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Stabilization of metal and metalloids from contaminated soils using magnesia-based tundish deskulling waste from continuous steel casting

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HIGHLIGHTS

- Tundish improves heavy metals retention conditions during leaching processes.
- Magnesium oxides makes tundish viable for stabilization of heavy metals in soils.
- Tundish and common stabilizer had similar effect on heavy metal retention in soil.
- Tundish offers environmental and economic advantages compared to current options.
- Use of tundish promotes the circular economy through industrial waste valorization.

G R A P H I C A L A B S T R A C T



tundish deskulling waste grinding

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ABSTRACT

This study presents a groundbreaking exploration into the potential use of refractory tundish deskulling waste (TUN), a magnesium oxide-based by-product from continuous steel casting, as a stabilizing agent for remediating metal and metalloids contaminated soils. Up-flow column horizontal percolation tests were conducted to measure the concentrations of metals and metalloids, pH, and electrical conductivity (EC) in the leachates of two different combinations of contaminated soil and stabilizer (95–5 wt% and 90–10 wt%). The effectiveness of TUN as a soil-stabilizing agent for contaminated soils with metals and metalloids was evaluated by comparing its leachates with those obtained from a sample of a well-established low-grade magnesium oxide (LG-MgO) by-product, which underwent the same testing procedure.

The findings revealed a significant correlation between the mobility of the examined metals and metalloids, and the water-soluble or acid phase of the contaminated soil, primarily governed by precipitation-solution reactions. While the stabilizing impact on non-pH-dependent metals, particularly redox-sensitive oxyanions, was less pronounced, both MgO-based stabilizers exhibited a favourable influence on soil pH-dependent metals and metalloids. They achieved this by establishing an optimal pH range of approximately 9.0–10.5, wherein the

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solubility of metal (hydr)oxides is minimized. Notably, metals like Zn and Cu, which have high leaching potential, experienced a remarkable reduction in leaching - Zn by over 99% and Cu by around 97% - regardless of the stabilizer content.

In a broader context, this research champions the principles of the circular economy by offering a technical remedy for treating soils contaminated with pH-dependent metals and metalloids. The proposed solution harnesses industrial waste - currently relegated to landfills - as a resource, aligning with sustainable practices and environmental responsibility.

1. Introduction

Soil is a complex and variable natural resource whose characteristics allow the development of ecosystems (Office of Communications FAO, 2015). This resource presents ecological functions such as biomass production, habitat, and genetic reserve for fauna and flora. In addition, soil allows environmental interaction such as storage, filtering, and transformation of matter, and energy reactions. Soil also promotes functions linked to human activity as a physical medium where social and economic activities take place and as a source of raw materials and cultural heritage (Directorate-General for Environment EU, 2021).

It has long been understood that the formation cycle of soil is extremely slow, which is why soils are non-renewable natural resources in human' terms. Therefore, immediate actions need to be taken to ensure that soils are cleaned and preserved (Directorate-General for Environment EU, 2021; Office of Communications FAO, 2023).

High rates of production in the industrial field release into the environment huge amounts of polluting compounds that affect the atmosphere, water, and soil (Hu et al., 2013). Considering that the measure of land degradation involves the decline or disruption of services offered by land ecosystems, such as the overall productivity of primary resources, satellite imagery data has revealed the presence of land degradation hotspots covering approximately 29% of the Earth's surface (UN, 2019). In this context, among the different pollutants that have been found in soils, polycyclic hydrocarbons (PHCs) and heavy metals (HMs) represent the greatest current environmental threat to this resource (Haque et al., 2022). Several studies have been conducted in the USA territory, where it has been reported that around 40% of contaminated soils contain high concentrations of organic pollutants and heavy metals (Ali et al., 2022; Sandrin et al., 2000).

Anthropogenic activities such as mining, the steel industry, waste incineration (including sludge treatment management, acid discharges and control of ashes), as well as poor management of electronic waste (e-Waste), introduce uncontrolled metals and metalloids into the soil matrix (Cormier et al., 2006; Yang et al., 2022). Furthermore, metals and metalloids are typically considered contaminants that can only be effectively addressed by extrinsic processes such as physicochemical or biological methods (Zhu et al., 2021).

Due to the persistent nature of these contaminants, metals and metalloids accumulate on the soil surface, impacting ecosystem dynamics. Additionally, they enter the food chain through plant roots, ultimately posing a potential risk to human health (Chellaiah, 2018; Haque et al., 2022; Puga et al., 2006). Consequently, it has been demonstrated that certain metals, including arsenic (As), cadmium (Cd), chromium (Cr), copper (Cu), lead (Pb), zinc (Zn), mercury (Hg), and nickel (Ni), are the most prevalent contaminants in soils. Often, their concentrations surpass the regulatory limits set for living organisms (Haque et al., 2022).

Soils contaminated with high concentrations of HMs are remediated using in-situ or ex-situ processes, such as bioremediation, physicochemical, electrical, or thermal treatments (Liu et al., 2018). Techniques like the utilization of biochar or stabilization/solidification treatment through the addition of alkaline reagents are effective in reducing HMs bioavailability and leaching in the soil (Zhang et al., 2013). Alkaline reactants like Lime (CaO) and ordinary Portland cement are commonly employed in stabilizing/solidifying contaminated soils due to their ease

of use and cost-effectiveness. In these cases, the pH level stabilizes around 12.2, controlled by the solubility equilibrium of portlandite (Ca (OH)₂). This equilibrium facilitates the precipitation and subsequent redissolution of pH-dependent metals, such as Pb or Zn. However, most pH-dependent metals and metalloids exhibit their lowest solubility within the pH range of 9.0–11.0, as determined by their respective Ksp values (Lide, 2003).

Thus, a potential strategy for stabilizing soil contaminated with pH-dependent metals involves employing MgO as a stabilizing agent (Li and Yi, 2019), given its solubility equilibrium within the optimal pH range (9.0–11.0). The use of pure magnesium oxides can be expensive, but low-grade MgO by-products (LG-MgO) offer a cost-effective alternative for soil remediation (García et al., 2004). LG-MgO is a by-product resulting from the calcination of natural magnesite (MgCO₃), collected from the kiln's air pollution system during the thermal process. Acting as a source of magnesium oxide, LG-MgO serves as a low solubility buffering agent in the pH range of 9.0–11.0, effectively stabilizing contaminated soils with minimal environmental impact (Carter et al., 2009; García et al., 2004; González-Núñez et al., 2012). Thanks to its low solubility and reactivity, LG-MgO provides a durable alkali reservoir for stabilization, avoiding pH alterations (Alloway, 2013; Wang et al., 2015).

