Stabilization and Solidification of Industrial Waste

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1. CHANG, H Oh. Hazardous and radiocative waste treatment technologies handbook. B.m.: CRC Press, 2001. ISBN 0-8493--9586-0.
2. *Industrial Waste Treatment Handbook*. Boston: Butterworth Heinemann, 2001. ISBN 0-7506-7317-6.
3. SIVASANKAR, B. *Instrumental methods of analysis*. New Delhi: Oxford University Press, 2012. ISBN 978-0-19-807391
4. CSUROS, Maria a Csaba CSUROS. *Environmental Sampling and Analysis for Metals*. Boca Raton: Lewis Publishers, 2002. ISBN 1-56670-572-x.
5. Scientific resources: such as Web of Science, ScienceDirect, SciFinder Scholar, Medline etc.

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ABSTRAKT

V této studii byla zkoumána stabilizace a solidifikace (S/S) odpadu z munice pocházejícího z výbušných komor, s použitím různých typů pojiv jako portlandský cement a úletový popílek. Metody byly otestovány za různých podmínek ovlivňující solidifikační směsi jako je například obsah vody, poměr voda-cement (Wa/C) a přídavek chloridů. Ve studii byla tělesa S/S připravena v různých poměrech odpadu ku obsahu pojiva (W/B) v solidifikační směsi: 80:20, 60:40, 40:60 a 20:80. Po 28 dnech tuhnutí byla pevnost v tlaku měřena pomocí hydraulického lisu. Kromě toho byly vzorky S/S podrobeny vyluhovacímu testu dle metodiky TCLP 1311 a koncentrace Pb a Cu byly analyzovány pomocí atomové absorpční spektrometrie (FAAS). Výsledky poté byly porovnány s evropským nařízením o ukládání odpadu na skládky 2003/33/EC. Ze získaných výsledků lze konstatovat, že vliv chloridu sodného na solidifikační směsi byl účinně otestován, což se projevilo stabilizací obsahu Pb a Cu o více než 99 %.

Klíčová slova: Stabilizace a solidifikace, pojivo, cement, popílek, pevnost v tlaku, Plamenová atomová absorpční spektrometrie (FAAS)

ABSTRACT

In this study, the Stabilization and Solidification (S/S) of ammunition waste, originating from semiautomatic explosion chambers using different types of binders along with the effect of environmental conditions, Water type, water-cement ratio (Wa/C), and the effect of chloride were investigated. The used binders are OPC (ordinary Portland cement) and FBCA (Fluidized Bed combustion ash). In the study, S/S solidified samples were prepared in a waste-to-binder (W/B) ratios: 80:20, 60:40, 40:60, and 20:80. After 28 days of curing, the compressive strength (CS) was monitored using a Laboratory Motorized Hydraulic Press. Furthermore, the S/S samples passed through the Toxicity Characteristic Leaching Procedure (TCLP 1311), and the leaching of Pb and Cu was analyzed by Flame Atomic Absorption Spectroscopy (FAAS). Then, the results were compared to European landfill regulation (2003/33/EC). From the result gained, the addition of chloride into OPC effectively stabilized the leaching of Pb and Cu from the waste, achieving a reduction of over 99 %.

Keywords: Stabilization and solidification (S/S), OPC (Ordinary Portland Cement), Fluidized Bed Combustion-fly ash (FBCA), Compressive strength (CS), Flame Atomic absorption spectroscopy (FAAS)

First, I give all my success to the Almighty God and my Savior, Jesus Christ. His unwavering guidance has made the seemingly impossible possible, helping me to pass all of life's challenges.

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1 INTRODUCTION

In the past, waste was only an inconvenience that required disposal. The large quantity of land available to the people and a tiny population, proper management was not a significant problem. The ecosystem could easily absorb the generated waste without any detrimental effects. However, the development of cities and industrial growth have increased the quantity and diversity of waste. This waste can take the form of solids, liquids, or gases, and the types of waste produced can vary depending on the type of industry, the raw materials used, and so on.

Landfilling has been the predominant method of waste disposal. However, this approach has raised many concerns due to improper waste management practices. Industrial wastes often contain hazardous substances that oppose natural degradation, and they are present in the environment for a long period of time. These substances are the main causes of both chronic and acute toxicity risks to humans, plant life, and animals.

In developed countries, these substances are classified as hazardous waste by various environmental agencies, such as the European Environmental Agency (EEA) and the US Environmental Protection Agency (USEPA). They are closely monitored before being disposed of in any landfill practice. The solidification and stabilization (S/S) of waste using different binders is one of the pre-landfill treatments that is used most of the time to ensure the health of the ecosystem and compliance with landfill regulations set by these environmental protection agencies.

However, countries found in developing continents like Africa exercise different trends because of lack of attention, weak enforcement of the law, and cheap landfilling cost of hazardous waste. Because of these factors, wastes produced in developed countries are easily transported to Africa for a small waste disposal fee, and this waste is dumped into landfills without any pre-landfill treatments. This trend is increasing over time and requires special attention. The contamination of Africa does not only affect Africa; it has global implications. Therefore, it is imperative to address this issue with urgency and implement effective waste management practices worldwide.

I. THEORY

2 WASTE

Most human actions produce waste. Nevertheless, since before recorded history, the generation of waste has consistently been a major source of worry. (Amasuomo and Baird 2016)

Waste (trash) generation has increased significantly, both in amount and rate of production. The Organization for Economic Co-operation and Development (OECD) estimates that 20 % of resources harvested worldwide are wasted and that the diversity of waste increases proportionately to waste volume. Unlike in the past, when appropriate management was not a major issue because there was a small population and a lot of space available to the people, waste was only a problem that needed to be disposed of. The environment at the time was able to easily absorb the quantity of waste produced without suffering any adverse effects. (Marek and Krejza 2023; Amasuomo and Baird 2016)

The influx of people into cities caused a population explosion, increasing the amount and variety of waste generated in cities. Then, things like metals and glass started to show up in significant amounts in the urban waste stream. Cities and localities with significant populations have seen an increase in indiscriminate waste and open landfills. Consequently, these dumps served as rats and other vermin breeding grounds, endangering public health. Unhealthy waste disposal procedures caused several epidemic outbreaks with high death rates. To protect public health, public officials started disposing of waste in a controlled manner in the eighteenth century. (Demirbas 2011; Amasuomo and Baird 2016)

Most waste resides outside the trash container and is not necessarily unattractive! Waste might take the form of pointless processing, input, or output. These are only a few examples of materials, stocks, equipment, facilities, labour hours, utilities, papers, costs, and movements. (Domingo 2015)

2.1 Classification of waste

Waste can take on many various forms, and there are many ways to characterize waste. The physical states (solid waste, liquid waste, and gas waste), physical qualities, reusable potentials, biodegradable potentials, source of production (Household/Domestic waste, Industrial waste, Agricultural waste, Commercial waste, Demolition or construction waste, and Mining waste), and level of environmental effect (hazardous and non-hazardous) are some typical features utilized in the classification of waste. (Amasuomo and Baird 2016)

Hazardous wastes include toxic materials (chemical waste from industrial, chemical, or biological processes that might harm or kill when consumed or absorbed via the skin), reactive (chemically unstable, reactive wastes react violently or explosively with water or air), ignitable, corrosive, infectious (materials from medical and research facilities that are considered infectious wastes include things like old bandages, hypodermic needles, and other items that could potentially harbour bacteria), or radioactive (ionizing radiation from radioactive wastes can damage living things). Examples of such wastes are spent fuel rods that contain fissionable materials used in nuclear power generation and isotopes of cobalt and iodine used in cancer treatment and other medicinal applications. (The Editors of Encyclopedia 2023)

2.1.1 Industrial waste

Industrial waste is leftovers from processing raw materials used to produce new goods. They emphasized that they might be in mines, industries, or mills. (Amasuomo and Baird 2016)

Industrial wastes are one of the causes of environmental contamination. These wastes can be extremely hazardous to living things since they consist of a wide range of highly poisonous organic and inorganic contaminants. (Woodard & Curran Inc. 2006; Bharagava, Saxena, and Mulla 2020)

Industries typically produce three types of waste: solid wastes (including hazardous wastes, which include some liquids), liquid wastes (such as process wastes, which go to an on-site or off-site wastewater treatment system), and air pollutants. Frequently, the three are managed by different people or departments. Depending on the traits of the wastes and the process of producing them, these wastes are managed and regulated accordingly. They are governed by different and independent sets of laws and regulations, and historically, as the times have changed, public and governmental attention has gone from one category, like wastewater, to another, like hazardous wastes. However, the three waste categories are related in how they affect the environment and how they are produced and managed by individual industries. (Woodard & Curran Inc. 2006)

Thus, the treatment of industrial waste comprises a variety of technical, regulatory, and environmental problems. Regardless of the industry, the assessment and selection of waste treatment technologies typically involves a logical progression of actions that contribute to the achievement of the objective of reducing waste toxicity and volume. These procedures begin with a high-level description and assessment of the waste-producing operations and proceed through a series of evaluations that get progressively more in-depth to find the best possible balance between effectiveness and cost, where cost includes both treatment and disposal. (Woodard & Curran Inc. 2006)

2.2 Ammunition Waste

Ammunition waste, comprising shells, cartridges, bullets, and explosive materials, was originally intended for military operations, training, or testing. Some examples of them are illustrated in **Figure 1**. (OSCE 2008; EPA 2004; Barker et al. 2021a) According to European regulations for waste categories, this waste falls into the category of granular hazardous waste. (European Commission 2003)

Ammunition waste presents environmental risks due to its hazardous metal content, such as Pb, Ni, As, Sb, W, and Cu. The fate, transport, and mobilization of these metals are complex processes influenced by a variety of environmental factors. **Table 1** provides an overview of the probable metal concentrations of this waste; these data are derived from soil sample studies conducted in both civilian and military shooting ranges. Notably, a significant proportion of these contaminated soil samples exhibit high concentrations of Pb. (Barker et al. 2021a)

Figure 1. *Unusable rocket motors (a) Ammunition(b)* (Shyman and Ustimenko 2009) *Military operation (c) and Typical small arms projectile (Bullet) and its cross section (d)* (Barker et al. 2021a)

Table 1. *Heavy Metal Concentration in Soil Samples Across Military and Public Shooting Ranges*. (Barker et al. 2021a)

Study Area	***Operation***	***pH***	***Concentration (mg/kg)***					
			Pb	***Sb***	***Cu***	***Zn***	***As***	***W***
Public rifle range Florida (USA)	*3 years*	*5.76*	*12,710*	*-*	*-*	*-*	*-*	*-*
public range (Switzerland)	*90 years*	*7*	*23,620*	*1,100*	*895*	*585*	*-*	*-*
Losone, swiss range (Switzerland)	*since 1960*	*3.2*	*80,900*	*4,000*	*189*	*-*	*-*	*-*
Rena range (Norway)	*-*	*7.6*	*30,000*	*2,900*	*2,300*	*-*	*-*	*-*
Test Beam (Alaska)	*1 firing event*	*5.34*	*458.8*	*12*	*62.8*	*71.7*	*14.5*	*-*
Murray Bridge (Australia)	*1970*	*9.29*	*12,167*	*325*	*3,555*	*735*	*8.83*	*-*
Military range (Botswana)	*since 1995*	*8.6*	*38,386*	*-*	*1,569*	*-*	*-*	*-*
Military range (Poland)	*since 1889*	*7.67*	*3,865*	*-*	*2,541*	*8,656*	*-*	*-*
Military range (South Korea)	*30 years*	*6*	*3,918*	*26*	*318*	*104*	*-*	*-*
Northwest, JAR military	*-*	*-*	*64,682*	*1,059*	*12,983*	*1,248*	*26*	*1,067*

2.3 Catalogue of waste

Commission Directive 2000/532/EC2 created a hierarchical list of waste descriptors known as the European Waste Catalogue (EWC). It is divided into twenty primary segments, some of which are based on materials and processes and most of which are industry-oriented. These all have two-digit codes that range from 01 to 20. A chapter can have one or more subchapters, each of which has four figure codes, the first two of which are two digits of the chapter. These contain codes for specific wastes, each of which is given a six-digit code. Entries containing an asterisk after the code designate hazardous waste. (The Environment Agency (UK) 2004)

It is used in information systems to relate waste stream characterization to implications on waste shipping, processing, and disposal. These class labels, or EWC tags, frequently help users find items of interest and match others with related interests. (van Capelleveen et al.

2021) Based on this, ammunition waste is categorized and identified under EWC Code 16 04 01*. (Commission of EU communities 2010)

3 STABILIZATION AND SOLIDIFICATION OF WASTE

The primary technology employed to handle the nation's waste products has been disposal to the land. Convenience, favourable rules, and economics all contribute significantly to the increased usage of land disposal. (Wiles 1987)

A pre-landfill waste treatment method called stabilization has been utilized for a variety of industrial wastes, but it is especially well suited to those that include heavy metals. Sludges and other aqueous hazardous wastes are treated using the solidification and stabilization (S/S) process, which employs chemically reactive formulations that combine with water and other chemical compounds or binders to generate stable solids. In addition to chemically solidifying the hazardous waste, the material employed for S/S also insolubilizes, immobilizes, encapsulates, destroys, sorbs, or otherwise interacts with certain waste components. Solids that are less toxic than the original waste are produced because of these reactions. Compressive Strength (CS) and leach resistance are essentially the two characteristics that define how effective these S/S products are. (Malviya and Chaudhary 2006; Hunce et al. 2012) S/S have often been employed to treat inorganic contaminants; however, certain organic contaminants have been effectively treated recently. In the S/S process, the immobilization of contaminants happens through three main mechanisms (Du et al. 2010):

1) physical adsorption of contaminants on the surface of different binder hydration products.
2) chemical fixation of contaminants by interactions between hydration products of binders and contaminants.
3) physical encapsulation of contaminants.

3.1 Stabilization

Stabilization is the use of additives or binders to reduce the toxicity, solubility, and mobility of hazardous materials found in the waste. These binders achieve this through chemical or physical means. A common method is adding chemicals that decrease the solubility of hazardous materials, which minimizes their leaching into the environment. For instance, non-hazardous sulfides, hydroxides, and phosphates are often used in binders and additives to transform highly soluble RCRA (As, Ba, Cd, Cr, Pb, Hg, Se, Ag) metal salts and oxides (e.g., $CdCl_2$ and $HgSO_4$) in mixed waste into relatively insoluble metal compounds (e.g., $Cd(OH)_2$ and HgS). (Chang H. Oh 2001)

The leachability of harmful chemicals from the encapsulated substance is a key indicator of stabilization efficiency. In the study of (Ferrazzo et al. 2023), the stabilization of metals found in Waste Foundry Sand (WFS) was compared between two binding materials: Alkaline Activated Binder (AAB) and Portland Cement Binder (PCB). The study focused on the metal leaching behaviour from WFS-AAB and WFS-PC using both batch and column test methods, respectively. As a result, all mixtures of WFS-AAB and WFS-PCB showed no metal toxicity. (Pattee and Pain 2003). (Pattee and Pain 2003)

Several factors contribute to the effectiveness of waste stabilization, including the waste-binder ratio W/B, waste type, pollutant type, and pollutant concentration. A study by (Vinter et al. 2016) also shows the importance of considering water as one parameter alongside the W/B ratio in the stabilization process. The study focuses on immobilizing pollutants found in hot dip galvanizing ash, which contains a high concentration of zinc. In the study, three different binders were used, Portland cement, fly ash, and coal fluidized-bed combustion. The positive results obtained from including water as a parameter alongside the W/B ratio give a positive result in the stabilization process.

