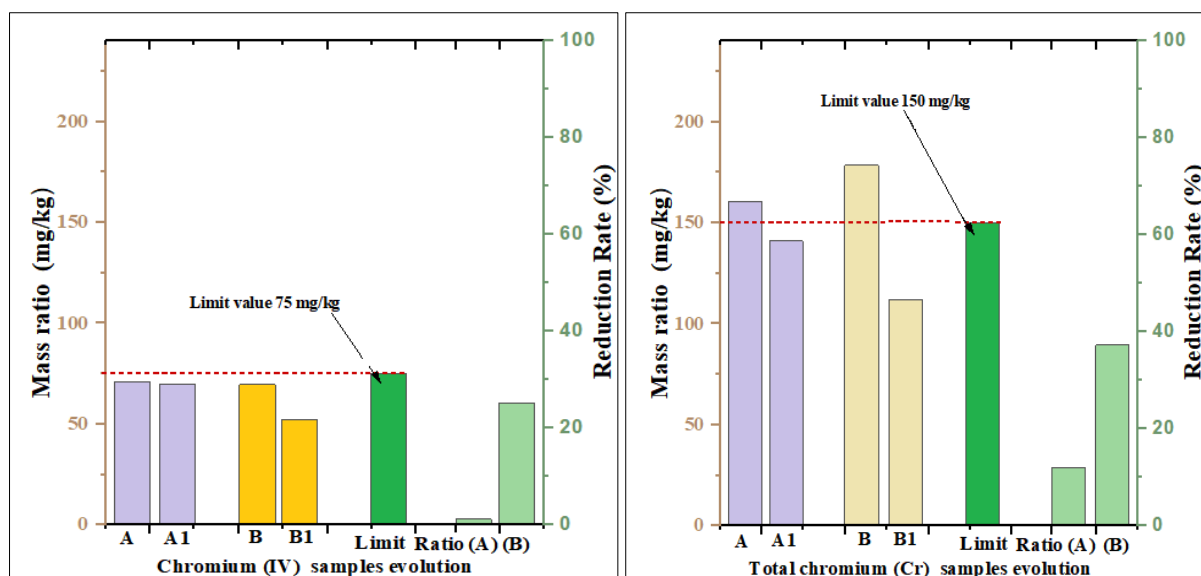


Fig. 3:Cr(VI) and Total Cr concentration before and after S/S processes

III.1.5.4 Zinc (Zn)

The S/S results show a substantial reduction in Zn concentrations, with levels significantly decreasing to below the regulatory limit value of 50 mg/kg after treatment. The initial concentration of Zinc was markedly high at 1025.69 mg/kg and was reduced to 110.65 mg/kg in the first measurement period. Although this represents a significant reduction, it's important to note that the post-treatment concentration in this instance slightly exceeded the limit value. In the second measurement period, the Zinc concentration was initially 82.45 mg/kg and was effectively reduced to 39.15 mg/kg after S/S treatment, well below the limit value. The mechanism behind the significant reduction of Zinc concentrations likely involves the immobilization of Zinc within the matrix formed by the reaction between Portland cement and sodium silicates. This process can bind heavy metals like Zinc into the structure of the solidified matrix, thereby preventing their leaching into the environment. The effectiveness of this treatment can be attributed to several factors, including the formation of insoluble Zinc compounds within the cement matrix, the physical encapsulation of contaminants, and the potential chemical stabilization provided by sodium silicate, which can enhance the overall binding capacity of the matrix. A recent work discusses the effectiveness of similar S/S methodologies in treating Zinc contamination by **Juan Dacuba et al. [23]** on the immobilization efficiencies of heavy metals using coal fly-ash/clay-based geopolymers. This study achieved immobilization efficiencies higher than 99% for Zinc, demonstrating the potential of alternative materials and methods for effective heavy metal immobilization in waste management.