The effectiveness of LG-MgO in stabilizing pH-dependent metals and metalloids for soil remediation has been demonstrated, offering a solution that mitigates the redissolution often associated with lime usage (García et al., 2004; Giro-Paloma et al., 2020). Additionally, the use of LG-MgO as a stabilizing agent aligns with circular economy principles, promoting the sustainable treatment of soils and the reutilization of industrial by-products (Huete-Hernández et al., 2021).

Regarding the LG-MgO industrial by-products, tundish deskulling waste (TUN) is a depleted refractory residue from the continuous steel casting process, characterized by its high MgO content. TUN constitutes the refractory mass coating layer of tundish directly in contact with the molten steel. This layer gradually wears down over time due to the casting process. Because of TUN fatigue, this refractory coating is periodically replaced for safety and to maintain production quality. Given the nature of the cast steel production process, substituting MgO refractories is challenging, resulting in the unavoidable generation of TUN waste. Moreover, worldwide, an estimated 5–7 million tons of TUN are generated annually and disposed of in landfills (Muñoz et al., 2020; Worldsteel, 2021). TUN contains significant impurities, posing challenges for its separation and recycling. However, the high MgO content of TUN, coupled with its widespread availability, makes it a potential alternative for stabilizing hazardous materials in contaminated soils.

The aim of this study is to assess the viability of utilizing TUN for the stabilization treatment of soils contaminated with metals and metalloids. To the best of the authors' knowledge, this study represents the inaugural lab-scale research into the utilization of magnesia-based waste from tundish deskulling in continuous steel casting (TUN) as a stabilizing agent. This research introduces an innovative, sustainable approach to soil stabilization in the presence of heavy metal contamination. By harnessing a highly abundant secondary resource, it aligns seamlessly with the principles of a circular economy, displaying a promising avenue for environmentally conscious solutions. The effectiveness of TUN, as a pH-dependent metal-contaminated soil-stabilizing agent, has been compared with that of LG-MgO, which has previously

demonstrated its efficacy. The possible reutilization of this residue for soil remediation was evaluated by measuring the concentrations of leached metals and metalloids, following the protocol outlined in the European technical CEN/TS 16637-3 specifications.

2. Materials and methods

2.1. Contaminated soil

The contaminated soil sample was sourced from an environmental sector company entrusted with the soil remediation of a former industrial site in the field of fertilizers. The site, spanning $36,000~\text{m}^2$, is situated along the coast adjacent to the metropolitan area of Barcelona, Spain. Historically, the industrial site was involved in chemical operations tied to the production of superphosphates, which entailed the use of sulfates and phosphates. This production process revolved around the reaction between finely ground phosphoric rock and concentrated sulfuric acid (65–75%).

In this method, sulfuric acid was primarily derived from sulfurbearing minerals, particularly pyrite (Habashi, 2006). The production sequence began with the extraction of sulfur dioxide through roasting, followed by its subsequent oxidation into sulfur trioxide using a catalytic process involving vanadium peroxide. The combustion of sulfur-bearing minerals led to the formation of considerable amounts of flue powder, which were subsequently separated from the gas stream. While pyrite roasting powder is primarily comprised of iron, it also contains notable quantities of copper, zinc, and lead, as well as traces of various heavy metals and metalloids (Habashi, 2006).

The roasting process generates two minor streams of pollutants: (i) ashes collected from kiln precipitators and (ii) sludge produced during acid gas washing. Additionally, ashes contain significant levels of arsenic, antimony, and selenium, all present in the form of trioxide (García et al., 2004). Conversely, the sludge is predominantly composed of copper sulfate, with smaller proportions of barium and tin sulfates (García et al., 2004).

For decades, the conventional practice among fertilizer companies involved the disposal of residues from the pyrite roasting process onto the soil surrounding their facilities. Over time, the extended exposure of these waste materials to the environment resulted in soil and groundwater contamination through leaching and percolation processes, respectively. The leachates produced under varying climatic conditions led to a significant reduction in pH levels, reaching acidic ranges up to 1.6 (García et al., 2004). This is evidenced by the heightened concentrations of metals and metalloids released into the environment through acid dissolution.

The soil under investigation primarily consists of heterogeneous sand and gravel. The soil matrix is predominantly composed of silica, with minimal silt content and the samples were collected by the company responsible for soil remediation (DAC Enviro, 2023; García et al., 2004). They conducted selective excavations in the industrial site area where the pyrite roasting residues had been deposited. All samples were obtained from the upper layer (0–100 cm) of the contaminated soil. After collection, 2.5 kg subsamples were taken and stored in high-resistance plastic bags. The pH of the soil samples used in the experiment was approximately 4.0, significantly lower compared to the pH values measured in nearby soils within the impact zone. The pH values of the surrounding soils were close to 6.0, indicating a substantial difference between the contaminated soil samples and the less affected soils in the vicinity.

The contaminated soil subsamples were meticulously mixed and then manually quartered. Once homogenized, subsamples were subjected to an oven at $105\,^{\circ}\text{C}$ for 24 h to determine their moisture content and particle size distribution implementing the methodology prescribed by the Spanish technical standards UNE 103-30093 and UNE 103101:1995, respectively (refer to Table A.1; Appendix A). Furthermore, to provide evidence of metal and metalloid contamination in the

industrial area's soil, elemental analysis of the homogenized samples was performed using the x-ray diffraction technique through a Panalytical Axios PW 4400/40 sequential wavelength dispersive x-ray fluorescence spectrophotometer (WD-XRF). Major, minor, and trace elements are summarized in Table 1, as well as the standard deviation (σ) for major and minor elements.

The contaminated soil displays notable concentrations of various elements, encompassing both major and trace elements. Notably, the predominant element is iron, attributed to its presence in pyrite. The contaminated soil also exhibits a high content of As, Ba, Cu, Pb, Sn, and Zn.

The different mineralogical phases within the contaminated soil were identified through X-ray diffraction (XRD) analysis. Utilizing a Bragg–Brentano PANalytical X'Pert PRO MPD alpha 1 powder diffractometer device with CuK α radiation, the analysis revealed several mineral phases in the contaminated soil (refer to Fig. A.1; Appendix A). These phases include various ferric oxides such as hematite (Fe₂O₃; PDF #01-080-2377) and ochre (Fe₂O₃; PDF #00-033-0664), as well as quartz (SiO₂; PDF #01-083-2465) and lead silicate (Pb₃SiO₅; PDF #00-029-0783). The presence of iron oxides, such as hematite and ochre, is consistent with the residues generated during pyrite roasting activities, aligning with historical industrial operations in the mentioned zone.

The elemental characterization (see Table 1) of the contaminated soil reveals a substantial abundance of iron oxides, accounting for 85.73 wt %. It is worth noting that the total iron content (Fe₂O₃) t typically falls within the range of 2–6 wt% in soils of the continental crust under normal conditions (Acevedo et al., 2004).