3.2 Solidification

The process of solidification is the transformation of waste from a sludge, semisolid, liquid, or particulate form into a solid structure (a form that holds its shape without a container) with the help of additives, binders, and admixture. (Chang H. Oh 2001)
The physical dewatering of the wastes and the enhancement of their physical attributes, like strength, compressibility, and permeability, are part of it. (R. Singh and Budarayavalasa 2021)

Typically, it will solidify into larger-sized forms than untreated waste. As a result, smaller area/volume ratios will Pb to lower rates of pollutant release. The permeability of the treated waste is usually substantially lower, which lowers the advective flow through the waste material. Fluids will flow around rather than through the treated material if their permeability is significantly lower than that of the surrounding material in the disposal zone. This will significantly minimize the number of pollutants released. (Batchelor 2006a)

Other than the type of waste and W/B ratio, the CS of a S/S material is highly affected by the water-cement ratio (Wa/C), especially if the binder is made of cement. Water is mostly needed to create cement hydration. Cement and other cementitious materials set and harden because of a chemical reaction that takes place between cement and water. several chemical reactions and physical transformations must occur to create hydrated cement paste (solid, long-lasting material). Within a few minutes of adding water, tiny crystals of calcium sulfoaluminate hydrate or ettringite ($Ca_6Al_2(SO_4)_3(OH)_{12}\cdot 26H2O$) will be formed, the ettringite changes into monosulfate hydrate. After two hours of the cementation process, Large prismatic crystals of calcium hydroxide and tiny crystals of calcium silicate hydrates (C-S-H) start to fill the vacant pores that were previously occupied by water and the hydrated cement particles. The product strength is largely contributed by the C-S-H formation. (John and Lothenbach 2023; Al-Jabari 2022)

The Wa/C ratio is a convenient measurement whose value is well correlated with PCC (Portland cement concrete) strength and durability. However, the addition of too much water can Pb to a weaker mix, increased porosity, and reduced durability. On the other hand, insufficient water may result in difficulty in placing and compacting the concrete mix. According to (ACI Committee 211 2002), the Wa/C of concrete should not exceed 0.5 for normal-weight concrete, 0.45 for concrete exposed to freezing, 0.4 for concrete exposed to salts, and 0.45 for concrete exposed to sulfates. In general, lower Wa/C ratios produce stronger, more durable PCC. According to (Kim et al. 2014) study, the Wa/C ratio increases from 0.45 to 0.60, the compressive strength is reduced by 24.4 %. However, a very low water level also results in poor workability. (S. B. Singh, Munjal, and Thammishetti 2015a)

According to (BS 8500-1 2016), it is recommended that the water-cement ratio (Wa/C) should be as lowas it can. However, specific conditions such as the type of cement, aggregate characteristics (size, shape, and gradation), and environmental conditions (humidity, temperature) will affect the water demand. **Table 2** shows the relationship between the Wa/C ratio and the resulting compressive strength CS. (BS 8500-1 2016; ACI Committee 211 2002)

Table 2. *Wa/C vs. CS for Various Cement Types* (BS 8500-1 2016)

Wa/C	***Cement type***	
	IIB-V, IIA	***IVB-V, IIB***
0.55	*CS (25-30)*	*CS (20-25)*
0.5	*CS (28-35)*	*CS (25-30)*
0.45	*CS (32-40)*	*CS (28-35)*
0.4	*CS (35-45)*	*CS (32-40)*
0.35	*CS (40-50)*	*CS (35-45)*

4 STABILIZATION AND SOLIDIFICATION TECHNIQUES

Many variables, including waste type, water content, reagent type, reagent addition ratio (mix ratio), curing time, and temperature, influence the development of a very wide range of strength and durability values in S/S processes. Reagent mix ratios can be changed in various processes to modify the final strength and durability values. (Bayar and Talinli 2013)

Primary and secondary stabilizing agents are the two categories of stabilizers used in the S/S process. To achieve the intended stabilizing effect, primary stabilizing agents alone may be used. The most often used stabilizers are lime and Portland cement. The cementitious properties of secondary stabilizing agents are negligible when used alone. In these situations, secondary stabilizing chemicals make up most of the stabilizer, and just a small amount of cement or lime is needed as an activator to start chemical reactions. (Haghsheno and Arabani 2024)

4.1 Cement method

Due to its alkaline qualities and strength, Ordinary Portland Cement (OPC) has historically been the most used material in S/S. (Chen, Nakamura, and Hama 2023). To create OPC-based S/S, cement is mixed with toxic waste, such as heavy metal aqueous solution or sludge, and the mortar is then allowed to cure to produce S/S samples. Ettringite and C-S-H gel are present in the final S/S product. (Tyagi and Annachhatre 2023a)

Too much Ettringite can Pb to cement expansion and cracking in specific situations. (Kogbara 2014) Nonetheless, other research revealed that the ettringite, generated throughout the cement hydration procedure, influences metal immobilization by substituting metal cations for Ca^{2+} ions. (Karamalidis and Voudrias 2007; Trezza 2007; Moon et al. 2010)

In the study of (Contessi et al. 2020), which investigates the formation of various hydration from different binders (OPC, CAC (calcium aluminate cement) and MK (geopolymer binder made of NaOH-activated metakaolin), in the result it was found that the formed C-S-H from the OPC could adsorb the Pb ions on its surface.

It has been demonstrated that using only OPC as a material for S/S technology to immobilize heavy metals works well. (J.-S. Li et al. 2014) evaluated the effectiveness of cement leaching of Pb-contaminated soil products. When the cement-to-dry soil ratio rose from 0.2 to 0.4, they discovered that the leaching concentration of Pb ions considerably decreased by 34.9

%. According to the findings of another research, (Oluwatuyi 2019) added OPC, which enhanced the soil products' ability to adsorb Pb pollutants. In the study (Fei et al. 2018), which investigated on-site S/S studies, a similar observation was made. It demonstrated OPC's (8 wt %) outstanding ability to stabilize Cd and Zn, whose immobilization percentages are 99.9 % and 99.4 %, respectively.

When choosing cement binder as a stabilizer of heavy metal-containing waste, one also needs to consider the number of heavy metals present in the waste material. For instance, fly ash and mine tailing waste materials can be efficiently solidified and stabilized when consisting of 35 – 40 % of heavy metals by weight. (Oner, Akyuz, and Yildiz 2005; Wei et al. 2015) However, caution is necessary when the heavy metal content exceeds 40 %. A study conducted by (Choi, Lee, and Park 2009) demonstrated that heavy metal leaching surpasses the allowable limit in waste containing more than 40 % of heavy metals.

Summing up all these conditions, applying cement-based S/S to wastes requires careful consideration of how much the waste's constituents obstruct cement hydration reactions. Numerous substances that are known to either speed up or slow down cement hydration have also been discovered to have comparable adverse effects on waste. These consist of sulphate, metals, halides, and organics, especially polar organics. One of the main goals of developing S/S technology is to prevent negative waste-binder interactions. Methods for handling these issues include putting an accelerator instead of a retarder and vice versa. Soluble silicate, for instance, has been widely utilized as a S/S admixture to decrease the effects of retarders. (Batchelor 2006b)

4.2 Pozzolan method

In the Pozzolan method, the binder is formed by mixing OPC or lime with pozzolans (fly ash, slag, rice ask ash). (Wiles 1987; Haghsheno and Arabani 2024)

The primary constituents of pozzolans are Fe_2O_3, SiO_2, and Al_2O_3. Pozzolanic reactions are typically enhanced by using materials rich in SiO_2 and Al_2O_3. (Haghsheno and Arabani 2024) According to (Sharo, Shaqour, and Ayyad 2021; Haghsheno and Arabani 2024) studies, Si, Al, and Fe should constitute at least 70 % of a pozzolanic material, which is a fundamental requirement for its effectiveness.

4.2.1 Fly ash

Several combustion technologies have advanced over the past century and are used worldwide to generate energy from coal combustion. Since 1920, pulverized coal combustion (PCC) has been the traditional combustion method. Conversely, since 1979, a more sophisticated method of burning coal has been developed to address PCC's limits regarding feedstock variety. This recent version is fluidized bed combustion (FBC) coal combustion technology. (Pei et al. 2023)

The waste products that are produced from these power plants are PCCA and FBCA. The primary differentiating factors lie in particle size, chemical composition, and the amorphous phase. PCCA particles are typically slightly finer, measuring between 1 and 200 µm, and have a higher amorphous phase than FBCA, which contains irregularly shaped particles ranging from 1 to 300 µm. Additionally, FBCA contains higher amounts of $CaSO_4$ and CaO than PCCA. (Chindaprasirt, Rattanasak, and Jaturapitakkul 2011)

Additionally, the CaO content plays a major role in classifying fly ash into two groups: Class C (with cementitious and pozzolanic properties) and Class F (non-self-cementing). Class F fly ash only serves as a pozzolanic material, while Class C fly ash exhibits both cementitious and pozzolanic qualities, which mostly contain a significant amount of lime. (Haghsheno and Arabani 2024)

According to (Kogbara et al. 2013) study, soil spiked with various heavy metals (Cd, Cu, Pb, Ni, and Zn) at concentrations up to 3000 mg/kg were treated with a composition of 1:4 cement to fly ash ratio, and the acceptable granular leachability of the stabilized sample were met by dosing above 20 % binder into the contaminated soil.

In another study by (M. Li et al. 2022), the reuse of oil-contaminated soil (OCS) in engineering applications requires strength stability. The study also examined how the coastal environment, like water, humidity, and temperature, affects the deformation and strength of OCS solidified with lime-fly ash. The findings showed that OCS's deformation, shear strength, and unconfined compressive strength (UCS) all improved after the treatment.

4.2.2 Rice husk ash

Rice husk ash (RHA) is a byproduct of agriculture made from the outer coating of milled rice grains. Amorphous silica makes around 85-95 % of rice husk ash (RHA). The primary factor influencing RHA's pozzolanic activity is the presence of this silica. (Haghsheno and Arabani 2024)

For example, the use of OPC with RHA as an overall binder system for S/S of Pb-contaminated soils. It reduces Pb leachability from treated samples more effectively than using a binder system with independent OPC. However, the compressive strength of solidified samples decreased when OPC was partially replaced by RHA in the binder system. (Yin, Mahmud, and Shaaban 2006)

4.2.3 Slag

Slag is a residue of the refining of iron ore. Although it requires longer curing times to reach appropriate strengths, it can be used in part as a cementing agent instead of cement. (Haghsheno and Arabani 2024)

4.3 Cement Kiln Dust

Cement kiln dust (CKD) is generated during the process of making cement clinker. It is a highly alkaline, fine-grained solid waste material. Silica, lime, cement, and other metal oxides are among its constituents. (Haghsheno and Arabani 2024)

CKD and fly ash solidification methods frequently produce friable, even granular products, which are typically preferred from a landfill's operational point of view. Additionally, CKD has typically been employed in operational situations when a need for fast solidification was necessary. (Conner and Hoeffner 1998)

In (Safari, Ansari, and Ghazban 2017) studies, a preliminary investigation was performed into the use of CKD as a binding agent to stabilize and harden mercury-containing waste. The findings showed that mercury concentrations were lowered to below the strict land disposal restriction of 25.0 ppb in the toxicity characteristic leaching method imposed by the US Environmental Protection Agency when roughly 36.0 % by dry mass of CKD was added to the waste where the initial concentration of the mercury inside the waste was 22.0 ± 5.00 ppm. It states that using CKD is advantageous for stabilizing or solidifying waste mercury since CKD by itself is a waste, and it can be partially absorbed during the process instead of being thrown away as waste.

In (Haghsheno and Arabani 2024) studies, CKD has a chemical composition like cement and exhibits similar performance when utilized independently. Furthermore, CKD demonstrates excellence in the S/S of oil-polluted soil compared to alternative binders. Interestingly, it has the capacity to enhance CS by at least 70 %.

4.4 Thermal techniques

In thermal treatment, the ultimate products are glass, ceramic, and glass-ceramic, which immobilize heavy metals. (Tyagi and Annachhatre 2023b)

4.4.1 Vitrification

Vitrification is a recognized effective method that turns waste materials into glass or materials that resemble glass. Moreover, it has been shown that this process effectively removes organic and inorganic compounds that are volatile or semi-volatile from glassy materials, as well as stabilises organic and inorganic pollutants. (Sanito et al. 2022)

There are benefits and drawbacks to vitrifying hazardous waste. For example, the process of mixing glasses involves a significant number of metals and ions that are used to trap components inside the inorganic amorphous network, which lowers the amount of waste material and prevents the production of hazardous materials post-treatment. Further, inert glass can be disposed of straight into landfills and has strong chemical resistance against ion leaching. Additionally, the vitrification-derived material can be utilized for roads and pavements to immobilize pollutants in metal slag and prevent them from leaking into the environment. The drawbacks of vitrification are that it requires more energy and money to set up than landfill disposal compared to cement-stabilized waste. (Sanito et al. 2022)

According to a study conducted by (Dellisanti, Rossi, and Valdrè 2009) involving field-scale joule heating vitrification to remediate a substantial quantity of soil contaminated with inorganic compounds and heavy metals. By progressively heating the contaminated soil to high temperatures, which induced melting, followed by rapid cooling, they produced a glassy monolith. This glassy structure effectively immobilized heavy metals such as Pb, Zn, and Zr, along with other inorganic contaminants.

5 CHLORIDE

Currently, the interactions between chloride and contaminants, especially with Pb in cementitious systems, have not been understood clearly. (Bobirică et al. 2018)

5.1 Effect of chloride on leaching

Studies have stated different things about the impact of chloride on the mobility and leachability of Pb from S/S samples. (Liu et al. 2018) studied the effect of chloride attack on Portland slag cement and fly ash stabilized soil samples in the form of NaCl. They immersed the samples in NaCl solutions at concentrations ranging from 0 % to 15 % for 0, 7, 28, and 90 days. Their findings indicated that the leached concentration of Pb decreased when the concentration of NaCl increased.

However, (Zhou, Ogawa, and Kawai 2023) stated in their study that heavy metal leaching from OPC-based solidified samples would be higher in a chloride-rich environment. Similarly, in (Bobirică et al. 2018) study, because chloride has high ionic strength, it has the capacity to increase the solubility of most solids. Consequently, the mobility of leached ions is increased through the formation of ion pairs. Given these conditions, it is expected that solidified waste exposed to chloride would show more significant leaching compared to samples in a low-chloride environment.

In the same study,(Bobirică et al. 2018) it was stated that chlorides can react with some of the hydrated phases of the cement to form chloride-bearing phases such as Friedel's salt ($3CaO.Al_2O_3.CaCl_2$), Kuzel's salt ($3CaO.Al_2O_3.1/2CaCl_2.1/2CaSO_4.10H_2O$) and a series of calcium oxychlorides ($xCa\ (OH)_2.\ yCaCl_2.zH_2O$). However, the effect of the formation of such solid phases on leaching behaviour remains undiscovered.

5.2 Effects of Chloride on Compressive Strength

The influence of chloride on the CS of cement-based materials, such as mortar and concrete, has been the subject of numerous studies. In fact, chloride accelerates the dissolution of portlandite and decalcification of calcium-silicate-hydrate (C-S-H) phases of cement. it is followed by the extraction of calcium ions from the matrix, Pbing to increased material porosity. Additionally, the growth and development of cracks occur due to the crystallization of chloride salts, mostly magnesium and calcium chlorides, within the capillaries of the matrix. (Kurdowski 2002; Marchand et al. 2001; Delagrave et al. 1996) These combined effects significantly impact the CS of solidified samples.

However, in the study of (Liu et al. 2018), the study tries to find theeffect of chloride on CS by immersing solidified samples in NaCl solutions. Interestingly, the CS of the samples initially decreased during the first 7 days of immersion into NaCl solutions, whereas after that, it is increased with longer soaking durations.