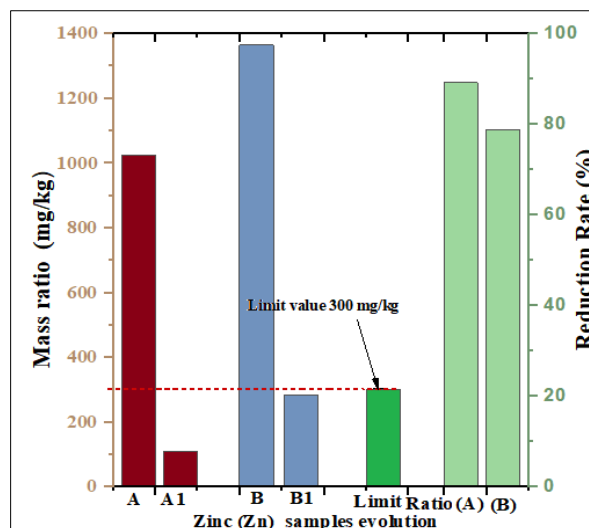


Fig. 3: Zinc(Zn) concentration before and after S/S processes

III.I.5.5 Iron (Fe)

The S/S process utilizing Portland cement and sodium silicates has demonstrated significant efficacy in reducing Iron (Fe) concentrations in ALZINC leachate discharges. The data presented shows:

- An initial Fe concentration of 1256.36 mg/kg on June 20th was reduced to 350.13 mg/kg following S/S treatment by September 22nd.
- For the October 14th measurement, the initial Fe concentration of 1459.58 mg/kg was lowered to 225.96 mg/kg after the S/S treatment.

These results indicate the S/S process's capability to significantly lower the Fe concentration in leachate discharges, with post-treatment levels for the October sample well below the regulatory limit of 350 mg/kg. The June sample's post-treatment level is precisely at the limit, suggesting the process's effectiveness across varying initial concentrations.

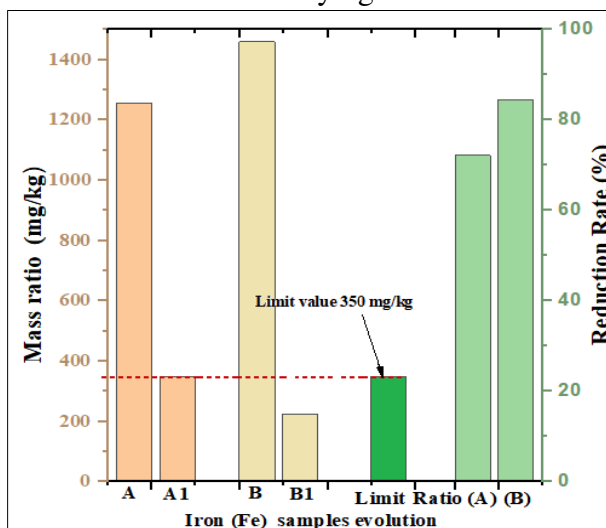


Fig. 3: Iron (Fe) concentration before and after S/S processes

III.I.5.6 Mercury

The S/S results for both samples show a considerable decrease in iron concentrations, highlighting the effectiveness of the S/S technique in immobilizing heavy metals in leachate. Initially, mercury concentrations were 6.59 mg/kg on 06/20 and 2.59 mg/kg on 10/14. After the S/S process on 09/22, the concentrations reduced to 0.56 mg/kg and 0.92 mg/kg, respectively. These results are significant as they demonstrate the process's ability to lower mercury levels

below the limit value of 1 mg/kg, thereby complying with environmental standards and reducing the potential for environmental harm.