To assess the potential release of metals and metalloids, the leaching test outlined in EN 12457–4, part of the European Standard for granular waste and sludges, was conducted (European Committee for Standarization, 2002). Additionally, to validate the soil contamination in the industrial area, a sample of nearby soil unaffected by industrial chemical activities underwent the same leaching test. To determine the content of metal (loid)s (As, Ba, Cd, Cr, Cu, Hg, Mo, Ni, Pb, Sb, Se, and Zn) in the eluates, the leachate samples were analyzed using inductively coupled plasma mass spectrometry (ICP-MS) with a PerkinElmer ELAN 6000 device. The results of the leaching test for both soils are presented in Table 2.

The EN-12457 standard is commonly employed to classify solid wastes, based on the criteria and procedures for waste acceptance in landfills described in the European Landfill Directive (Council of the European Union and 2003/33/EC, 2003). Table 2 provides a summary of the limits defined in the waste acceptance criteria for landfills. It classifies waste into three levels based on its leaching potential. Inert solid waste is characterized by having all the analyzed parameters below the values specified in the first column of Table 2. Non-hazardous waste must demonstrate that all the analyzed parameters are lower than those described in the second column. Hazardous waste, conversely, necessitates concentrations below the values provided in the third column of the table.

A pronounced disparity in the release of heavy metals and metalloids is evident between soil impacted by industrial activity (contaminated soil) and its adjacent unaffected counterpart, as illustrated in Table 2. Metals released from the unaffected soil remained below the threshold for classification as inert waste, while the contaminated soil exceeded concentration limits for some metal (loid)s. The leaching of specific metal (loid)s surpassed the threshold for inert waste and should be categorized as non-hazardous waste (e.g., Cu and Pb) or hazardous waste (e.g., Zn). It is worth noting that the pH levels of the contaminated and unaffected soil samples differ significantly due to the oxidation of pyritic sulfides and the leaching of sulfuric acid from waste deposition onto the contaminated soil.

The unexpectedly low leaching of certain trace elements, such as As, Ba, Cu, Pb, or Zn, can be attributed to their predominant presence in less soluble mineral phases rather than their initial concentration. Previous research has demonstrated that many heavy metals exist in highly

Table 1
Major, minor, and trace element composition of the contaminated soil.

	Major and n	ninor elements (w	t.%)							
	Fe ₂ O ₃ ^a	MnO	TiO_2	CaO	K_2O	P_2O_5	SiO_2	Al_2O_3	MgO	Na ₂ O
	85.729	0.003	0.039	0.211	0.338	0.134	11.447	1.061	0.169	0.454
$\sigma(\pm)$	0.164	0.001	0.004	0.015	0.029	0.068	0.271	0.001	0.060	0.099
	Trace eleme	ents (mg·kg ⁻¹)			· <u></u>		·			
	As	Ва	Ce	Co	Cr	Cu	La	Мо	Ni	Pb
	247	2161	0.01	23.8	41.1	1257	6.25	20.3	9.5	4117
	Rb	Sc	Sn	Sr	Th	v	W	Y	Zn	Zr
	19.2	3.75	272	33.5	8.37	36	77.4	13.5	810	46.3

^a The content of iron is expressed as total iron oxide, calculated by stoichiometry from the iron signal, as usual, is reported for results from XRF spectrometry analysis.

Table 2
Leaching (EN 12457–4) chemical composition of contaminated and unaffected soils. Limit values established by the European landfill directive to classify solid waste for its admission to landfills.

Parameter	Contaminated soil	σ (±)	Unaffected soil	σ (\pm)	Limit value	es	
					Inert	Non-Hazardous	Hazardous
pН	4.05	0.02	5.90	0.02	n.r ^a	n.r ^a	n.r ^a
As (mg·kg ⁻¹)	< 0.025	0.002	0.021	0.003	0.5	2.0	25
Ba (mg·kg ⁻¹)	0.268	0.007	0.187	0.001	20	100	300
Cd $(mg \cdot kg^{-1})$	0.155	0.013	0.015	0.001	0.04	1.0	5
Cr (mg⋅kg ⁻¹)	< 0.025	0.001	< 0.080	0.001	0.5	10	70
Cu (mg·kg ⁻¹)	11.595	1.047	0.065	0.006	2	50	100
Hg (mg·kg ⁻¹)	< 0.005	0.001	< 0.005	0.002	0.01	0.2	2
Mo (mg⋅kg ⁻¹)	< 0.025	0.003	< 0.01	0.001	0.5	10	30
Ni (mg·kg ⁻¹)	0.138	0.016	< 0.077	0.005	0.4	10	40
Pb (mg⋅kg ⁻¹)	0.479	0.171	0.006	0.001	0.5	10	50
Sb (mg·kg ⁻¹)	0.010	0.009	0.021	0.007	0.06	0.7	5
Se (mg L ⁻¹)	0.056	0.022	< 0.040	0.001	0.1	0.5	7
Zn (mg·kg ⁻¹)	55.742	0.552	0.774	0.009	4	50	200

a Not required.

insoluble forms in the contaminated soil, primarily associated with neoformed silica phases or high-temperature calcined iron oxides (García et al., 2004). For example, it's common for As to be incorporated into the structure of sintered iron oxides, which reduces its solubility (Chimenos et al., 2012; García et al., 2004). Similarly, the presence of sulfates resulting from the oxidation of pyritic sulfides likely contributes to the formation of low-solubility barium sulfates in the case of Ba.

2.2. MgO-based stabilizer reactants

Two secondary resources from the industrial sector, both characterized by a high magnesium oxide content, will serve as stabilizing reagents for remediating contaminated soil. In this research, low-grade magnesium oxide (LG-MgO) obtained from magnesite calcination will be used as a reference product, based on its proven effectiveness as a stabilizer in soil remediation in previous studies (del Valle-Zermeño et al., 2015; García et al., 2004; Giro-Paloma et al., 2020). On the other hand, the material of study will be TUN, a by-product from the cast steel industry, chosen for its high magnesium oxide content and the need for valorization routes.

2.2.1. Low-grade magnesium oxide (LG-MgO)

The LG-MgO utilized in this study was supplied by Magnesitas Navarras, S.A. (Navarra, Spain). This LG-MgO by-product was obtained from fabric filters integrated into the exhaust gas pollution control system. These filters capture fine particles emitted during the calcination process of natural magnesite in a rotary kiln, which is used to produce commercial MgO products. These products find applications in the agricultural and livestock sectors, as well as the steelmaking industry, where they are used in the formulation of refractory materials.

The major and minor elemental composition of LG-MgO was analyzed using X-ray fluorescence (XRF). Additionally, the particle size

distribution (PSD) was determined using a Beckman Coulter LS 13320 particle size analyzer, while the specific surface area was measured by the BET (Brunauer, Emmett, and Teller) method, conducted with a Micromeritics Tristar 3000 instrument. The overall buffering capacity against acidification of LG-MgO was evaluated using the acid neutralization capacity (ANC) method, as per the European standard CEN

Table 3Chemical characterization of LG-MgO and TUN, particle size distribution (PSD), and other physical and chemical parameters.