In addition to the various conditions which is listed above, disposal of high chloride content has several adverse effects on both human infrastructure (Corrosion of Steel and Pipes) and some effects on the ecosystem (soil salinity, freshwater salinity, and animal poisoning. (Duan et al. 2024)

6 HEAVY METALS

The physical characteristics of metals, such as their heat conductivity and electrical resistance, are directly correlated with temperature, malleability, ductility, and even lustre, which are frequently used to define and distinguish them from nonmetals and metalloids. (Appenroth2010)

Chemically speaking, metals with an atomic mass greater than 20 and a specific gravity greater than 5 are considered heavy metals. From a biological point of view, the group of metals and metalloids that can be poisonous to both plants and animals, even at deficient concentrations, are referred to as "heavy". (Rascio and Navari-Izzo 2011)

Some examples are Cu, Zn, Cr, Pb, Fe, Co, Ni, Mn, and others. Even though some of these metals are necessary for biological processes like the production and proper operation of hormones, enzymes, cells, and metabolism, humans only require trace amounts of these substances. They may have adverse impacts on human health if their levels in the circulatory system increase. In general, it is important to consider heavy metals as being both biologically significant in trace amounts and having a high density. (Naveed, Oladoye, and Alli 2023)

As a result of growing urbanization and industrialization, the number of heavy metals in our natural environment has rapidly increased over the past several decades, generating severe concerns around the world. According to many studies, industrial and consumer items release more than 300 million tons of heavy metals annually, both necessary and unnecessary, that end up in the soil and water. Furthermore, metal contamination becomes a major issue when these wastes are improperly disposed of in landfills. Some metals have incredibly lengthy biological half-lives, which effectively turn them into cumulative toxins. Some metals are naturally carcinogenic as well. Electronic scraps, medical waste, metal finishing industrial waste, used petroleum catalysts, battery wastes, and fly ash are some of the main industrially produced wastes. (Naveed, Oladoye, and Alli 2023; Jadhav and Hocheng 2012)

6.1 Effect of heavy metals on living organisms

Heavy metal contamination of soil is a global issue impacting several nations. It is brought on by the release of waste from mining, industry, and agriculture, the use of pesticides and fertilizers without proper scientific study, and the irrigation of sewage. Because heavy metals are poisonous, their accumulation in agricultural soils can seriously affect the environment and pose a risk to food safety. Even in low quantities, highly toxic heavy metals can cause significant ecological threats to soil and water, and many of them can cause cancer in humans. (Jiang et al. 2022) as illustrated in **Figure 2 and Figure 3**, heavy metals in the soil damage ecosystems and can cause several diseases when ingested by humans via the food chain.

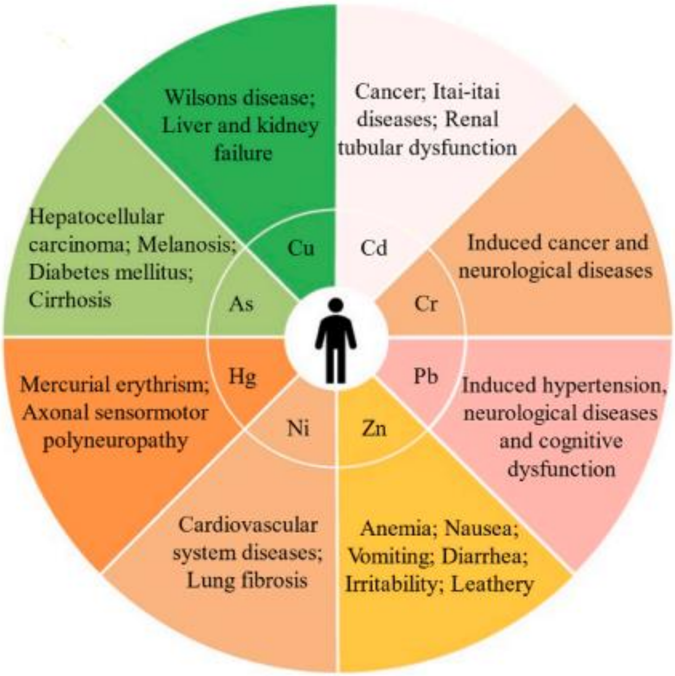

Figure 2. *Effect of heavy metal on humans* (Jiang et al. 2022)

It only becomes harmful when its level in the plant exceeds a predetermined threshold, as illustrated in **Figure 3**. This is especially significant considering the second truth, which states that some substances, referred to as micronutrients, serve crucial roles in plant cells. This has been demonstrated for Co, Cu, Fe, Mn, Mo, Ni, and Zn. They do not exhibit harmful effects until the internal concentration surpasses a specific threshold, at this point, they are referred to as "heavy metals." As far as we know, all these plant micronutrients are transitional components. For biosynthesis, growth, nucleic acids, growth agents, chlorophyll and secondary metabolites, carbohydrates, lipids, and stress tolerance, the functioning of membranes also depends on a sufficient intake of micronutrients. (Appenroth 2010)

Other heavy metals, such as Hg, Pb, and Pu, are toxic and have no known physiological or biological effects on living things. Their accumulation over time in the bodies of animals can result in life-threatening diseases. For some creatures or in some environments, certain substances that are typically harmful are advantageous. V, W, and even Cd are among examples. (Hawkes 1997)

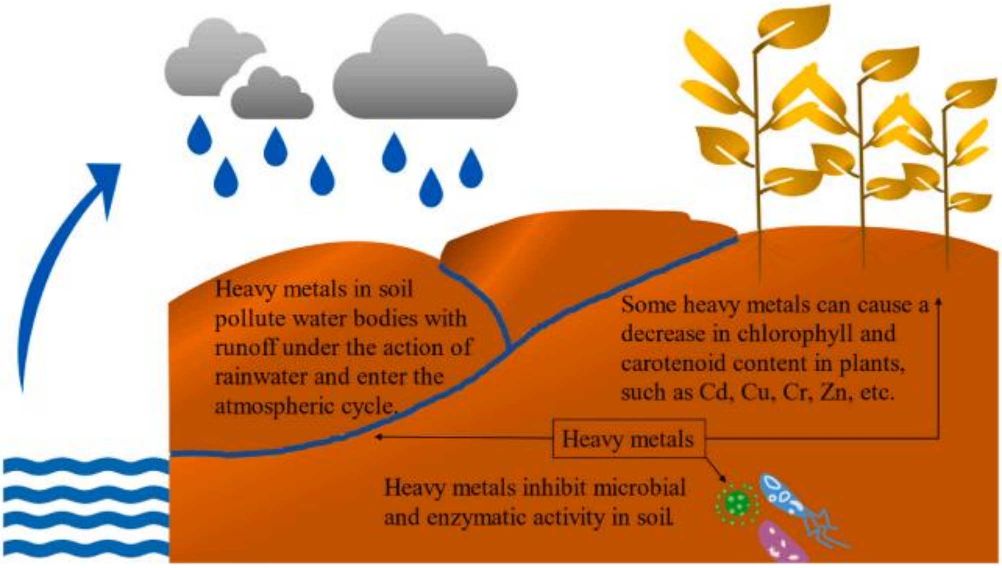

Figure 3. *Effect of heavy metals in the ecosystem*(Jiang et al. 2022)

7 LEAD

One of the simplest metals to mine is Pb, which can be melted at only modest temperatures. As a result, Pb has been used by humans for thousands of years. Pb was utilized by the Egyptians more than 7000 years ago for ceramic glaze, cooking utensils, cooking piping, weights, and anchors. Pb was also frequently utilized by the Romans. (Pattee and Pain 2003)

Despite the long history of usage of Pb, the demand rose significantly during the Industrial Revolution of the 18th and 19th centuries, and then again after the introduction of organic Pb compounds as antiknock agents in gasoline (first in 1923, then widely used after World War II). (Pattee and Pain 2003)

Today, Pb and its derivatives are used extensively, and the global commerce in this metal, whether impure or refined, as well as its minerals and compounds, has grown significantly. Pb is a very important commodity due to the quantity of the metal that is produced, the great economic worth of its trade, and the fact that its production and transformation employ a massive number of people. (Casas and Sordo 2006)

Pb is a significant component of more than 200 minerals and is both dense (11.34 g/cm^3) and extremely soft (35 diamond pyramid hardness). It is a relatively rare metal with an average concentration of 0.016 g Pb/kg soil in the earth's crust. (Pattee and Pain 2003)

The element is a group 14 heavy metal that is bluish-white and glossy. Pb crystals have a small Pb-Pb distance of 3.49 A and are face-centred cubic crystals. (Casas and Sordo 2006)

There are four stable isotopes of Pb: ^{204}Pb, ^{206}Pb, ^{207}Pb, and ^{208}Pb. The last three result from the corresponding radioactive series decay of ^{238}U, ^{235}U, and ^{232}Th. Contrary to gold, for instance, Pb is more frequently found in the compounds galena (PbS), carbonate ($PbCO_3$), and anglesite ($PbSO_4$). (Hynes and Jonson 1997; Casas and Sordo 2006)

It is extremely rare to find Pb as a pure element and it is usually present as Pb (II) in deposits with different origins, it is combined with other elements (sulfur and oxygen) or in various minerals with a wide range of compositions. (Casas and Sordo 2006) The main Pb minerals are summarized in **Table 3**.

Table 3. *Different types of minerals and compositions of Pb* (Casas and Sordo 2006)

Sulphides		**Other minerals**	
Mineral type	***Composition***	***Mineral type***	***Composition***
Galena	PbS	**Clausthalite**	$PbSe$
Geoeronite	$Pb_5(Sb, As)_2S_8$	**Altaite**	$PbTe$
Beegerite	$Pb_6Bi_2S_9$	**Penroseite**	$(Ni, Cu, Pb)2Se_2$
Bournonite	$PbCuSbS_3$	**Litharge**	PbO
Meneghinite	$CuPb_{13}Sb_7S_{24}$	**Massicot**	PbO
Boulangerite	$Pb_{2-5}Sb_{2-4}S_{5-11}$	**Minium**	Pb_3O_4
Cosalite	$Pb_2Bi_2S_5$	**Cerussite**	$PbCO_3$
Selenocosalite	$Pb_2Bi_2(S, Se)_5$	**Anglesite**	$PbSO_4$
Kobellite	$Pb_2(Bi, Sb)2S_5$	**Wallenite**	$PbMoO_4$
Selenokobellite	$Pb_2(Bi, Sb)_2(S, Se)_5$	**Crocoite**	$PbCrO_4$
Franckeite	$Pb_5Sn_3Sb_2S_{14}$	**Pyromorphite**	$Pb_3(PO_4)_3Cl$
Cylindrite	$Pb_3Sn_4Sb_2S_{14}$	**Vanadinite**	$Pb_5\ (SO_4)_3Cl$
Jamesonite	Pb_4FeSb_6Su	**Plumbogummite**	$PbAl_3(PO_4)_2(OH)_5\text{-}H_2O$
Semseyite	$Pb_9Sb_8S_{21}$	**Tsumebite**	$Pb_2Cu\ (OH)_3(PO_4)\text{-}_3H_2O$
Zinkenite	$Pb_6Sb_{14}S_{27}$	**Percyclite**	$Pb_3(CO_3)\ Cl_2$
Plagionite	$Pb_5Sb_8S_{17}$	**Phosgenite**	$Pb_2Cl_2CO_3$
Nagyagite	$Pb_5Au\ (Te, Sb)_4S_{5-8}$	**Boleite**	$Pb\ (Cu, Ag)\ Cl_2(OH)_2\text{-}H_2O$
Wittite	$Bi_6Pb_5(Se, S)_{14}$	**Argentiam**	$(Pb, Ag)\ Fe_3.6(SO_4)_{2-4}(OH)_{6-2}$
Fizelyite	$Pb_3Ag_2Sb_8S_{18}$	**Plattnerite**	PbO_2

7.1 Production of lead

Currently, Pb is utilized for Pb-acid storage batteries, alloys, cable sheathing, radiation shielding, construction (as sheets and pipes), paint pigments, glass, glazes, and enamels, as well as utilizable ceramics and other minor applications. (Casas and Sordo 2006) as is shown in **Figure 4**.

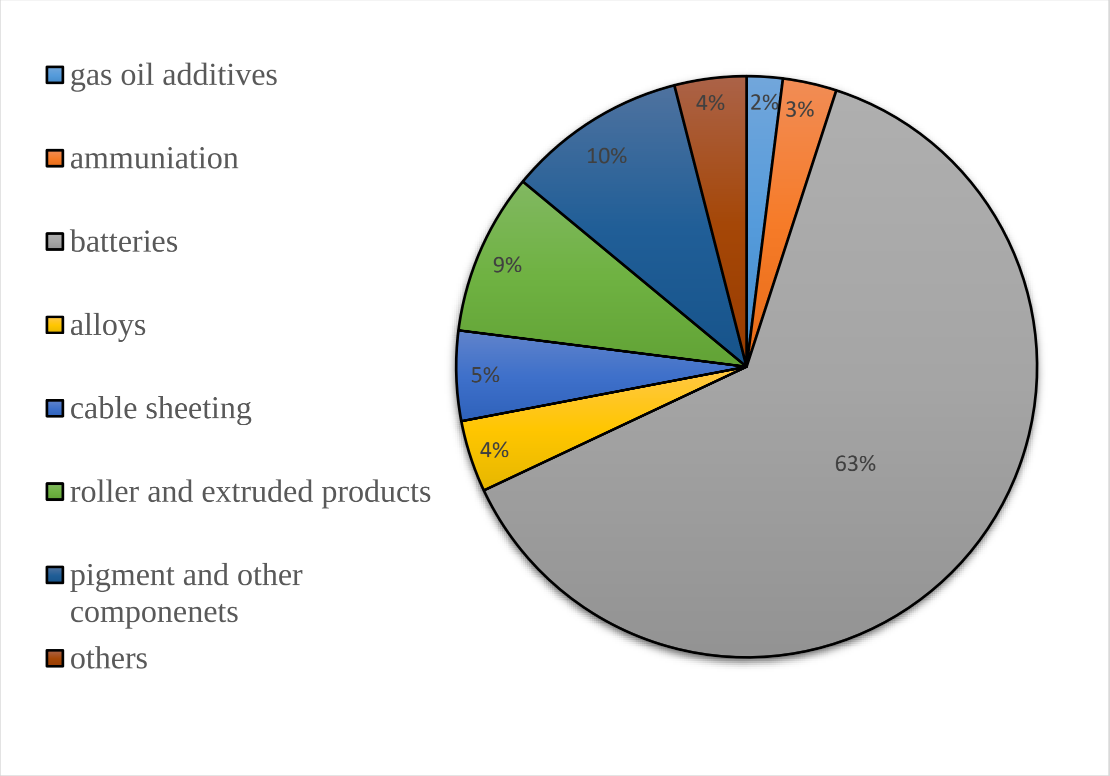

Figure 4. *Application of Pb worldwide* (Hynes and Jonson 1997)

Raw materials for producing Pb include both primary Pb ores, primarily galena-rich (PbS), and secondary resources, primarily used Pb-acid batteries. Resources for Pb in developed nations primarily originate from secondary Pb recovered during the recovery process. In the United States, secondary Pb accounts for more than 80 % of Pb production, while secondary Pb accounts for 90 % of Pb production in Europe. In emerging economies such as China, recycled Pb comprised 42 % of the total Pb output in 2016. Around 60-66 % of secondary Pb is produced globally. (Pan et al. 2019)

When primary Pb and secondary Pb are produced, substantial amounts of Pb slag are also formed. By way of illustration, a primary Pb smelting plant that produces 1 t of Pb produces

7100 kg of Pb slag. For every tonne of metallic Pb produced during the secondary Pb recycling process, 100–350 kg of slag is produced. The World Bureau of Metal Statistics reports that Pb production was 11.1 million tonnes in 2016 and that the production of Pb slag was over 5.5 million tonnes. (Pan et al. 2019)