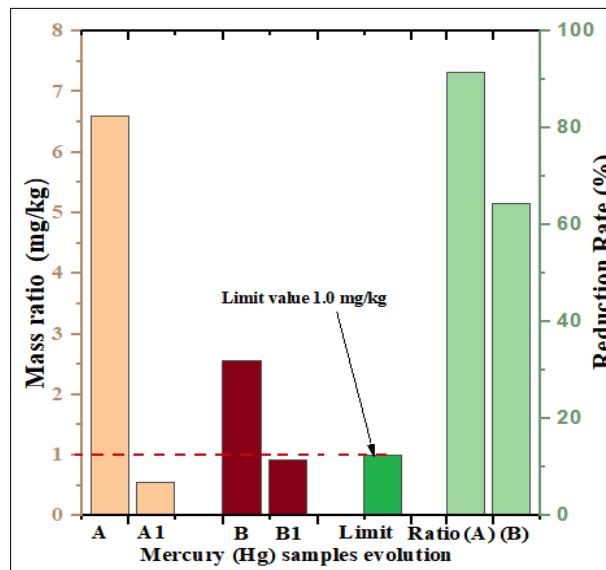


Fig. 3: Mercury (Hg) concentration before and after S/S processes

III.1.5.7 Lead (Pb)

The S/S results indicate a significant reduction in lead concentrations, demonstrating the efficacy of this method for heavy metal immobilization. Initially, lead concentrations were 396.56 mg/kg on 06/20 and 198.69 mg/kg on 10/14. Following the S/S process on 09/22, the concentrations were reduced to 70.15 mg/kg and 88.00 mg/kg, respectively. These outcomes are noteworthy as they show that the process effectively lowers lead levels below the regulatory limit of 100 mg/kg, thereby mitigating potential environmental and health risks associated with lead contamination, **Kang et al. [24]** studied the effect of Carbonation on the Leachability of Solidified/Stabilized Lead-Contaminated Expansive Soil, **Song et al.[20]** used a novel binder incorporating bone meal and fly ash for sustainable stabilization/solidification of Cd and Pb in industrially heavy metal-contaminated site soils and shows an effectiveness of Modified Portland Cement (MPC) in stabilizing soils contaminated by industrial activities, indicating its strong potential as a viable binder for on-site stabilization/solidification (S/S) processes.

This research findings can provide valuable insights into enhancing the S/S process's effectiveness for treating leachate discharges, like those from ALZINC, particularly in reducing lead concentrations to adhere to environmental standards.

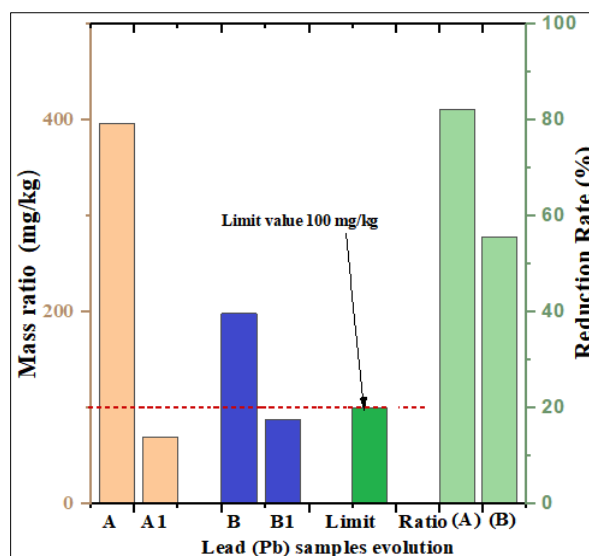


Fig. 3: Lead (Pb) concentration before and after S/S processes

III.II Comparing with other studies

Based on recent studies (2019-2021) regarding the impact reduction of heavy metals present in leachate discharges by stabilization-solidification using Portland cement and sodium silicates, the table below provides a comparative overview of various research findings. These studies explore different materials, methods, and outcomes related to the stabilization-solidification process.