Compound (wt. %)	LG-MgO	σ (±)	TUN	σ (±)
MgO	64.710	0.185	62.500	0.187
CaO	4.870	0.005	9.500	0.065
SiO_2	2.200	0.005	10.300	0.083
Fe ₂ O ₃	2.240	0.030	6.600	0.056
Al_2O_3	0.390	0.020	5.100	0.019
K ₂ O	0.290	0.009	-	_
MnO	0.150	0.013	-	_
P_2O_5	0.080	0.010	0.100	0.001
TiO ₂	0.020	0.005	-	_
Na ₂ O	0.060	0.003	0.300	0.002
SO_3	4.090	0.054	0.300	0.001
Cr ₂ O ₃	_	_	0.200	0.002
LOI ^a	16.33	0.86	2.600	0.24
		σ (<u>±</u>)		σ (±)
d ₁₀ ^b (μm)	5.29	0.81	0.89	1.51
d ₅₀ ^b (μm)	22.67	4.66	16.92	1.62
d ₉₀ ^b (μm)	58.15	1.75	92.83	2.04
Specific surface area (m2·g−1)	12.777	(±0.094)	2.874	(±0.015)
ANC ^c (mol H ₃ O ⁺ ·kg by-product)	28.670	(±0.330)	23.780	(±1.181)

^a Loss on ignition at 1050 °C.

^b Accumulated fraction lower than the particle size.

^c Acid neutralization capacity (CEN 14997).

14997. The results of the characterization of LG-MgO are presented in Table 3.

Magnesium oxide constitutes the predominant element in LG-MgO, accounting for 64.71 wt% of its composition. It is followed by sulfur (4.09 wt% as SO₃) and calcium (4.87 wt% as CaO). The presence of sulfur can be attributed to the use of petroleum coke as a fuel source during the MgO production process in the rotary kiln (Formosa et al., 2011), while the calcium content mainly originates from the dolomite and calcite present in the natural feedstock. The high loss of ignition determined at 1050 °C (16.33 wt%) can be ascribed to the presence of magnesium and/or calcium carbonates in the LG-MgO. The primary crystalline phase identified in LG-MgO through XRD analysis was periclase (MgO, PDF #01-078-0430). Major mineral phases include brucite (Mg (OH)₂, PDF #01-083-0114), dolomite (MgCa (CO₃)₂, PDF #01-083-1766), magnesite (MgCO₃, PDF #01-071-1534), calcite (CaCO3, PDF #01-072-1214), anhydrite (CaSO4, PDF #01-072-0503), and calcium oxide (CaO, PDF #01-077-2376). Minor phases detected encompass fluorite, quartz, and certain silicates.

PSD analysis of LG-MgO revealed that most particles had diameters below 60 μm . Remarkably, despite undergoing a high-temperature thermal process, LG-MgO exhibited a substantial specific surface area of 12.8 $m^2\ g^{-1}$. Additionally, the product demonstrated a significant acid neutralization capacity (ANC), primarily influenced by the equilibrium solubility of Mg (OH)2, as reported by del Valle-Zermeño et al. (2015).

Both LG-MgO and TUN underwent the leaching test outlined in EN 12457–4 of the European Standard for granular waste and sludges (European Committee for Standardization, 2002). The leachates obtained were subjected to ICP-MS analysis to determine the content of metals and metalloids in the eluates (refer to Table A.2; Appendix A). The results indicated that all metal and metalloid concentrations fell below the limits specified for inert waste classification (refer to Table 2). Furthermore, the determined pH values in the LG-MgO and TUN leachates (10.69 and 11.96, respectively) confirm that the alkaline pH levels observed in the leachates are attributable to the Mg(OH)₂ content in the stabilizers.

2.2.2. MgO-based tundish deskulling waste (TUN)

In the continuous casting process, a tundish, which is refractory-lined, serves as an intermediate vessel for transferring liquid steel from a steel-teeming ladle to the mould. Positioned above the mould, the tundish plays a crucial role in regulating the steel feed. Notably, the tundish's refractory lining accounts for the highest consumption of refractories in the steelmaking process, representing 42% of the total (Madias, 2010).

Tundish refractory linings can be categorized based on their application mode into wet and dry systems. Wet systems are employed in approximately 70% of steel plants worldwide and utilize gunning or sprayable materials. Conversely, dry systems employ a resinous bond activated at low temperatures (García-Zubiri et al., 2011). In dry systems, a dry powder is introduced into the gap between the tundish's permanent lining and the former. While the dry system allows for easy deskulling of the lining, it has lower insulation properties due to its higher density, necessitating more frequent renewal.

Indeed, the refractory lining of a tundish has a finite lifespan, determined by factors such as the quality of the lining materials and the characteristics of the tundish slag. As a result, a significant quantity of waste, referred to as tundish deskulling (TUN), is generated during the process.

The TUN sample used in this study was supplied by Magnesitas Navarras, S.A. (Navarra, Spain), a company that provides MgO-based refractory masses to a steel mill in Basauri (Bizkaia, Spain), where the sample originated. This steel mill has an annual steel production capacity of approximately 700 kt and consumes roughly 2.7 kt of MgO-based tundish masses. After collection, the sample underwent a series of processes aimed at achieving homogenization and a particle size

suitable for use as a stabilizing agent. These processes included sieving, demagnetization, crushing (particle size <3 mm), and grinding (particle size distribution <100 μ m) (refer to Fig. A.2; Appendix A).

TUN is also characterized by a high MgO content (62.5 wt%) (refer to Table 3), making it a low-grade magnesium oxide source. In comparison to LG-MgO, TUN exhibits higher concentrations of calcium, silicon, iron, and aluminium. Elevated calcium levels can be attributed to the presence of dolomite in the refractory mass formulation, as well as the diffusion of calcium from secondary ladle slags. The silicon content is attributed mainly to its occurrence in raw materials and, notably, to the interactions of refractory materials with silica-based slag during the steelmaking process. The inclusion of aluminium in the refractory mass formulation explains the higher aluminium content. Furthermore, the presence of iron is primarily associated with the diffusion of iron from molten steel in contact with the refractory material (Siadati and Monshi, 2009).

Despite having a lower d50 value than LG-MgO, TUN has a lower specific surface area (refer to Table 3). This characteristic can be attributed to its composition of high-temperature sintered materials and its higher densification. Consequently, despite its higher alkali oxide content and pH (refer to Table A.2; Appendix A), TUN exhibits a lower acid neutralization capacity (ANC) than LG-MgO (refer to Table 3).