The fluxes, impurities in the coke and iron, and the ore all affect the composition of primary Pb slag. The compositions of primary and secondary Pb slag are illustrated in **Table 4 and Table 5**. (Pan et al. 2019)

Table 4. *The composition of primary Pb slag.* (Pan et al. 2019)

Compounds/Elements	***Composition (%)***
Fe_2O_3	*2.07-32.47*
FeO	*9.49–28.90*
SiO	*14.68–43.09%*
CaO	*3.05–23.11%*
Al_2O_3	*1.73–6.22%*
MgO	*0.15–5.44%*
PbO	*2.82–11.11%*
ZnO	*11.11%*
S	*0.2–9.0%*

Table 5. *The composition of secondary Pb slag.* (Pan et al. 2019)

Elements	***Composition (%)***
Fe	*20.1 - 55.68%*
Ca	*1.3 - 22.43%*
Si	*2.6 - 20.57%*
Zn	*0.12 - 1.1%*
Pb	*1.15 - 21.97%*
Cu	*0.25 - 1.3%*
S	*0.52 - 20.5%*

Pb slag is mostly employed in rough disposal methods that need a lot of land, such as stockpiling and landfilling. Statistics show that more than 670 m^2 of land will be required to accumulate 10,000 t of waste residue. Pb, zinc, and cadmium are among the highly migrating hazardous metals found in Pb slag. Mineral phases in slag have an impact on the release of hazardous substances under weathering and leaching conditions. The primary determinant of the release of hazardous components from Pb slag is also the pH of the leachate. The soil and groundwater in the immediate vicinity will become contaminated by the landfill's hazardous materials and the accumulation process. (Pan et al. 2019)

7.2 Treatment of lead slag

There have been two attempts to address the Pb slag concern. The first step is to reduce the possibility of reducing the harmful substances in the Pb slag. Both pyrometallurgy and hydrometallurgy can be employed for eliminating toxic components, and they can also be immobilised in a S/S product such a geopolymer. Due to its advantageous mechanical and physical qualities, Pb slag is being used as an aggregate for concrete and road building, which is the second attempt to reduce the amount of Pb slag.(Pan et al. 2019)

7.2.1 Pyrometallurgy

It is an efficient method for recovering a high concentration of iron and the volatile elements zinc and Pb from primary Pb slag. The slag has an average iron content of above 30%. (Pan et al. 2019)

Since iron mostly exists as the minerals magnetite (Fe_3O_4) and fayalite (Fe_2SiO_4), iron concentration can be obtained via direct reduction and magnetic separation. Carbon monoxide, pyrolysis gas, carbon, and other reductants are used to decrease Pb components and zinc compounds so they can volatilize into flue gas as dust. For the treatment of Pb slag and the recovery of important metals, the direct reduction followed by the magnetic separation method is appropriate. (Pan et al. 2019)

7.2.2 Hydrometallurgy

A growing amount of focus has been placed on the recovery of Pb slag through the hydrometallurgical process, specifically for the secondary Pb slag, due to the tightening regulations around the discharge standard of pyrometallurgy. (Pan et al. 2019)

Metallic Pb (Pb) and galena (PbS) are the primary Pb compounds found in secondary Pb slag. Various methods, including acetic acid leaching systems, chloride leaching systems, and HNO_3-based leaching systems, are used to leach galena and metallic Pb to recover Pb. (Pan et al. 2019)

8 TOXICITY OF LEAD

At least as early as the second century B.C., when the Greek physician Nikander recorded the colic and paralysis that accompanied Pb intake, warnings of Pb's deadly characteristics were first made. Wine drinkers and Pb workers were the primary early victims of Pb intoxication. Due to its sweet flavour, Pb was useful in winemaking to balance the astringent taste of grape tannic acid. Pb-sweetened Wine, with up to 20 mg of Pb per litre, was a significant component of the diet of the Roman aristocracy. (Needleman 2004)

Landfilling and stockpiling are the primary methods of disposing of Pb slag; both require large amounts of land and intensify several environmental problems. Pb slag's environmental stability is dependent upon several parameters, including pH variations, the slag's mineral phase, atmospheric influences, and the duration of the slag-water interaction. Pb slag weathers easily with water and releases zinc, iron, and calcium more readily in acidic environments. (Pan et al. 2019)

Pb concentrations in the environment are not necessarily closely correlated with the amounts of Pb that enter and are absorbed by plants and animals from the atmosphere, soil, and water. Numerous aspects include the chemical and physical structure of the substance, the route of exposure, and the exposed organism's biology. Plants can absorb Pb through both wet and dry deposition. Surfaces, such as soil splash and road surfaces, as well as by uptake from roots. Pb that is inorganic reaches the earth for animals primarily by food and inhalation, and skin or gill absorption is significant for aquatic creatures. All animals have the potential to absorb organic Pb through their skin, but such Uptake is usually negligible. (Pattee and Pain 2003)

8.1 Toxicity of lead in plant

Pb's toxic effects on plants are most likely to happen close to point sources of Pb emission, in extremely high environmental concentrations, or when Pb is easily available for plant absorption (for example, in conditions of low soil or water pH, low soil calcium and phosphate, etc.). (Pattee and Pain 2003)

In the case of Pb slag, As the leaching time is extended, the concentration of hazardous components increases when the oxygen in the open air accelerates oxidative weathering and encourages the development of carbonate and secondary oxide phases, which make it simpler to release harmful elements. If anti-seepage methods are not perfect, toxic elements like Pb and Zn in the slag may seep into the soil with weathering and rainfall. The hazardous components in the soil will move to the plant body and affect the growth of nearby plants and animals since they are difficult for microorganisms to break down. (Pan et al. 2019)

There have been numerous reports of Pb's effects on plants, including disruption of cell membranes and mitosis, inhibition of plant growth, reduction of ATP (adenosine triphosphate) synthesis and structural protein formation, reduction of photosynthesis, water absorption, and transpiration rates, lengthening of generation times, and reduction in pollen germination and seed viability. (Pattee and Pain 2003; Naveed, Oladoye, and Alli 2023; Sardar et al. 2013)

When Pb was administered at 100–200 ppm concentrations, sugar beetroot plants showed a decrease in growth and chlorosis. (Naveed, Oladoye, and Alli 2023) 7-Week-old seedlings of autumn olive (*Elaegnus umbellata*) and loblolly pine (*Pinus taeda*) showed decreased transpiration and photosynthesis (by 10 to 25%) after being exposed to 320 ppm Pb in potting medium for weeks. (Pattee and Pain 2003)

8.2 Toxicity of lead in animals and human

Aquatic organisms are exposed to different effects of Pb depending on their species, exposure duration, tolerance development, Pb concentration, and environmental conditions that affect Pb solubility, like pH and water hardness. (Pattee and Pain 2003)

For example, the LC_{50} (concentration of total Pb needed to kill 50% of individuals) ranges from 612 µg Pb/mL with a water hardness of 54 mg $CaCO_3$/L to 1910 µg waste for daphnia magna exposed for 96 hours.

For aquatic organisms, Various sublethal effects can happen at deficient water Pb concentrations (7 µg/L), and water Pb concentrations of 10 µg/L can inhibit the activity of some hematopoietic enzymes, even though the concentration of Pb that causes lethality varies greatly depending on the chemical form of Pb (with organic forms tending to produce toxic effects at lower concentrations than Pb^{2+}) and composition of the water. (Pattee and Pain 2003)

Cattle that consume 5 to 7 mg of Pb per kilogram of body weight per day will either die from sublethal Pb poisoning or experience Pb poisoning.(Pattee and Pain 2003)

At the molecular level, Pb is a non-specific toxin that prevents many enzymes from doing their functions normally in the body. The effects of Pb on the hematological system, brain, neurological system, learning and behaviour, reproduction, and survival are those that have been the subject of the most research in the case of humans.(Pattee and Pain 2003; Needleman 2004; Casas and Sordo 2006; Sardar et al. 2013) Some of the effects of organic Pb are illustrated in **Table 6**. Due to their propensity for pica (use of their hands and mouths) and increased intestinal absorption and retention rate, children are more exposed to Pb exposure than adults. (Needleman 2004; Casas and Sordo 2006)

Table 6. *The effect of organic Pb in human beings.* (Gidlow 2004)

Toxicological effect	***Concentration***	***Description***
Reproductive	*>=50 µg/100ml (in sperm samples) in some cases, >= 40 µg/100 ml (in sperm samples)*	*Affect sperm morphology and function.*
Neurotoxicity	*>= 40 µg/100 ml (in Blood samples)*	*It affects child neuropsychological development at blood Pb levels above 20 µg/100 ml.*
Carcinogenicity	-	*Stomach cancer, lung cancer*
Renal function	*>= 40±13 µg/100 ml (in Blood samples)*	*Affect sperm morphology and function.*
immunology	*>= 50 µg/100 ml (in Blood samples)*	*An increased percentage and increased absolute count of B lymphocytes*
Toxicokinetic	*>= 40 µg/100 ml (in Blood samples)*	*Inhibition of ALAD activity*

9 AMENDMENTS FOR LANDFILL OF HAZARDOUS WASTE

Current concerns include the creation of hazardous waste on an international level and its effective mitigation. The Solidification and Stabilization process is one of the most common ways to physically and chemically treat waste that cannot currently be used in an effective way, and it can considerably improve the quality of waste disposal. These methods are distinguished by a reduction in waste surface area while maintaining a hazardous material content. Hazardous compounds are chemically bonded to a matrix of inert organic or inorganic molecules, forming a barrier between them and the environment around them. It builds physical and chemical barriers that keep these pollutants from entering the environment rather than reducing the number of contaminants present in the waste. (Vacenovska and Drochytka 2012)

Many nations have their laws. However, leachability, free liquid content, and permeability are requirements for the disposal of solidified waste in landfills. (Hunce et al.,2012)

9.1 Amendment in Europe

The disposal of hazardous waste, which is stable, non-reactive waste, means that its leaching behaviour stays the same over time, under landfill design conditions, or as a result of foreseeable accidents: in the waste alone (for instance, by biodegradation), under the influence of long-term ambient conditions (for instance, water, air, temperature, mechanical constraints), or the influence of other wastes (including waste products like leachate and gas). (European Commission 2003) The requirements for the disposal of hazardous waste in Europe are summarized in **Table 7 and Table 8**.

9.1.1 Leaching requirement

Table 7. *Leaching limits values of elements for hazardous waste* (European Commission 2003)

Elements	***L/S = 2 L/Kg***	***L/S = 10 L/Kg***
	mg/kg dry substance	***mg/kg dry substance***
As	*6*	*25*
Ba	*100*	*300*
Cd	*3*	*5*
Cr	*25*	*70*
Cu	*50*	*100*
Hg	*0.5*	*2*
Mo	*20*	*30*
Ni	*20*	*40*
Pb	*25*	*50*
Sb	*2*	*5*
Se	*4*	*7*
Zn	*90*	*200*
Cl-	*17,000*	*25,000*
F-	*200*	*500*
sulphate	*25,000*	*50,000*
DOC	*480*	*1,000*
TDS	*70,000*	*100,000*

The waste may also be evaluated at L/S = 10 L/Kg and a pH of 7.5-8.0 if the DOC values are not met at the material's pH. If the assessment yields a result below 1,000 mg/kg, the waste may be considered to meet the DOC acceptance requirements.

The TDS values can be utilized instead of the sulfate and chloride values. (European Commission 2003)

9.1.2 Additional requirements for Hazardous waste

Table 8. *The additional parameters for hazardous waste* (European Commission 2003)

Parameters	***Values***
LOI	*10%*
TOC	*6%*
ANC	*must be evaluated*

Either LOI or TOC must be evaluated. If this value is not achieved, a higher limit value may be admitted by the competent authority, provided that the DOC value of 1 000 mg/kg is achieved at L/S = 10 L/Kg, either at the material's own pH or at a pH value between 7.5 and 8.0. (European Commission 2003)

9.2 Amendment in Africa and Ethiopia

According to the Organization for Economic Cooperation and Development (OECD) report, the cost of Hazardous waste disposal in developed countries ranges from USD 100 to USD 2000 per ton, while these costs ranged from USD 2.50 to USD 50 per ton in African countries.

Due to the high cost of disposing of such wastes in their countries and due to the less stringent environmental rules and regulations in Africa, the large amounts of hazardous wastes generated in rich countries are typically transferred across to African nations. (Akpan and Olukanni 2020)

The main drawback of the landfill method in Africa starts with sorting at the place of generation, even though it is said to be a simple and affordable form of waste disposal. Because of this, it is easy to find hazardous waste products in African landfills, which in some cases have caused groundwater contamination. Furthermore, handling hazardous wastes is a major weakness for African landfills. (Akpan and Olukanni 2020) A summary of some of the African countries' hazardous waste disposal is shown in **Table 9**.

Ethiopia has some regulations for controlling the environmental impacts of industrial wastes, including hazardous ones. However, the enforcement of these rules is weak, and the waste management system is inadequate. The Hazardous Waste Management and Disposal Control Proclamation No. 1090/2018, has two major principles. The first section is minimizing the release of hazardous waste by reducing or eliminating the hazardous substances in the raw materials during the production process and monitoring the production process by:

a) controlling the production of hazardous waste.

b) creating conditions necessary for the collection and reusability or recyclability of the product after its expiry period.

The second section is that one of the responsibilities of hazardous waste producers is to collect, segregate, and dispose or cause to be collected, recycled, or disposed of hazardous waste by an authorized body, whereas, like the European Council, there is no limit of landfill disposal of hazardous waste.

Table 9. *A review of a landfill in Africa and their ratings, based on the agreement of international rule* (Akpan and Olukanni 2020)

Level of landfill control	***Rating***	***Country and land fill location***	***Characteristics***
Zero level of control	*0*	*Mebellewa (Cameroon)* *Antula (Guinea Bissau)* *Awotan (Nigeria)* *Lapite (Nigeria)* *Eneka (Nigeria)* *Ajankanga (Nigeria)* *Aba-Eku (Nigeria)* *Unguwan (Nigeria)* *Wakaliga (Uganda)* *Bakoteh (Gambia)* *Kadhodeki (Kenya)* *Gachororo (Kenya)* *Kosha (Ethiopia)*	*limited controlled functions, uncontrolled burning, open dumping and No leachate collection system* ***Note: -*** *Not capable of Handling Hazardous Waste*
Semi-controlled	*5*	*Solous (Nigeria)* *Musaka (Nigeria)* *Mpape (Nigeria)* *Epe (Nigeria)* *Granville (sierra Leone)*	*No leachate Collection Facilities* ***Note:*** *-Not capable of Handling Hazardous Waste*

		Kingtom (sierra Leone) *Grankuwa (south Africa)* *Nduba (Rwanda)* *Hatherley (South Africa)* *Vingunguti (Tanzania)*	
Medium or controlled	*10*	*Olusosun (Nigeria)* *Dompoase (Ghana)*	*A degree of the trained workforce who follow a set of instructions in daily operations. Facilities are available to capture particulates; equipment may be managed appropriately.* ***Note:*** *- Not capable of Handling Hazardous Waste*
Medium to High (professionally controlled)	*15*	*Costal Park (South Africa)* *Bellville south (South Africa)* *Robinson Deep (South Africa)* *Gamodubu (Bostwana)*	*A high level of planning is taken in the location, daily operation, and emission control.* *Daily cover materials are utilized, leachate collection systems are available to a certain degree, and a method for gas collection is put in place.* ***Note:*** *- Capable of Handling Hazardous Waste*
Highly Controlled	*20*	*None*	*These are state of the art facilities that comply with international regulations and standards. Efficient Hazardous waste management potential, leachate, and gas harnessing are sustainable; post-closure plans are put in place.* ***Note:*** *- Capable of Handling Hazardous Waste*

10 EVALUATION AND DETERMINATION OF LEAD WASTE

10.1 Leaching procedures

10.1.1 Types of Leaching Test

In the field of environmental engineering, two primary types of leaching tests are commonly used, according to (Timothy Townsend Yong-Chul Jang Thabet Tolaymat Department of Environmental Engineering Sciences University of Florida 2003) The first category consists of batch leaching tests, which include the Extraction Procedure Toxicity (EP-Tox), Toxicity Characteristic Leaching Procedure (TCLP), Synthetic Precipitation Leaching Procedure (SPLP), Waste Extraction Test (WET), American Society for Testing and Materials extraction test (ASTM D 3987-85), and Multiple Extraction Procedure (MEP). These batch tests mostly involve mixing small-size waste with an extraction solution and agitating the mixture. Due to their relatively short duration (it takes hours or days), they are often referred to as short-term tests. The key differences between these tests are the choice of leaching solution, the liquid-to-solid (L/S) ratio, and the number and duration of extractions.