Study Title	Key Findings	Ref.
Green remediation of Cd and Hg contaminated soil using humic acid modified montmorillonite (2020)	Utilization of HA-Mont for Cd and Hg contaminated soil showed significant reduction in metal concentrations and proved to be a green S/S method with long-term stability.	[25]
Comparison of reactive magnesia, quick lime, and ordinary Portland cement for stabilization/solidification (2019)	MgO, CaO, and OPC were compared for S/S of heavy metal-contaminated soils, with varying efficiencies across different heavy metals.	[26]
Calcium aluminate cement as an alternative to ordinary Portland cement (2021)	This study elucidates the mechanisms involved in the retention of heavy metals using different binders, highlighting the role of ettringite and CSH in metal immobilization.	[27]
Leachate composition of lead and cadmium ions from solidified mortar mixed with Nanosilica (2021)	Nanosilica effectively reduces the leachability of Pb and Cd ions, indicating its potential in improving S/S processes.	[28]
Stabilization/solidification of lead- and zinc-contaminated soils using MgO and CO ₂ (2019)	Zn slows MgO carbonation; Pb unaffected. MgO+CO ₂ strengthens and reduces Pb leach but equals PC in Zn soil.	[29]
Performance of chemical chelating agent stabilization and cement solidification on heavy metals in MSWI fly ash (2019)	Chelating agents and cement solidification reduce heavy metal leaching from MSWI fly ash, with dithiocarbamate showing the best performance.	[30]

These studies provide insights into various aspects of the stabilization-solidification (S/S) process, including alternative materials to Portland cement, the effectiveness of nanomaterials like Nanosilica, and the role of chelating agents in enhancing the stabilization and solidification

of heavy metals in contaminated soils and wastes. Our results further confirm that the S/S process is a highly effective method for reducing the environmental impact of heavy metals. By immobilizing heavy metals within the matrix of stabilizing agents such as Portland cement, alternative cements, or through the use of additives like nanosilica, the leachability of these contaminants is significantly reduced. This reduction in leachability directly translates to a decrease in the risk these metals pose to the environment and public health. The S/S process, therefore, serves as a critical tool in the management of contaminated sites, offering a path towards mitigating the adverse effects of heavy metals and contributing to the broader goal of environmental preservation and safety.

IV Conclusions

The stabilization/solidification (S/S) treatment of ALZINC leachate discharges using Portland cement and sodium silicates has demonstrated significant efficacy in reducing the concentrations of various heavy metals, including Cadmium (Cd), Nickel (Ni), Chromium (*Cr(VI)*), Zinc (Zn), Iron (Fe), and Lead (Pb), to levels that meet or are well below the respective regulatory limit values. These results underscore the effectiveness of the S/S process in immobilizing heavy metals, thereby mitigating their leachability and potential environmental impact.

For Cadmium and Nickel, the treatment achieved concentrations below the regulatory limits, showcasing the process's capability in handling metals known for their toxicity and mobility. The slight reduction in Chromium (*Cr(VI)*) concentrations, although modest, remained within safe limits, highlighting the challenges and potential areas for optimization in treating specific metal forms. The substantial decreases observed in the concentrations of Zinc, Iron, and Lead post-treatment not only met regulatory standards but also demonstrated the process's broad applicability and efficiency across a range of heavy metal contaminants.

The inclusion of sodium silicates in the S/S process appears to enhance the immobilization capabilities of the cement matrix, suggesting that the chemical composition and physical properties of the S/S matrix are crucial factors in the successful treatment of contaminated leachates. These findings are supported by recent research, including studies on coal fly-ash/clay-based geopolymers, which offer insights into alternative materials and methods for heavy metal immobilization, highlighting ongoing advancements in the field.

In conclusion, the application of Portland cement and sodium silicates in the S/S treatment of ALZINC leachate discharges presents a viable and effective method for the immobilization of a wide range of heavy metals, ensuring environmental compliance and reducing the risk of metal contamination.

Declaration of competing interest

We declare that we have no financial and personal relationships with other people or organizations that can inappropriately influence our work; there is no professional or other personal interest of any nature or kind in any product, service and/or company that could be construed as influencing the position presented in, or the review of, the manuscript entitled.

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