Diffraction patterns reveal periclase (MgO, PDF #045–0946) as the main crystalline phase in TUN. Minor phases include corundum (Al $_2$ O $_3$, PDF #046–1212), brucite (Mg(OH) $_2$, PDF #044–1482), calcite (CaCO $_3$, PDF #005–0586), forsterite (Mg $_1$.8Fe $_0$.2(SiO $_4$), PDF #079–2184), merwinite (Ca $_3$ Mg(SiO $_4$) $_2$, PDF #035–0591), monticellite (Ca $_3$ Mg(SiO $_4$) $_2$, PDF #035–0590), potassium aluminum silicate (KAlSi $_2$ O $_6$, PDF #031–0967), aluminum iron oxide (AlFeO $_3$, PDF #030–0024) and gehlenite (Ca $_2$ Al $_2$ SiO $_7$, PDF #035–0755).

Regarding the potential release of metals and metalloids, TUN exhibited higher leaching of Se and Pb compared to LG-MgO (see Table A.2; Appendix A). Although the Pb content remains below the threshold for inert materials, the concentration of Se exceeds the limits specified for non-hazardous (refer to Table 2). It is likely that both metals have diffused from the molten steel.

2.3. Experimental procedure

To evaluate the effectiveness of TUN as a stabilizing agent for contaminated soils, two leaching tests were carried out. Firstly, a batch granular leaching test (EN-12457) was conducted. Secondly, a horizontal up-flow percolation test (CEN/TS 16637–3) was performed to simulate water percolating through stabilized soil, providing additional insights into potential leaching behaviour.

2.3.1. Granular batch leaching test (EN-12457-4)

In the batch experiments, the EN-12457-4 leaching test was conducted using varying proportions of LG-MgO and TUN (5 wt%, 10 wt%, 15 wt%, and 20 wt% on a dry basis) to stabilize the contaminated soil, aiming to identify the most effective percentages of the stabilizing agent.

The contaminated soil was initially homogenized and then quartered (1/16), resulting in different sub-samples for conducting various leaching tests. The granular batch leaching tests involved the extraction of water-soluble substances that are released through continuous exposure to water. These tests were performed on sub-samples with particle sizes smaller than 10 mm, allowing for the prediction of potential metals and metalloids release.

To carry out the granular leaching tests, duplicate closed polyethylene reaction vessels with a capacity of 0.5 L were utilized. The samples underwent continuous stirring at a rate of 5–10 rpm at room temperature while maintaining a liquid-to-solid (L/S) ratio of $10\,L\,kg^{-1}.$ After 24 h of mixing, the suspensions were filtered using 0.45 μm nitrocellulose filters to obtain the leachates. These duplicate leachates were then analyzed using ICP-MS to determine the concentrations of metals and metalloids present in the eluates, including As, Ba, Cd, Cr,

Cu, Hg, Mo, Ni, Pb, Sb, Se, and Zn.

2.3.2. Horizontal up-flow column percolation test (CEN/TS 16637–3)

The effectiveness of different proportions of soil and stabilizer was further assessed over an extended duration using the horizontal up-flow percolation test as outlined in the European Committee for Standardization CEN/TS 16637–3. This experiment involved the use of five methacrylate (PMMA) columns, each with a diameter of 50 mm and a height of 340 mm (refer to Fig. A.3 in Appendix A). In each column, 1.0 kg of sample material was added.

Cotton was placed on top of the columns to prevent the passage of particles from the leachate, ensuring a consistent soil matrix throughout the experiment. One column was filled solely with contaminated soil, serving as a reference to assess the impact of water on soil washing. The remaining columns were filled with mixtures of soil and stabilizer (either TUN or LG-MgO) in varying proportions based on the best-performing ratios determined in the batch leaching test.

The column test was conducted for a period of 20 days at a flow rate of 20 mL $h^{-1}.$ At specific cumulative liquid-to-solid ratios of 0.1, 0.2, 0.5, 1.0, 2.0, 5.0, and $10.0\,L\,kg^{-1},$ seven leachate samples were collected from each column. These leachates were then filtered through nitrocellulose filters with a pore size of 0.45 μm and subsequently analyzed using ICP-MS to quantify the concentration of metals and metalloids present in the eluates.

3. Results and discussion

3.1. Granular leaching test

The contaminated soil exhibited a moisture content of 10.30 wt%, an acidic pH close to 4.05, and grain sizes where more than 51% of the sample had diameters exceeding 1.5 mm (as detailed in Table A.1 in Appendix A). The granular batch leaching test conducted on the contaminated soil revealed elevated concentrations of Cu, Pb, and Zn. Based on the criteria outlined in the European Landfill Directive, the contaminated soil is categorized as hazardous waste primarily due to the concentration of Zn detected in the leachate (as indicated in Table 2).

In contrast, the results obtained from the granular batch leaching test demonstrated that both stabilizing agents (LG-MgO and TUN) had low concentrations of metals and metalloids (refer to Table A.2 in Appendix A). Despite both stabilizers originating from industrial sources, they can be classified as non-hazardous solids according to the European Landfill Directive (Council of the European Union and 2003/33/EC, 2003). Consequently, the concentrations of metals and metalloids observed during the leaching experiments are primarily attributed to the release of these elements from the contaminated soil.

The comparison between the levels of metals and metalloids leached from the contaminated soil and those from the unaffected soil in the surrounding area, as presented in Table 2, revealed significantly higher concentrations of metals such as Cd, Cu, Pb, and Zn, exceeding them by at least 10 times. Consequently, these metals were considered critical factors in this study.

Table 4 provides the concentrations of metals and metalloids in the leachates obtained from the granular leaching tests using various soil-stabilizer proportions. These results offer valuable insights into the leaching behaviour of these contaminants and the influence of MgO-based stabilizer agents on their release.

The batch leaching test results highlighted the substantial impact of the stabilizers on the soil's pH. Even minor additions of either stabilizing agent (e.g., 2.5 wt%) increased the pH of the stabilized soil above 10.5. In general, for equivalent percentages of stabilizing agents, the pH of the soil stabilized with TUN was slightly higher than that of the soil stabilized with LG-MgO. However, this pH never exceeded 11.3, primarily governed by the solubility equilibrium of Mg (OH)₂. This observation was consistent with the application of higher quantities of both TUN and LG-MgO, ranging from 10 to 20 wt%, which consistently maintained the

Concentration of metals and metalloids in the leachate from the remediated soil, in accordance with European Standard EN 12457-4.