The second type is the column or lysimeter test, which tries to simulate the behaviour of waste materials. In this test, the waste material is placed in a column or lysimeter, and a leaching solution is continuously added to produce leachate. Unlike batch leaching tests, where the solution remains static, this approach more closely represents field conditions. However, controlling the experimental conditions of this test is challenging. Operational issues like channeling and column clogging may happen and a negative result can be gained.

10.1.2 Toxicity characteristic leaching (TCLP 1311)

An essential technique for determining the mobility of organic and inorganic analytes found in liquid, solid, and multiphasic hazardous wastes is the Toxicity Characteristic Leaching Procedure (TCLP). It helps assess the environmental impact of these elements through their leaching potential. The TCLP extract is the liquid that remains after being filtered through a glass fibre filter measuring between 0.6 and 0.8 µm. Suppose the waste contains less than 0.5% dry solid material. The liquid phase is separated from the solid phase in wastes comprising more than or equal to 0.5% solids, and the solid phase is extracted using an extraction fluid volume (20 times the weight of the solid phase). An extraction fluid selection is necessary based on the solid waste's alkalinity. For instance, volatile analytes are examined using a special extractor bottle. The solid phase is subsequently filtered out of the liquid extract. The waste is deemed hazardous without additional examination if an analysis shows that a controlled compound is present in higher amounts. (U.S. Environmental Protection Agency (EPA) 1992)

10.1.3 European Norm (EN 12457)

Waste leaching is thoroughly characterized by the EN 12457 standard. It consists of compliance testing for sludge and granular waste material leaching as follows:

Section 1: One-stage batch test for materials with a high solid content and a particle size of less than 4 mm (with or without size reduction), conducted at a liquid-to-solid ratio of 2 L/Kg.

Section 2: One-stage batch test (with or without size reduction) for materials whose particle size is less than 4mm at a liquid-to-solid ratio of 10 L/Kg.

Section 3: Two-stage batch test for materials with a high solid content and particle sizes less than 4 mm (with or without size reduction), at liquid-to-solid ratios of 2 L/Kg and 8 L/Kg.
Section 4: One-stage Batch test at a liquid-to-solid ratio of 10 L/Kg for materials with particle size below 10 mm (with or without size reduction). (BS EN 12457 2024; European Commission 2003)

10.2 Instrumental Determination of Pb

10.2.1 Spectrometry determination

Some analytical equipment with high-sensitivity detection capabilities is available to determine Pb at ppm or sub-ppm levels, such as graphite furnace atomic absorption spectroscopy (GFAAS) and inductively coupled plasma mass spectroscopy (ICP-MS). Ion chromatography has also determined Pb in different matrices, whereas GFAAS and ICP-MS are recommended for sensitivity. However, their price is extremely high, for instance, the price of an ICP-MS apparatus typically varies from $250,000 to $750,000, and the cost of operation each day can exceed $1000. Additionally, ICP-MS and GFAAS require a very clean working environment because only a small quantity of sample solution can be put into the instrument. This increases the expense of maintenance for operating the instruments, especially an ICP-MS. Due to this, many analytical facilities are unable to purchase an ICP-MS. Furthermore, even though GFAAS equipment costs less than $20,000, it is not economically beneficial for labs where Pb analysis is not a regular activity. (Lang Lang, Konghwa Chiu, and Qingyong Lang 2008)

In the case of environmental samples with a Pb concentration above 0.2 mg/L, it is possible to use FAAS (Flame Atomic Absorption Spectroscopy), which has a performance characteristic of sensitivity of 0.5 mg/L, detection limit 0.1 mg/L and optimal concentration range from 1 to 20 mg/L and it is cheaper compared to ICP-MS and GFAAS, but it requires extraction. (Csuros and Csuros 2002)

For analysis of samples with a higher concentration of elements, higher sample dilution is required, which would result in significant mistakes because of this it is recommended to find a quick and precise method for identifying the constraints. Rapid, multi-element chemical composition analysis is possible with XRF, which has found widespread application in fields such as metallurgy, geology, environment, biology, food, and so on. (Tian et al. 2018)

10.2.2 X-ray fluorescence analysis

One of the modern spectroscopic techniques to determine a substance's crystalline phase composition is X-ray fluorescence (XRF) analysis, which measures the emission of the distinctive fluorescent X-rays emitted by a substance that has absorbed high-energy X-ray radiation. The excited state of the atoms in the irradiated material is brought about by interaction with high-energy photons. The atom recovers to a ground state after becoming excited for approximately one femtosecond. The extra energy is now released as a photon or transmitted to another electron from the outer shells when vacancies (K, L, M, etc.) are filled with electrons from the outer shells. Only transitions that follow the guidelines for choosing electric dipole radiation from outer shells or subshells are permitted. The element can be identified using the group of distinctive X-rays from each element, including all transitions. (Kirichkov et al. 2023)

The geochemical sample analysis covers a broad concentration range of 0.0001% to 80% for elements ranging from Na to U. The detection limits for medium Z elements range from 20–1000 μg/g and for high Z elements, from 1 to 20 μg/g depending on sample preparation. (Kirichkov et al. 2023)

II. ANALYSIS

11 CHEMICALS AND LABORATORY EQUIPMENT

11.1 Laboratory Equipment

- Elva, X-Ray Fluorescence Spectrometer, Ukraine
- Atomic absorption spectrometer ContrAA 800, Analytikjena, Germany
- Analytical balances Kern ABJ 220-4NM, Germany
- Electromagnetic mixer MM4, Lavat, Czech Republic
- pH meter 720 WTW series InoLab - combined pH electrode: pH electrode SenTix 41, WTW, pH range 0-14 /0-80 °C/ store in 3 mol/l KCl, Germany TBU in Zlín, Faculty of Technology 37
- Laboratory furnace MP 05-1.0, Laboratory furnace Martínek, Czech Republic •
- RZR 2020 overhead stirrer (Heidolph & Co.KG. Germany)
- Laboratory Motorized Hydraulic Press (BSML 21 – Brio Hranice s.r.o.).
- TOC-L (SHIMADZU-Total Organic Carbon Analyzer)
- Polypropylene container 30*25 mm
- Digital caliper and brushing papers
- glass fibre filter paper (0.45 µm). (Papirny Pernstejn Ltd., Czechia)

11.2 Chemicals

- Acetic acid, CH_3COOH (Penta chemicals, Czechia)
- Portland Cement (CEM 1 42.5 R, Cement Hranice, Czechia)
- Single element standard (1g L^{-1}) – Cu, Pb, Ni (ASTASOL Czechia)
- Multi-element standard ANM1004 (10 mg L^{-1}) (ASTASOL Czechia)
- Nitric Acid, HNO_3, 65% (Penta chemicals, Czechia)
- Sodium Chloride, NaCl (Penta Chemicals, Czechia)
- Silver nitrate, $AgNO_3$ (Penta Chemicals, Czechia)
- FBCA - fluidized bed combustion ash

12 WASTE CHARACTERIZATION

The waste sample comes from the semi-automatic, discontinuous KVE-2 explosion chamber, a technological apparatus that consists of two hemispheres that open hydraulically and have an internal volume of 1.9 m^3. Although the chamber is intended to blow 2 kg of explosives, it cools down to an outlet temperature of 50°C, producing a maximum of 2 Nm^3 of gaseous products at an initial temperature of 2000°C. (Bc. Ondřej Hrubý 2008; Cervinkova et al. 2007)

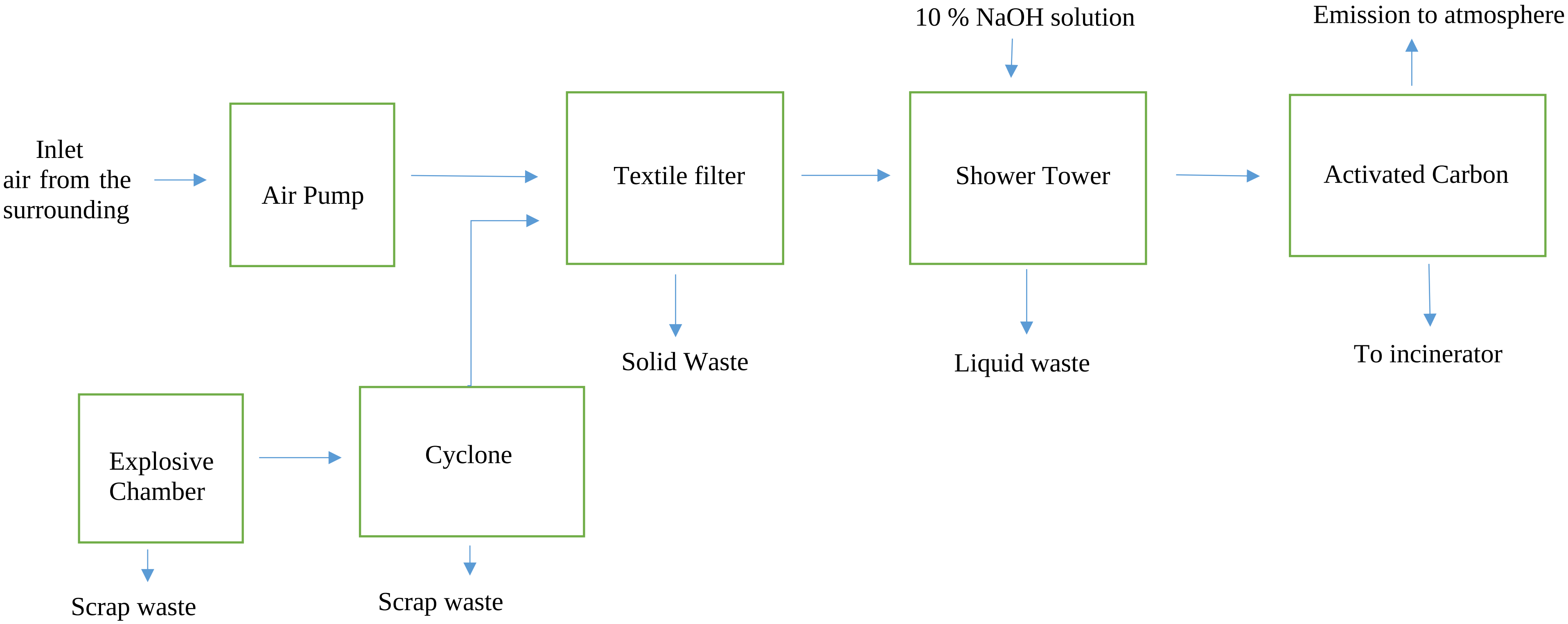

Figure 5. *The scheme of industrial process of ammunition waste.* (Bc. Ondřej Hrubý 2008; Cervinkova et al. 2007)

13 METHODOLOGY

13.1 Sample preparation

Under Hazardous Waste standards, samples were extracted using a leachate composed of acetic acid and distilled water. Following the TPLC 1311 standard and EN 12457-4 norm, acetic acid-leached samples were prepared with a ratio of 1:20 (10 g of sample in 200 ml of acetic acid) and a particle size of ≤ 1 mm. A liquid-solid ratio of 10:1 was used for distilled water-leached samples, with a particle size of ≤ 10 mm for the mixture preparation.

after that, the prepared mixture underwent automatic agitation at 150 RPM for 24 hours (for distilled water-leached samples) and 18 ± 2 hours (for acetic acid-leached samples). Then the agitated mixture was filtered through glass fibre sheets with a pore size of 0.45 µm. Finally, the filtered samples were presented for FAAS analysis.

The pH of the leaching liquids used in the leaching process was measured to be 2.88±0.05 (acetic acid) and 7.84 (distilled water). Additionally, for XRF determination, a sample mass of 20 g was utilized.

13.2 Total Dissolved solid (TDS)

Six tannery dishes were first dried overnight at 105°C in an oven, and their weight was recorded. Each set of three containers was labelled to a specific sample, along with its corresponding leaching liquids (acetic acid and distilled water). After that, 25 ml of the filtered, leached sample was dispensed into each pre-weighed tannery dish. After another overnight drying cycle at 105°C, the weight of each tannery dish was recorded. The Total Dissolved Solids (TDS) content was then calculated using Equation 1. (Vinter et al. 2016)

$$TDS = \left(\frac{W_2 - W_1}{V_0}\right) * 1000 \quad [g/L] \qquad (1)$$

Where: TDS – total dissolved solids (g/L)

W_2 – weight of tannery dishes (g)

W_1 – weight of tannery dishes with samples after oven-dry (g)

V_0 – sample volume (L)

13.3 Total Organic Carbon (TOC) and Dissolved Organic Carbon (DOC)

To evaluate the content of the TOC and DOC of the Leached waste sample, a TOC-L (SHIMADZU-Total Organic Carbon Analyzer) was used. This instrument operates via the TOC-Control L computer software. The selected system in the software was TOC + ASI. Before measurement, all samples go through filtration using a 2.5 µm filter paper. This filter paper was initially washed with hot water and dried for at least 2 hours in an oven dryer to ensure complete dryness.

13.4 Metal content determination

13.4.1 FAAS (Flame Atomic Absorption Spectrophotometer)

The waste samples and calibration solutions were analysed using an air-acetylene flame on the contrAA 800D atomic absorption spectrophotometer manufactured by Analytical Jena in Germany. To minimize interference in the process of analysing in the FAAS system, distilled water, and nitric acid were utilized. The targeted elements were measured at specific wavelengths, as detailed in **Table 10**. Additionally, the concentration of unknown samples was determined by applying linear regression to the constructed calibration curve.

***Table 10**. Detected Metals and their respective wavelengths.*

Wavelength (nm)	***Element***
327	*Cu*
228	*Cd*
213	*Zn*
232	*Ni*
248	*Fe*
313	*Mo*
217	*Pb*
196	*Se*
206	*Sb*
357	*Cr*

Additionally, all of the analysed samples from FAAS measurements unit were changed to mg/kg using **Equation 2**. (F.James Holler & Stanley R. Crouch 2016)

$$c_a = \frac{c_b * V}{m} \qquad (2)$$

Where: c_a – calculated concentration in (mg/kg)

c_b – analysed concentration from FAAS (mg/L)

$V(mL)$ – Volume of leachate (ml)

$m(g)$ – mass of the S/S sample used for leaching (g)

13.4.1.1 Lead, Zinc and Copper Determination

The concentration of Pb was determined from acetic acid-leached samples and distilled water-leached samples at a wavelength of 217 nm, using a selected dilution factor of 100×. Additionally, five calibration solutions were prepared, covering a concentration range from 0-50 mg/L. Moreover, the zinc content was determined at wavelength 317 nm, and five calibration standards were prepared with a concentration range of 0-5000 mg/L. Also, Cu was determined at a wavelength of 327 nm, and five calibration solutions were prepared with a concentration range of 0-10 mg/L.