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	Contaminated soil	م (∓)	TUN 2.5 wt%	و (共)	TUN 5.0 wt%	α (‡)	TUN 10.0 wt %	α (+)	TUN 20.0 wt %	α (‡)	LG- MgO 2.5 wt%	α (‡)	LG- MgO 5.0 wt%	σ(±)	LG-MgO 10.0 wt	σ (±)	LG-MgO 20.0 wt %	α (∓)	
$As (mg kg^{-1})$	<0.025	0.003	<0.030	0.002	0.030	0.002	0.040	0.006	0.060	0.009	<0.030	0.002	<0.030	0.002	<0.030	0.001	<0.030	0.006	
2d (mg kg ⁻¹)	0.155	0.013	< 0.010	0.001	<0.010	0.003	<0.010	0.006	<0.010	0.002	<0.010	0.001	<0.010	0.003	<0.010	0.003	<0.010	0.002	
$Cr (mg kg^{-1})$	<0.025	0.008	< 0.030	0.004	0.030	0.001	0.050	0.001	0.070	0.001	<0.030	0.004	<0.030	0.001	<0.030	0.002	<0.030	0.004	
Su (mg kg ⁻¹)	11.595	1.047	0.030	0.003	<0.030	0.002	<0.030	0.005	0.050	0.033	<0.030	0.001	0.030	0.002	<0.030	0.004	0.030	0.004	
Hg (mg kg ⁻¹)	<0.005	0.008	<0.010	0.001	<0.010	0.001	<0.010	0.003	<0.010	0.001	<0.010	0.003	<0.010	0.004	<0.010	0.001	<0.010	0.001	
${ m Mo}\ { m (mg}$ ${ m kg}^{-1})$	<0.025	0.005	0.100	0.005	0.120	0.001	0.130	0.001	0.150	0.003	<0.030	0.005	<0.030	0.002	<0.030	0.002	<0.030	0.002	
$Ni \text{ (mg kg}^{-1})$	0.138	0.016	< 0.030	900.0	<0.030	0.005	<0.030	0.002	<0.030	0.005	<0.030	0.003	<0.030	0.001	<0.030	0.003	<0.030	0.003	
Pb (mg kg ⁻¹)	0.479	0.171	<0.050	0.004	<0.050	0.003	<0.050	0.004	090.0	90000	<0.050	0.004	<0.050	0.003	<0.050	0.005	<0.050	0.004	
$sb (mg kg^{-1})$	0.010	0.009	0.030	0.002	0.030	0.001	0.030	0.001	0.030	0.001	0.010	0.001	0.010	0.001	0.010	0.001	0.010	0.001	
se (mg kg ⁻¹)	0.056	0.022	0.420	0.018	0.440	0.031	0.430	0.002	0.500	0.018	0.220	0.012	0.200	0.024	0.170	0.002	0.150	0.015	
$^{ m Zn}$ (mg $^{ m kg}^{-1}$)	55.742	0.552	0.110	0.021	<0.050	0.003	<0.050	900.0	090.0	0.008	<0.050	0.004	<0.050	0.004	<0.050	0.003	<0.050	0.001	
H	4.05	±0.02	10.77	±0.02	10.74	±0.02	11.14	±0.02	11.28	±0.02	10.92	±0.02	10.62	±0.02	10.74	±0.02	10.75	±0.02	., .

pH level near 11.0. Consequently, the pH remained practically unchanged irrespective of the amount of stabilizer added. This pH range has been established as optimal for minimizing the solubility of pH-dependent metals, including the elements considered critical in the context of this soil (Cui et al., 2019; García et al., 2004; Zhao et al., 2023).

Although soil mixtures with LG-MgO exhibited lower concentrations of leached metals, both soil stabilizers reduced the leaching of Cd, Cu, Pb, and Zn by 99% (as shown in Table 4). After remediation, regardless of the percentage of stabilizing agent added, the soil could be categorized for non-hazardous landfill management, aligning with the limits specified by the European landfill directive (Table 2).

Some metals, such as Se or Cr, showed increased concentrations in the leachate as the amount of tundish added increased. It is plausible to consider that the source of these metals lies within the stabilizing agent itself. Certain metals and metalloids, capable of oxyanion formation, exhibit redox sensitivity (e.g., As, Cr, Se, Mo, Sb, V, and W). While their solubility remains independent of pH, their leaching behaviour may be enhanced under alkaline conditions through the dissolution of mineral phases in which they are adsorbed (Cornelis et al., 2008). Nevertheless, the concentration of these metals remained below the limit established for their classification as non-hazardous material.

The ability to use significant quantities of a stabilizer agent while keeping the pH of the stabilized soil within the optimal range offers the advantage of creating an alkaline reservoir. This reservoir ensures long-term soil stability while maintaining conditions of minimal solubility for pH-dependent metals. Considering both the potential release of metals and economic factors, the soil-stabilizer proportions chosen for soil stabilization in the horizontal up-flow column percolation test were 5 wt % and 10 wt%.

3.2. Horizontal up-flow percolation test

The column percolation test allows for predicting the behaviour of onsite soil remediation. Figs. 1 and 2 show the variation of pH and electrical conductivity (EC) at each cumulative L/S ratio, respectively.

During the column leaching test on the stabilized soil with various proportions of stabilizer, there was a noticeable increase in pH levels observed in all leachates compared to the initial pH of the contaminated soil (Table 2). The changes in pH at the different cumulative ratios showed that even when no stabilizing agent was added, this parameter increased and reached values very close to neutrality at cumulative L/S ratios from $0.5 \, \text{L kg}^{-1}$ and beyond. However, when stabilizers were used for the remediation of the contaminated soil, the pH levels achieved at a

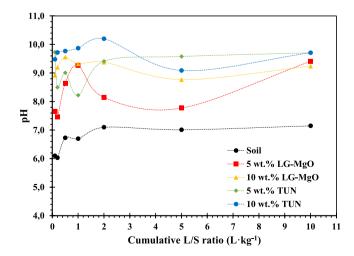


Fig. 1. pH of the contaminated soil leachates and their treatment with stabilizers in the different cumulative ratios of the column leaching test.

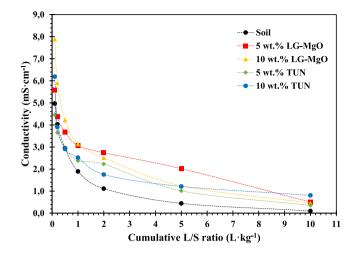


Fig. 2. Electrical conductivity (EC) of the contaminated soil leachates and their treatment with stabilizers in the different cumulative ratios of the column leaching test.

cumulative L/S ratio of 10 ranged from approximately 9.0 to 9.7. This pH range remained consistent across all proportions of stabilizers assessed.

It's worth noting that the pH levels attained in the column test were slightly lower compared to the pH values determined in the granular batch leaching test (Table 4). The pH obtained when adding TUN as a stabilizer was slightly higher compared to the pH values obtained using LG-MgO, likely due to the higher lime content present in TUN. Importantly, the pH achieved is not significantly affected by the percentage of stabilizer reactant added, indicating that MgO-based stabilizing agents provide a reservoir of stabilizing reactant without affecting the optimum pH conditions. These pH levels achieved in the stabilized soil samples, regardless of the quantity or type of stabilizer reactant used, are conducive to the minimum solubility levels of most pH-dependent metal hydroxides (Cui et al., 2019; García et al., 2004; Gu et al., 2022; Nędzarek et al., 2015).