13.4.1.2 Other Heavy Metal Determination

To determine other heavy metal presence in the sample a QCM (quality certified material) - ANM 1004 was used. The concentration of the leached samples (water and Acetic acid) was measured without dilution. The prepared calibration solution had a concentration range from 0-10 mg/L.

13.4.2 XRF (X-ray Fluorescence Spectrophotometer)

Elemental analysis was carried out by energy dispersive X-ray fluorescence spectrophotometer equipped with a Rhodium X-ray source. It was manufactured in Ukraine by the company ELVATECH. It is controlled by the computer software ElvaX 2.8.2. Both tasks were implemented light (tube current 25 uA tube voltage 10 kV) and heavy (tube current 10 uA and tube voltage 45 kV) to measure the waste samples. To prevent interference, mainly between the reaction of light metals with air, helium gas was also used during the measurement. The analysis time was set to 120 seconds, and the samples were analysed as powders in a special container made from polypropylene with a diameter of 30 mm and a height of 20 mm.

13.5 Stabilization and Solidification of waste

13.5.1 S/S of waste without considering Wa/C ratio (Method 1)

In this study, a solidifying mixture was created by combining waste and binder in different compositions. The binder used was Portland cement (CEM 1 42.5 R) from Cement Hranice. Sample weights were determined based on the waste-cement (W/C) ratio. In the experiment, three blank samples with a composition of 1:3 (cement to sand) and seven W/C compositions were prepared. These compositions covered a waste content range from 20 % to 80 % by weight. For each composition, two waste samples and three blank samples were meticulously prepared.

The waste and cement were mixed for approximately ten minutes using an overhead stirrer (RZR 2020). During sample preparation, distilled water (16-40 ml) was added to enhance the workability of the paste and for the creation of cement hydration. Subsequently, the paste was cast into 30 x 50 mm cylinder moulds and stored in a dark environment for 28 days. The total weight of the solidifying mixture was 50 g.

After a 28-day curing period, the compressive strength of the S/S samples was recorded using the Laboratory Motorized Hydraulic Press (BSML 21 – Brio Hranice s.r.o.). Before measurement, the top surface of the solidified material was meticulously smoothed to achieve a flat surface. This was achieved by rubbing the solidified material on a concrete brick.

Finally, the S/S samples underwent leaching tests according to the TCLP 1311 protocol (refer to sub-chapter 10.1). The samples were presented for FAAS measurement after removing suspended solids using a 0.45 μm glass fibre filter.

13.5.2 S/S, considering water as one parameter, also controls the Wa/C ratio (Method 2)

In this study, the procedures closely follow those outlined in Subchapter 10.3.1. However, a key distinction lies in the added amount of distilled water is also seen as one parameter as is shown in **Figure 6**. Besides that, the Wa/C ratio was controlled to be in the range of 0.3 to

0.5. Three (90:10, 85:15, 80:20) solid-water (S/Wa) composition was selected, and for each composition, two samples of W/C were prepared, resulting in a total of six distinct combinations in which the waste composition ranges from 30 % to 70 % by weight.

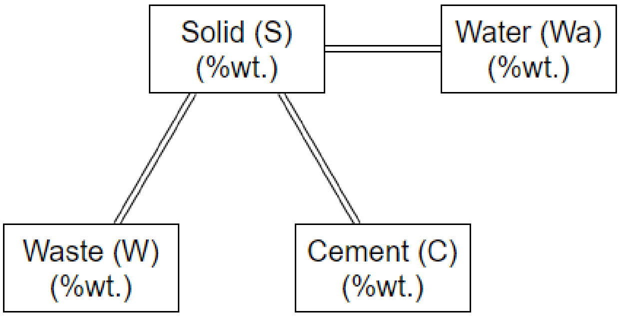

Figure 6. *Scheme of preparation of samples.*

13.5.3 S/S of waste by adding NaCl (Method 3)

In this study, a S/Wa composition of 80:20 and a W/C composition of 30:70 was selected. The study aimed to find the impact of different water types, environmental conditions, and the effect of Chloride on the S/S process. The addition of chloride was in the form of NaCl. The water-cement ratio was controlled (within the range of 0.3 to 0.5), the used water type was considered as one parameter and 80:20 S/Wa was selected. Four different conditions were tested:

Condition 1: Samples prepared with distilled water exposed to sunlight. **(Cond 1)**
Condition 2: Samples prepared with tap water exposed to sunlight. **(Cond 2)**
Condition 3: Samples prepared with distilled water placed in a dark environment. **(Cond 3)**
Condition 4: Samples prepared with tap water placed in a dark environment. **(Cond 4)**

Each water type contained a calculated amount of dissolved NaCl. The NaCl amount was calculated based on stoichiometry calculation (1 mol of Pb = 2 mol Cl) from the potential reaction of Pb with Cl ($2NaCl + Pb \rightarrow 2Na + PbCl_2$). The initial Pb concentration in the waste served as the foundation for calculating the mass of NaCl, which was subsequently determined using FAAS. For each combination, two samples were prepared.

13.5.4 S/S of waste by adding NaCl (Method 4)

Three distinct combinations were prepared, the waste content ranging from 40% to 80% by weight. In each combination, tap water and distilled water were employed, and all samples were exposed to sunlight. Furthermore, the water-cement ratio was carefully controlled within the range of 0.3 to 0.5. For each combination, a total of two samples were prepared.

13.5.5 S/S of waste by Pozzolan method (Method 5)

In this method, the binder was composed of a combination of FBCA and OPC. Four distinct combinations were prepared, with waste content ranging from 30% to 60% by weight. The cement content constituted 10% of the total binder content in each combination. Additionally, distilled water was utilized to enhance the workability of each mixture.

13.6 Compressive strength (CS)

To evaluate the compressive strength, all the brushed samples underwent a 100 kN force for 60 seconds using the Laboratory Motorized Hydraulic Press (BSML 21 – Brio Hranice s.r.o.) until they fractured. Subsequently, CS was computed using **Equation 3**. (S. B. Singh, Munjal, and Thammishetti 2015b) Additionally, to determine the surface area, the diameter of the samples was measured using digital micrometres.

$$CS = \frac{F}{A} \qquad [MPa] \qquad (3)$$

Where: CS – compressive strength of a material (MPa)
F – Applied load (kN)
A – Surface Area (mm^2)

13.7 Chloride Content

A total of eight compositions of solidifying mixtures, each comprising two samples, were tested to assess the chlorine content. These samples were derived from S/S materials that utilize NaCl and comply with European landfill regulations.

The argentometric titration method was used to find the concentration of chlorine in each sample. This method depends on the reaction between the Cl^- in the samples and Ag^+ to form AgCl. The occurrence of this reaction was visualized using K_2CrO_4 as an indicator. After measuring the titration volume, the concentration of chloride in the samples was calculated using **Equation 4** (Vinter et al. 2016) then the founded g/L results were converted to mg/L according to **Equation 2**. Each sample was measured three times, 10 ml of the sample was used for every titration.

$$c_{Cl^-} = M_{Cl} * V_{AgNO_3} * c_{AgNO_3} * f_D * \frac{1}{V_{sample}} \qquad g/L \qquad (4)$$

Where: c_{Cl^-} - concentration of NaCl in the prepared solution (g/L)

M_{NaCl} – the molar mass of NaCl (g/mol)

C_{AgNO_3} – concentration of AgNO3 (mol/L)

V_{AgNO_3}– endpoint volume of volumetric solution of AgNO3 (mL)

f_D - dilution factor

V_{sample} – volume of sample analysed (mL)

13.8 Statistical analysis (SA)

In this study all the gained data from every analysis was arranged according to statistical analysis using confidence interval calculation as shown in **Equation 5**, and the assumed Confidence interval was 95 %. (Chunlong Zhang 2007)

$$CI = \widetilde{X} \pm Z\frac{s}{\sqrt{n}} \qquad (5)$$

Where: CI – confidence interval (95 %)

$\widetilde{X}$ – sample mean

Z – confidence level value (0.05)

s – standard deviation of samples

n – sample number

14 RESULT AND DISCUSSION

14.1 FAAS results

14.1.1 Lead Concentration

Table 11. *The leached concentration of Pb in different leachates.*

LT	c_{Pb} (mg/kg)	pH	TOC (mg/kg)	DOC (mg/kg)	TDS
DW_{LT}	ND	7.82±0.32	1197.2±60	950.4	5,960±448
AA_{LT}	61,540±156.8	5.82±0.04	-	-	-

Following the findings presented in **Table 11**, it is observed that the Pb concentration exceeds the permissible limit of 50 mg/kg, as stipulated in the 2003/33/EC decision by the European Commission. Furthermore, the pH level of the acid-leached samples (AA_{LT}) is below 6, while the distilled water-leached samples (DW_{LT}) remain within acceptable limits. Additionally, the DOC, TOC, and TDS analysis shows that the waste remains well below the permissible limit specified by the European Union landfill regulations. (European Commission 2003)

14.1.2 Other heavy metals

Table 12. *The presence of heavy metals in the sample.*

Elements	LT		EU standard for Lf (L/S =10 L/Kg)
	W_{LT} (mg/kg)	AA_{LT} (mg/kg)	mg/kg
C_{Cd}	0.1395	235.6	5
C_{Cu}	ND	6620	100
C_{Zn}	ND	518.8	200
C_{Ni}	0.138	1056	40
C_{Fe}	ND	ND	-
C_{Mo}	18.85	15.95	30
C_{Se}	7.438	7.788	7
C_{Sb}	4.382	2.766	5
C_{Cr}	ND	ND	70

Based on the AAS analysis, which is shown in **Table 12**, the samples leached with acetic acid showed concentration levels of specific elements (Cd, Cu, Zn, Se, and Ni) that surpass the permissible limits established by European regulations. However, the remaining elements remain within acceptable limits. Notably, the samples leached with distilled water, only Se exceeded the permissible limit, while the other elements remained below the specified limit. (European Commission 2003) Consequently, using acetic acid for leaching is seen as a successful strategy for further experimental evaluations.

14.2 X-Ray fluorescence

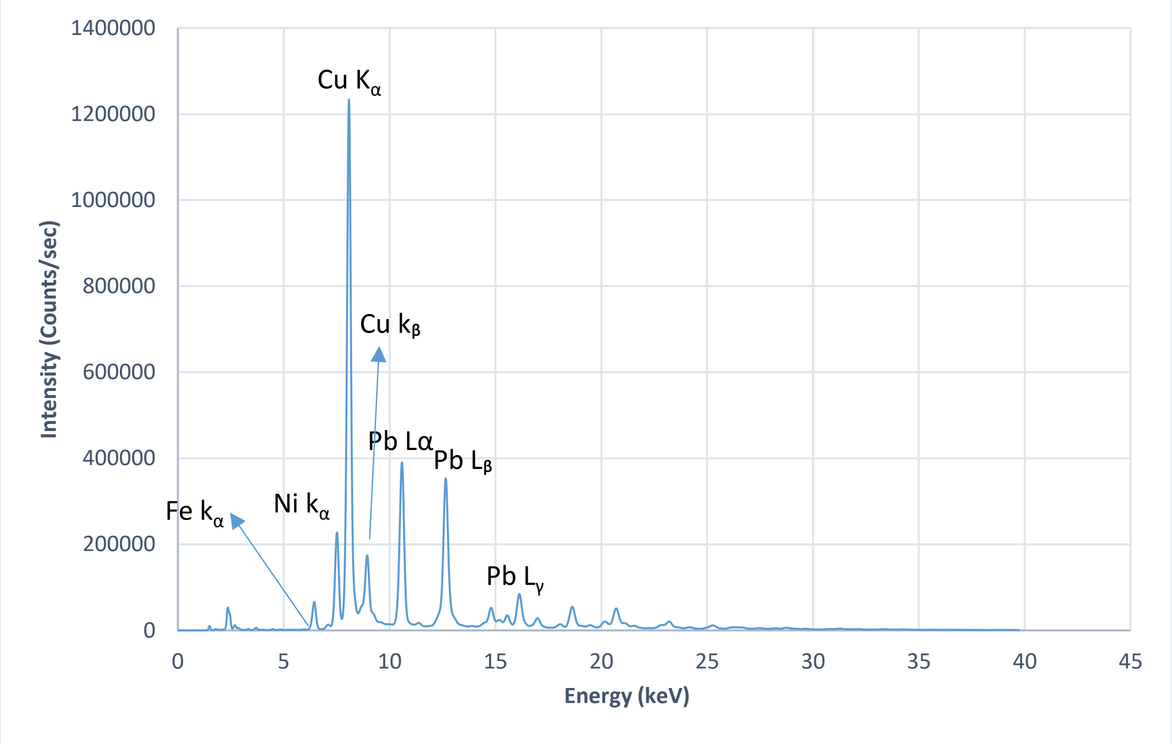

Figure 7. *The XRF spectrum of the sample is in the combined (heavy and light) arrangement.*

The XRF spectrum shows the presence of specific heavy metals, namely Cu, Pb, Ni, and Fe, within the analyzed sample. Additionally, minor elements such as Al, Cr, Mn, Se, and Th were also detected in the XRF analysis with lowered intensity values compared to the primary metals, which is shown in **Figure 7**. These results align with the results of various studies, which mention the occurrence of these heavy metals in similar waste materials. (Lima et al. 2011; Tešan Tomić et al. 2018; EPA 2004; Barker et al. 2021b)

14.3 Compressive strength

14.3.1 Method 1

Table 13. *Method 1 Compressive Strength results*

W/C	*Wa/C*	*A (m^2)*	*F (kN)*	*CS (MPa)*	*Note*
Blank	*0.3*	*615.44*	*7.1±0.16*	*11.38±0.26*	
80:20	*1*	*615.44*	*NM*	*NM*	*fragile*
70:30	*0.53*	*615.44*	*NM*	*NM*	*fragile*
60:40	*0.5*	*615.44*	*1.65±0.69*	*2.68±1.12*	
50:50	*0.5*	*615.44*	*1.65±0.69*	*2.68±1.12*	
40:60	*0.5*	*615.44*	*1.8*	*2.92*	
30:70	*0.5*	*615.44*	*1.15±0.29*	*1.87±0.48*	
20:80	*0.44*	*615.44*	*NM*	*NM*	*fragile*

According to the compressive strength result, which is summarized in **Table 13**, the blank sample result, which follows a typical mix ratio of 3:1 (cement to sand), has been found to exhibit a compressive strength ranging from 10 MPa to 20 MPa after 28 days of curing, this range falls within acceptable limits. (Dehghan et al. 2019; S. B. Singh, Munjal, and Thammishetti 2015b) Indicating that the remaining measured samples give logical results.

Among the measured samples, the composition consisting of 60:40 (W/C) has a higher compressive strength result of 2.92 MPa compared to other mix ratios. This mix ratio has a Wa/C ratio of 0.5. Unfortunately, the compressive strength of the samples composed 80:20, 70:30, and 20:80 (W/C) was measured due to its fragility.

14.3.2 Method 2

Table 14. *Method 2 Compressive Strength results*

S/Wa	*W/C*	*Wa/C*	*A (mm^2)*	*F (kN)*	*CS (MPa)*	*Note*
90:10	***75:25***	*0.44*	*615.44*	*NM*	*NM*	*fragile*
	70:30	*0.37*	*615.44*	*NM*	*NM*	*fragile*
85:15	***62:38***	*0.46*	*615.44*	*2*	*4.23±1.91*	
	50:50	*0.35*	*615.44*	*0.9±1.76*	*2.68±0.47*	
80:20	***40:60***	*0.4*	*615.44*	*2.6±0.19*	*4.23±0.32*	
	30:70	*0.36*	*615.44*	*1.7±0.19*	*2.84±0.60*	

As indicated in **Table 14**, a mix ratio composed of 80: 20 (S/Wa) with 40:60 (W/C) has a higher CS result of 4.23 ± 0.32 MPa and a mix ratio composed of 85:15 (S/Wa) with 62: 38 (W/C) produces a close value of compressive strength of 4.22 ± 1.90 MPa. Notably, the samples also sustain a load of 2.6 ± 0.19 MPa and 2.6 ± 1.18 MPa respectively. In this specific composition, Wa/C was maintained at 0.4 and 0.46, respectively.

It was also observed that when the Wa/C ratio drops below 0.4 the tested sample's CS decreases and even becomes fragile.

Additionally, observations from both **Table 13** and **Table 14** reveal that, at times, samples with a higher waste content produce samples that have a greater CS than those with lower waste content. This suggests that the concentration of the waste, especially Pb, positively influences CS when it is present in some amount. For example, in **Table 13**, a 40:60 (W/C) combination produces a higher compressive value of 2.92 MPa compared to a sample with a 30:70 (W/C) ratio, which has a compressive value of 1.87±0.48 MPa. Similarly, in **Table 14**, a comparison can be made between samples with 30:70 (W/C) and 40:60 (W/C). Notably, the compared samples have similar or close values of Wa/C ratios. This analysis is also mentioned in the study by (Liu et al. 2018).

Overall, the study showed that samples prepared by considering water as one parameter while controlling the Wa/C ratio alongside produced a higher compressive strength than the others, which does not consider, as illustrated in **Figure 8**.

The compressive strength of samples prepared according to method 3, method 4, and method 5 was not recorded due to the samples' fragility after 28 days, which makes it challenging for the CS measurement.

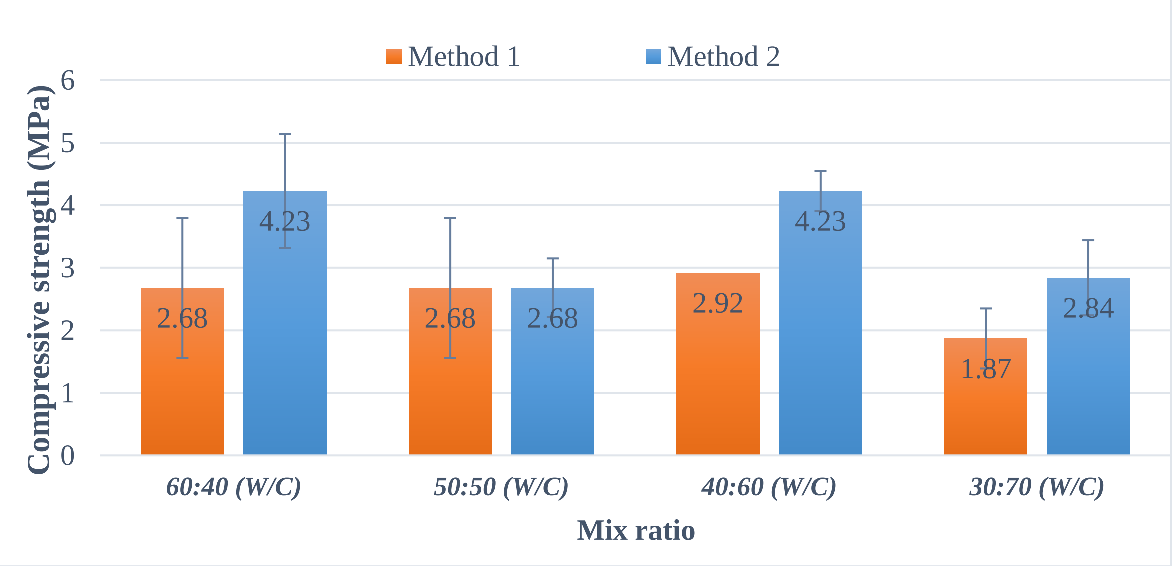

Figure 8. *Compressive strength comparison*

14.4 Leached Metals (Pb & Cu)

14.4.1 Method 1

Table 15. *Metal Leaching Results from Method 1 Samples*

W/C	pH	c_{Pb} (g/kg)	c_{Cu} (g/kg)
Blank	7.4±0.4	ND	ND
80:20	4.72±0.01	5.52±0.19	0.94±0.46
70:30	4.52±0.12	4.5±0.06	0.71±0.13
60:40	5.05±0.2	4.5±0.18	1.11±0.30
50:50	5.1±0.03	3.59±0.09	0.81±0.05
40:60	4.96±0.06	3.22±0.22	0.79±0.12
30:70	5.1±0.32	2.47±0.3	0.78±0.09
20:80	4.99±0.56	1.8±0.03	0.5±0.09

Following the data presented in **Table 15**, it is evident that all the prepared S/S samples exhibit a pH value below 6, except for the blank sample. Furthermore, concerning the leached concentration of metals, particularly Pb and Cu, these samples fail to comply with European landfill regulations. Which states that the permissible concentration of Pb should not exceed 50 mg/kg, while for Cu, the limit is 100 mg/kg. (European Commission 2003)

14.4.2 Method 2

Table 16. *Metal Leaching Results from Method 2 Samples*

S/Wa	W/C	pH	c_{Pb} (g/kg)	c_{Cu} (g/L)
90:10	**75:25**	5.01±0.16	6.23±0.26	1.32±0.1
	70:30	5.2±0.18	5.95±0.02	1.28±0.09
85:15	**62:38**	4.85±0.41	4.54±0.06	0.86±0.1
	50:50	6.04±0.07	3.94±0.08	0.7±0.2
80:20	**40:60**	5.47±0.01	3.31±0.1	0.67±0.07
	30:70	6.54±0.23	1.53±0.09	0.34±0.1

Like the samples outlined in **Table 15**, the S/S samples, prepared according to Subchapter 10.3.2, show non-compliance with European landfill regulations, as indicated in **Table 16**. However, the pH levels of certain samples (50:50 (W/C) and 30:70 (W/C) ratios) have improved compared to Method 1, resulting in values exceeding 6. Apart from that, the leached concentration of Pb is not affected by the conditions of assuming water as one parameter alongside controlling the Wa/C ratio, as is illustrated in Figure 9. The stabilization of Pb is more effective in Method 1 compared to Method 2 based on their leaching results. In the case of Cu, the stabilization was improved compared to Method 1; however, in 70:30

compositions, Method 1 had more effective Cu stabilization than Method 2, as illustrated in **Figure 10**.

Figure 9. *The comparison of the effective stabilization of Pb*

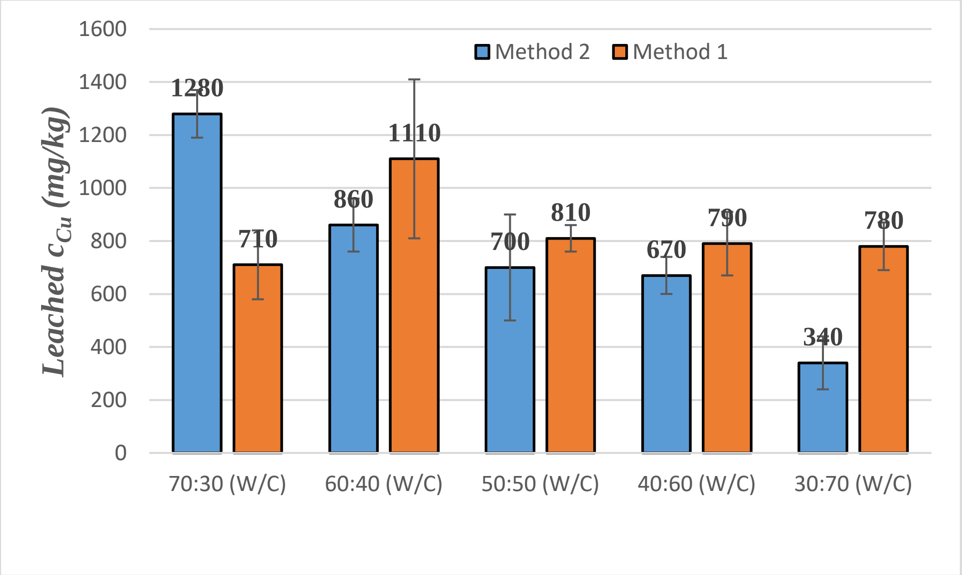

Figure 10. *The comparison of the effective stabilization of Cu*

14.4.3 Method 3

Table 17. *Metal Leaching Results from Method 3 Samples*

Condition	*Wa/C*	*pH*	c_{Pb} *(mg/kg)*	c_{Cu} *(mg/kg)*
1	*0.36*	*8.76± 0.34*	*ND*	*ND*
2	*0.36*	*8.32± 1.3*	*15.8±31*	*5.4±10.4*
3	*0.36*	*7.17± 1.3*	*588.9±174.24*	*105.92±46.9*
4	*0.36*	*8.79± 2.42*	*13.8±27.4*	*15.2±29.8*

Investigating S/S samples prepared through the addition of NaCl, remarkable outcomes have been observed as shown in **Table 17**. Except for Condition 3, all other conditions produce leaching concentrations of metals below the permissible limits stipulated by European landfill regulations, as indicated in **Figure 11**. Notably, across all S/S samples, there is a consistent reduction in the leaching of heavy metals. As indicated in **Figure 12,** the S/S samples treated with NaCl exhibit a substantial decrease in the leaching of Pb and Cu, reaching a value of 99 %.

Additionally, all the S/S samples in different condition produce a pH value above 6 even if, some of the data contain high margin of errors in pH values.

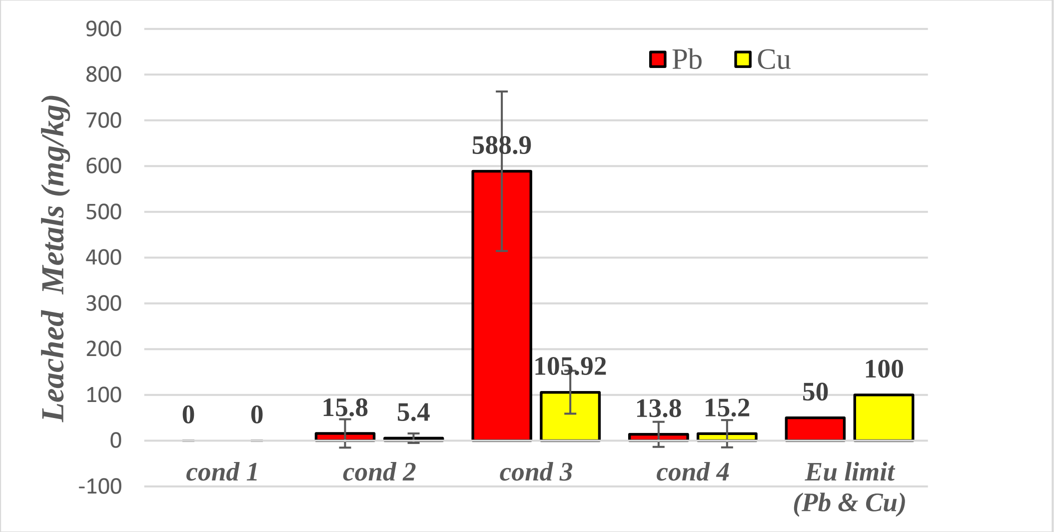

Figure 11*. Comparison of Leached concentration of metals from S/S samples with EU limit*

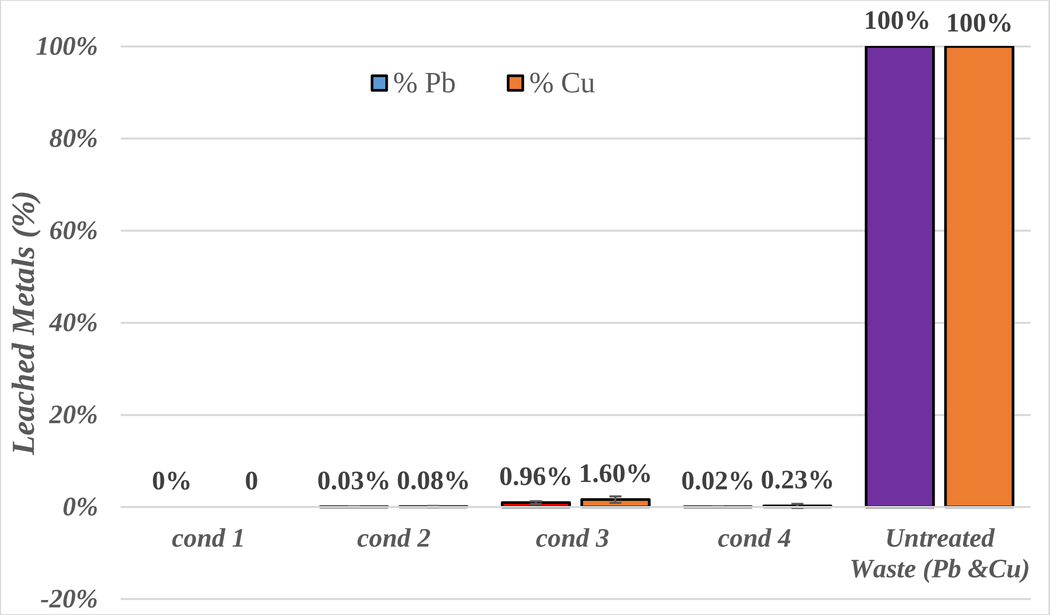

***Figure 12**. Comparison of leached metals from the S/S sample with the untreated waste*

14.4.4 Method 4

***Table 18**. Metal Leaching Results from Method 4 Samples*

Cond	W/C	Wa/C	pH	c_{Pb} (mg/kg)	c_{Cu} (mg/kg)
1	80:20	0.5	5.32±0.21	12,898±1,003.5	3,390±1,517
	60:40	0.4	8.83±0.45	ND	ND
	50:50	0.35	10.71±0.74	ND	ND
	40:60	0.33	9.92±2.38	ND	ND
2	80:20	0.5	6.95±0.03	55.4±30	4.21±3.72
	60:40	0.4	7.94±4.46	25.2±49.2	4±4.2
	50:50	0.35	6.87±0.45	421±236	163.6±131
	40:60	0.33	9.79±2.93	15.61±30.59	4.15±8.14

According to the findings presented in **Table 18**, except for a combination of 80:20 (W/C) ratio, all S/S samples prepared according to condition 1 presented undetected values of both Pb and Cu. However, S/S samples prepared according to condition 2, showed measurable concentrations of leached Pb and Cu This discrepancy likely arises from the fact that tap water contains ions, as is shown in **Table 19,** that can compute with Pb^{2+} and Cu^{2+} to form bonds with Cl^-, in contrast, there are no ions in distilled water that computes with Pb^{2+} and Cu^{2+}.

Table 19. *Zlín tap water mineral composition*

Parameter	***Units***	***Higher limit***
NO_3^-	*mg/l*	*50*
Fe	*mg/l*	*0.2*
Mg	*mg/l*	*0.05*
Al	*mg/l*	*0.2*
F^-	*mg/l*	*1.5*
Pb	*mg/l*	*0.025*
Hg	*mg/l*	*0.001*
Se	*mg/l*	*0.01*
NO_2	*mg/l*	*0.5*
NH_3^+	*mg/l*	*0.5*
Ca^{2+}	*mg/l*	*40-80*
Mg^{2+}	*mg/l*	*20-30*
pH	-	*6.5-9.5*

As is shown in **Figure 13**, all the S/S samples under condition 2 showed a detectable value of Pb above the European regulation. However, only a mix ratio of 50:50 (W/C) had a concentrated value of Cu that surpassed the permissible limit set by the European regulation. Additionally, a significant reduction in the leaching concentration of both Pb and Cu was seen compared to the untreated waste. This reduction in leaching is illustrated in **Figure 14**, where the leaching concentration of Pb reaching a maximum reduction of 99 %, while that of Cu also showed an impressive reduction range from 75 % to 99 %. Overall, the pH levels of all samples in both conditions are above 6, except the S/S sample with an 80:20 (W/C) ratio found in condition 1.