The electrical conductivity (EC) values observed during the column leaching test showed a consistent trend. Initially, there was a decrease in EC with each increase in the cumulative ratio (Fig. 2 and Table A.3 in Appendix A), which is consistent with the soluble fraction in the contaminated soil dissolving rapidly during the initial stages of water percolation. This solubilization of ions like Ca^{2+} , K^+ , Mg^{2+} , and SO_4^{2-} from the soil contributed to the high initial EC values (Chen et al., 2010; Simón et al., 1999).

However, it's interesting to note that in the column containing 10 wt % TUN as a stabilizer, the EC values increased slightly after reaching a cumulative ratio of 10 L kg $^{-1}$. This may be attributed to the higher content of soluble fraction present in the TUN stabilizing agent itself.

In summary, the EC values decreased as water percolated through the soil, but in the case of the column with TUN, there was a slight increase in EC at higher cumulative ratios, likely due to the properties of the stabilizing agent.

Table 5 presents the cumulative release $(mg \cdot kg^{-1})$ of various metals at a cumulative L/S (liquid-to-solid) ratio of 10 L kg^{-1} from the up-flow column leaching tests conducted using both MgO-based stabilizing agents. It is important to note that many of the concentrations of the analyzed metals in the aliquots obtained are below the detection limits. For these cases, the detection limit itself has been considered for calculating the cumulative concentration. Therefore, the real cumulative release is expected to be lower than the represented value.

Regardless of the percentage of stabilizing agent used, the effect of the addition of the LG-MgO was evident, particularly in those metals with high leaching potential (Zn and Cu). This results in a reduction of

Table 5 Cumulative metal release (mg·kg $^{-1}$) corresponds to the cumulative L/S ratio of 10 L kg $^{-1}$.

	Cumulative metal release (mg·kg ⁻¹)										
	Cd	Ва	Pb	Ni	Zn	Cu	Se	Sb	Cr	Мо	As
Contaminated soil	0.1303	0.3580	0.0696	0.1697	45.381	4.9190	0.0759	< 0.0068	< 0.0103	< 0.0052	< 0.0109
$\sigma(\pm)$	0.0101	0.0010	0.0015	0.0759	0.6475	0.0239	0.0019	0.0001	0.0003	0.0001	0.0002
5 wt% TUN	< 0.0052	0.1055	< 0.0294	0.0183	< 0.1262	0.1140	0.7213	< 0.0185	< 0.0110	0.0423	0.0354
$\sigma(\pm)$	0.0002	0.0011	0.0009	0.0007	0.0110	0.0011	0.0109	0.0003	0.0007	0.0012	0.0014
10 wt% TUN	0.0084	0.2481	< 0.0900	< 0.0114	< 0.1266	0.0944	0.5736	0.0413	< 0.0117	0.0144	< 0.0264
$\sigma(\pm)$	0.0002	0.0016	0.0057	0.0004	0.0130	0.0008	0.0113	0.0005	0.0007	0.0004	0.0004
5 wt% LG-MgO	< 0.0052	0.1651	< 0.0334	< 0.0111	< 0.1245	0.0445	0.1955	0.0262	< 0.0103	< 0.0052	< 0.0112
σ (±)	0.0003	0.0016	0.0002	0.0001	0.0122	0.0006	0.0038	0.0002	0.0014	0.0001	0.0004
10 wt% LG-MgO	< 0.0052	0.1606	< 0.0453	< 0.0101	< 0.1255	0.0694	0.2681	0.0277	< 0.0103	< 0.0056	< 0.0121
σ (±)	0.0002	0.0014	0.0230	0.0005	0.0143	0.0007	0.0023	0.0002	0.0012	0.0002	0.0004

released metal exceeding 99% for Zn and over 97% for Cu (Fig. 3). For Ni, Cd, and Ba, although the release from the untreated soil was already very low, the addition of the stabilizer agents further reduced their release. A Singular mention should be made for the metal (loid)s (i.e., Sb, Mo, As, and Se). All of them exhibited very low releases from the column test with the contaminated soil sample. However, the addition of both MgO-based stabilizer agents slightly increased their release. For all these metal (loid)s, although at very low concentrations, it can be concluded that their main origin comes from the stabilizing agent. The presence of these metal (loid)s was higher in TUN than in LG-MgO (Table A.2; Appendix A). Consequently, the column leaching test revealed higher metal (loid) release in soil samples stabilized with TUN. Surprisingly, except for Sb, the release of metal (loid)s is higher when the TUN percentage is lower (5 vs. 10 wt%). This phenomenon could be attributed to the lower pH of the soil sample stabilized with 5 wt% TUN in the initial aliquots generated during the column leaching test. In this regard, it is important to highlight that this metal (loid)s can exist in different oxidation states, wherein the lower valence states are influenced by pH, while the higher valence states (i.e. Sb(V), As(V), Se(VI), Mo(VI), and Cr(VI)) form pH-independent oxyanions, behaving as nonmetals. Nonetheless, the leaching behaviour of these redox-sensitive elements may be heightened under alkaline conditions due to the dissolution of the mineral phases in which they are adsorbed (Cornelis et al., 2008).

Fig. 4 illustrates the cumulative release of different metals as a function of cumulative L/S (liquid-to-solid) ratios from the up-flow column leaching tests conducted using both MgO-based stabilizing

agents. The metals presented in Fig. 4 are those from the contaminated soil whose release significantly exceeds the limits for non-hazardous materials (Zn and Cu), exhibit significant variation in the stabilized soil (Cd and Ni), or show anomalous behaviour compared to previous metals (Pb).

It should be noted that, in the case of Pb, the addition of 10 wt% of TUN has resulted in an increase in the release of this metal (Fig. 4), indicating a negative reduction. Emphasize that, regardless of the stabilizer utilized, there is a reduction in the release of Zn, Cu, Ni, and Cd by more than 92%. Although the initial release of Ba from the contaminated soil sample was not very significant (0.36 mg kg⁻¹), its reduction was slightly over 50%. To justify this lower reduction, it should be noted that the stabilizers themselves (LG-MgO and TUN) already exhibit a release of Ba (Table A.2; Appendix A). On the other hand, although its concentration is not very significant, only Pb shows a slight increase because of adding 10 wt% of TUN stabilizer. In this case, it should be considered that the release of Pb from TUN was significantly higher than that of LG-MgO (Table A.2; Appendix A), so higher additions of this stabilizer may also contribute to the release of Pb.

Comparing the results of the stabilized soil with those of the contaminated soil without any stabilizer reactants provides valuable insights into the effects of the stabilizers on the leaching behaviour of the metals. This comparison helps assess how effectively the stabilizers mitigate the release of metals from the soil.

It can be observed from the contaminated soil samples that the release of metals took place in the initial aliquots of the column leaching test. Starting from the fifth aliquot (cumulative L/S ratio of $2 L kg^{-1}$), the

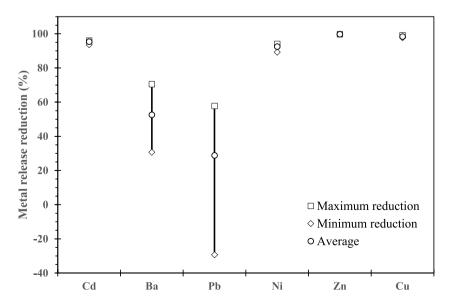


Fig. 3. Reduction of pH-dependent metal release from the stabilized soil samples using MgO-based stabilizer agents in the up-flow column leaching test.

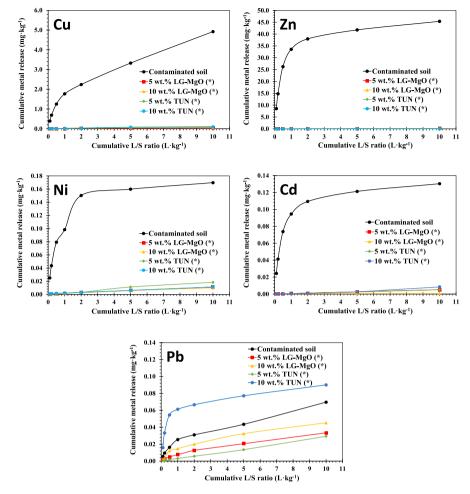


Fig. 4. Cumulative release of metals in column test from the contaminated soil and remediated soil using different percentage of LG-MgO or TUN.

release of metals significantly decreased due to the gradual depletion of metals in the contaminated soil. The addition of stabilizing agents drastically decreased their release, likely pH values close to 9.5 reduced the solubility of these metals. This indicates the effectiveness of the stabilization process in mitigating the leaching of these metals from the soil. Consequently, significant reductions in the cumulative release of Zn and Cu can be observed. Similar behaviours were also observed for Cd and Ni, where their release from the stabilized soil samples was significantly lower compared to the contaminated soil without stabilizing agents. No significant difference in metals released was observed between the experiments using LG-MgO or TUN as stabilizer reactants, as the concentration values were very similar. Although the maximum values were below 0.1 mg kg⁻¹, the cumulative release of Pb is higher in the soil sample stabilized with 10 wt% TUN than in the contaminated soil without the addition of any stabilizer reactant. For the rest of the stabilized soil samples, whether obtained with 5 wt% TUN or with any of the two studied percentages of LG-MgO, although they present lower Pb values, these do not significantly differ from those of the affected soil without the addition of stabilizers.

4. Conclusions

This study demonstrates that MgO-based tundish deskulling (TUN) can be effectively employed for the remediation of contaminated soils. Several key findings and conclusions can be drawn from the research:

- Effectiveness of TUN: TUN, due to its high MgO content and resulting alkaline pH range (9.0–10.5), effectively improves conditions for retaining metals and metalloids during leaching processes. This favourable medium created by TUN allows for long-term soil stability.
- Comparison with LG-MgO: The remediation efficacy of TUN was compared to that of LG-MgO, which has previously demonstrated its efficiency. The study found no significant differences in pH values between soil samples stabilized with TUN and LG-MgO.
- **Reduction in Metal Leaching:** In up-flow column leaching tests, the addition of 5 wt% or 10 wt% of TUN resulted in a significant reduction (over 95%) in the release of metals like Zn, Cu, Ni, and Cd, achieving similar results to LG-MgO. This indicates that TUN is highly effective in mitigating metal leaching.
- Pb Anomaly: An anomaly was observed in the case of Pb, where the
 release of this metal was higher in soil stabilized with 10 wt% TUN
 compared to the contaminated soil. A similar trend was observed for
 some metalloids (Sb, As, Se, Mo, and Cr), which exhibited slightly
 higher releases in stabilized soils, but at very low and insignificant
 concentrations.
- Eco-Friendly Solution: TUN represents a potentially cost-effective and eco-friendly solution for remediating contaminated soils. Its viability as an alternative to conventional stabilizing agents opens up opportunities for advancing environmental restoration practices.

Overall, this study underscores the promising potential of MgObased TUN as a soil remediation agent, particularly for mitigating the

release of metals and metalloids. Further research and practical implementation of TUN-based soil remediation strategies could have significant positive impacts on environmental restoration efforts.

4.1. Limitations

While this study demonstrates the efficacy of MgO-based tundish deskulling (TUN) in the remediation of contaminated soils, there are certain limitations and areas for future consideration:

- Application Specificity: The findings are based on the specific conditions and parameters employed in this study. Further investigations are required to evaluate the effectiveness of TUN in diverse soil types and varying environmental conditions.
- Pb Anomaly Investigation: The anomaly observed in the case of Pb requires further in-depth research to comprehend the underlying factors influencing the release of this metal in the presence of TUN.
 Identifying the precise mechanisms at play is crucial for optimizing the application of TUN in soil remediation practices.
- Long-Term Effects Assessment: The long-term stability and sustainability of TUN-based soil remediation methods warrant extensive monitoring and assessment to ascertain the enduring impact of this approach on soil quality and ecological health over time.

4.2. Future perspectives

In light of the research outcomes and identified limitations, several key perspectives can be outlined for future studies and practical applications:

- Comprehensive Field Studies: Conducting large-scale field studies under various environmental conditions can provide a more comprehensive understanding of the efficiency and ecological implications of TUN application in real-world soil remediation scenarios.
- Mechanistic Studies: Undertaking detailed mechanistic studies can aid in elucidating the intricate processes governing the interaction between TUN and specific contaminants, thereby facilitating the development of more targeted and efficient soil remediation strategies.
- Sustainability Analysis: Performing comprehensive sustainability assessments, encompassing economic, environmental, and social factors, is essential to gauge the overall feasibility and long-term viability of TUN as a sustainable solution for soil remediation on a broader scale.

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Author contribution statement

Alex C. Quintero-Payan: Investigation, Validation, Writing – Original Draft; S. Huete-Hernández: Investigation, Validation, Writing – review & editing; V.B. Aguilar-Pozo: Investigation, Validation, Writing – review & editing; S. Astals: Validation, Writing – review & editing, Funding acquisition; J.M. Chimenos: Conceptualization, Supervision, Visualization, Resources, Writing – review & editing, Funding acquisition.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.chemosphere.2023.140750.

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