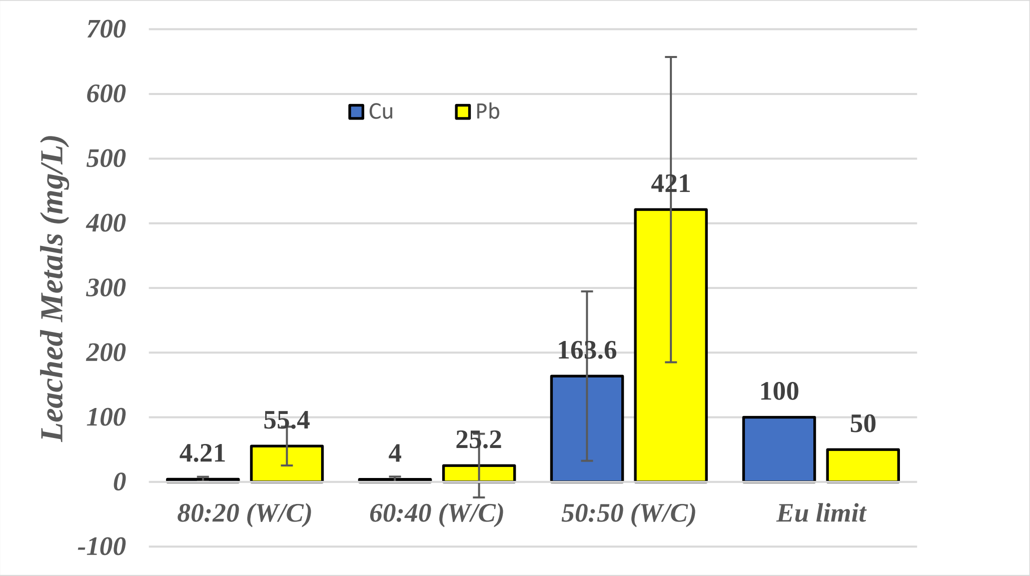

Figure 13. *Comparison of leached metals in condition 2 of different ratio of W/C with the EU limit*

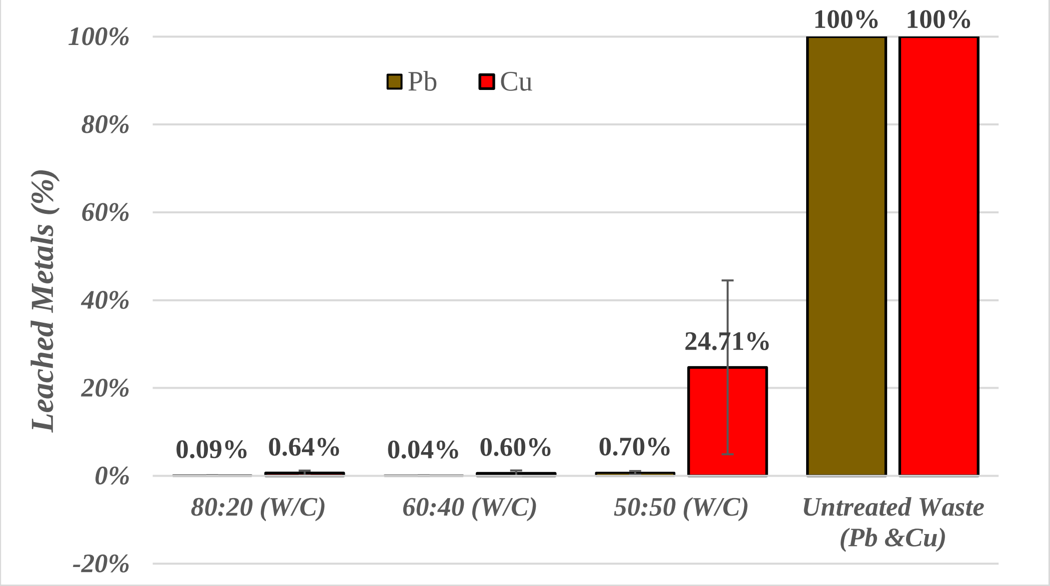

Figure 14. *Comparison of leached metals in condition 2 with different ratio of W/C with untreated waste*

14.4.5 Method 5

Table 20. *Leached metals from the FBCA*

pH	c_{Pb}*(mg/kg)*	c_{Cu}*(mg/kg)*
12.3±0.01	*8.88±14.47*	*ND*

As shown in **Table 20** the leached FBCA samples originally contained a detectable concentration of Pb, while the concentration of Cu is undetected.

Table 21. *Metal Leaching Results from Method 5 Samples*

W/B	*pH*	c_{Pb} *(mg/kg)*	c_{Cu} *(mg/kg)*
60:40	*5.94±2.29*	*17.77±34.88*	*3.34±6.53*
50:50	*11.49±0.85*	*1394.8±2311.19*	*11.64±23.29*
40:60	*12.06±0.13*	*4619.4±4854.05*	*ND*
30:70	*12.2±0.12*	*4442±372.39*	*ND*

In **Table 21**, it was observed that the data showed a significant margin of error, particularly concerning Pb concentration. Furthermore, the results indicated that the leached concentration of Pb increased as the binder ratio increased. This phenomenon could be attributed to the initial measurable amount of Pb present in the used FBCA sample, as shown in **Table 20**. Regarding Cu, the FBCA has effectively stabilized it, and the values are below the permissible limit. However, none of the tested samples complied with the European landfill regulation because of the leached amount of Pb.

14.5 Chloride content of S/S sample

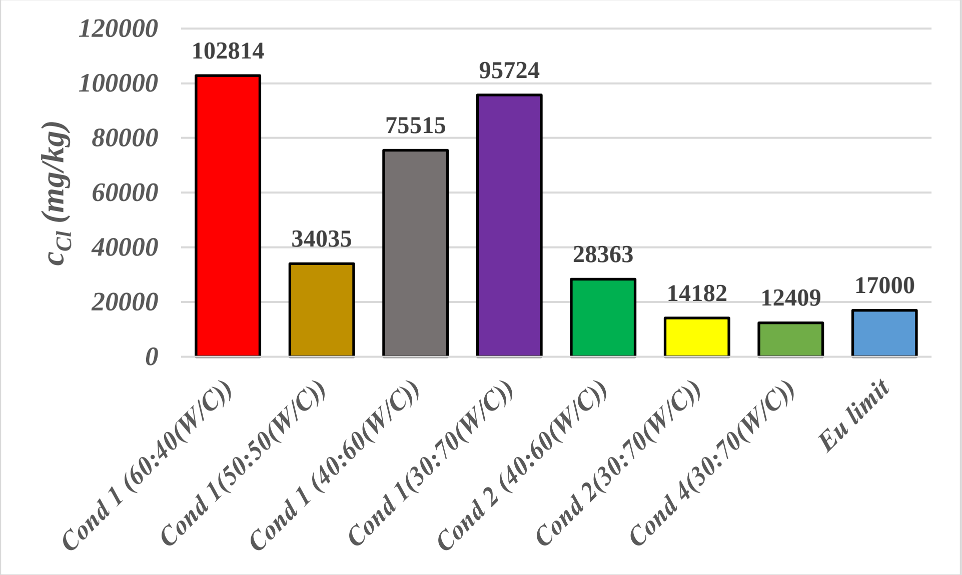

Figure 15*. Comparison of chloride content in S/S with EU regulation*

Figure 15 shows that only conditions 2 and 4 fall below the European chloride content regulation for landfills, while the remaining conditions exceed the specified limit.

14.6 Other leached metals

Table 22. *Leached metals from the best S/S samples*

Cond	***S/Wa***	***W/C***	***Wa/C***	***c_{Cd}(mg/kg)***	***c_{Ni}(mg/kg)***
2	***80:20***	*30:70*	*0.33*	*ND*	*142.91±112.4*
4	***80:20***	*30:70*	*0.33*	*ND*	*141.6±177.56*

In **Table 22**, it is evident that Cd was fully stabilized under both conditions. However, concerning Ni, the findings reveal a higher margin of errors among the samples. Additionally, the concentration of Ni exceeds the limit set by the European landfill regulation, as it is shown in **Figure 16**. Despite this, a noticeable decrease in the leaching concentration of both Cd (100 %) and Ni (85 %) is visually apparent when comparing the treated waste to the untreated waste, as illustrated in **Figure 17**.

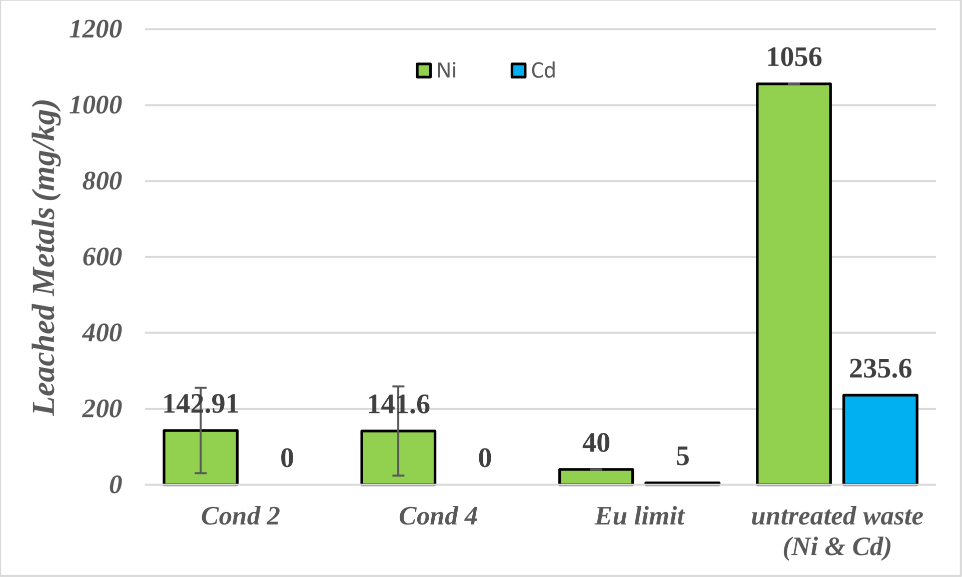

Figure 16. *Comparison of Leached metals (Ni & Cd) with Eu limit and untreated waste*

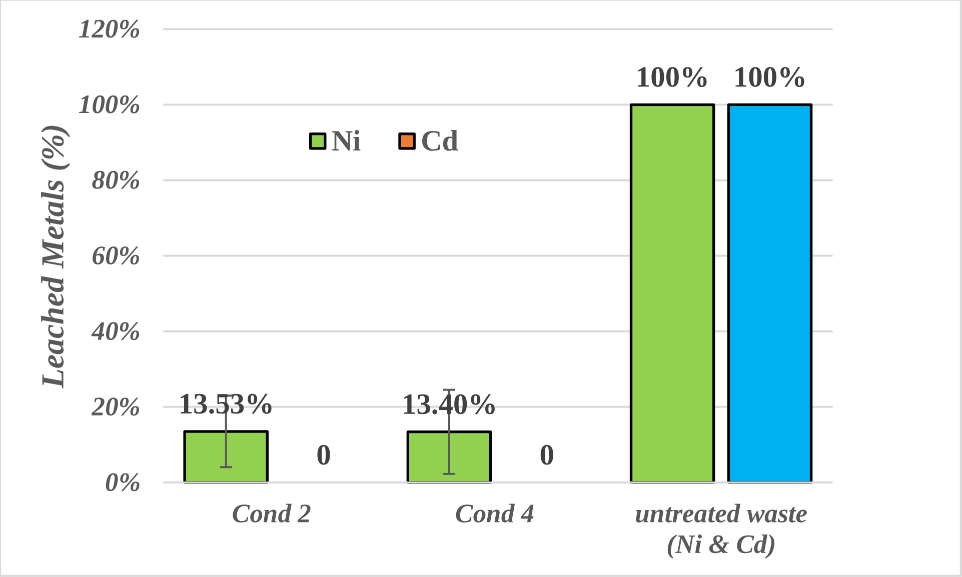

Figure 17*. Percentage reduction in leaching of metals*

CONCLUSION

In this study, the S/S of ammunition waste has been studied by implementing various S/S techniques. From different analyses and from the gained results, the following points can be said as a conclusion:

Based on the XRF and FAAS analysis, the waste contains higher concentrations of heavy metals (Pb, Cd, Cu, and Ni) above the permissible limit set by European landfill regulation. Notably, Pb and Cu exhibited higher concentration values, with Pb at 61,540±156.8 mg/kg and Cu at 6620 mg/kg, respectively.

It has been observed that the CS is highly affected by the W/B and Wa/C ratios. Notably, water emerged as a crucial parameter in enhancing the CS. The samples produced according to Method 2 demonstrated a CS value nearly double that of the samples prepared based on Method 1. Among all the samples, the highest CS was recorded in a sample created with an 85:15 (S/Wa) ratio and a 62:38 (W/C) ratio, producing a CS value of 4.23±1.91 MPa and a bearing load of 2.6±0.19 kN. However, the S/S samples prepared with the addition of NaCl (Methods 3 and 4) and with combined binders (cement plus FBCA) (Method 5) did not produce any CS.

The findings of this study indicated that the application of FBCA for the S/S of this type of waste or waste with a high concentration of Pb is not advisable. This recommendation arises from the observed increment in the leached amount of Pb as the ratio of FBCA in the binder content increases. On the other hand, FBCA yields promising results in the stabilization of Cu. All the S/S samples, with W/B ratios of 60:40, 50:50, 40:60, and 30:70, achieved successful stabilization. Importantly, these samples comply with the European regulatory limits for Cu landfills. (2003/33/EC).

This study indicates that chloride has a positive impact on stabilizing the leachability and mobility of heavy metals such as Pb, Cu, Cd, and Ni. The most effective samples were generated by integrating chloride, in the form of NaCl, under conditions 2 and 4 (Method 3) with a ratio of 80:20 (S/Wa) and 30:70 (W/C), resulting in high stabilization efficiency, with values reaching 99 % for Pb, 99 % for Cu, 86 % for Ni, and 100 % for Cd, compared to untreated waste. Furthermore, the chloride contents of these samples were to be found at 14,182 mg/kg and 12,409 mg/kg, respectively, which is low compared to the European regulation for chloride landfills 2003/33/EC. However, it was observed that the presence of chloride affects the CS.

Finally, none of the S/S samples prepared using various methods met the European landfill regulations. This happened because the Ni content was not successfully stabilized below the stipulated limit set by the European landfill regulation 2003/33/EC.

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LIST OF ABBREVIATIONS

AA_{LT} – Acetic Acid Leaching

CKD – Cement Kiln Dust

CS – Compressive Strength

C-S-H – Cement-Silicate-Hydrate

DOC – Dissolved Organic Carbon

DW_{LT} – Distilled Water Leaching

EC – European Commission

EN – European Norm

EPA – Environmental Protection Agency

EWC – European Waste Catalogue

FAAS – Flame Atomic Absorption Spectroscopy

FBCA – Fluidized Bed Combustion Ash

GFAAS – Graphite Furnace Atomic Absorption Spectroscopy

ICP-MS – Inductive Coupled Plasma – Mass Spectroscopy

ND – Non-Detected

OSCE – Organization for Security and Cooperation in Europe

OPC – Ordinary Portland Cement

RHA – Rice Husk Ash

S/Wa – Solid-Water ratio

TCLP – Toxicity Characteristics Leaching Procedure

TOC – Total Organic Carbon

W/B – Waste-Binder ratio

W/C – Waste-cement ratio

Wa/C – Water-cement ratio

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