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Effect of Different Physical and Geochemical Parameters on Mobilisation of Metals: A Crucial Step Towards Resource Recovery from Waste

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ABSTRACT

The concept of using accelerated supergene processes in repository engineering (ASPIRE) has been proposed to create ‘anthropogenic ores’ of critical or valuable metals and to supply ‘clean’ aggregates to meet future needs. This repository concept is a paradigm shift from the historical practice of ‘store and contain’ to ‘store, contain, clean and concentrate’ to extract resources from solid wastes that are generated in millions of tonnes per year by the industrial, mining and mineral processing sectors. Resource extraction efficiency largely depends on three processes: metal mobilisation, transport, and trapping within the ‘ore’. However, the complexities and lack of comprehensive understanding of the major physical and geochemical processes associated with these three processes (mobilise, transport and trap) in a multiphase geomaterial pose a significant challenge. This paper considers, based on synthesis of the literature, the physical and geochemical processes associated with the mobilisation of elements within an ASPIRE storage. The influence of the several physico-bio-chemical parameters, including pH, particle size, redox state of elements, chemistry of lixiviants, organic matter, mineral composition and aging is highlighted. Particular attention is given to municipal solid waste incinerator (MSWI) ash and coal fly ash, and literature data for this material is used to estimate leachability of metals. It is very challenging to estimate leaching concentration based solely on physico-chemical parameters, and additional kinetic studies are urgently required. Finally, the feasibility of nature-based approach to accelerate mobilisation by supplying root exudates is discussed.

Keywords: Physical and geochemical parameters, mobilisation, resource recovery, accelerated supergene

1. INTRODUCTION

In the era of the ‘Sustainable Development Goals’, ‘Circular Economy Concept’ and ‘Carbon Neutrality’, appropriate management of industrial, mining and mineral wastes (IMMWs), including combustion ashes from biomass and MSWI plants, contaminated dredge sediments and sludges, is of utmost importance. Major fractions of IMMWs are managed by disposing in either secured or non-secured landfills in line with the concept of ‘store and contain’, which delays the contamination risk of surrounding environments and is not ideal due to the risk of leaching of contaminants from landfills either in short or long term. Numerous studies have been conducted via laboratory tests to determine the long-term leaching of heavy metals from IMMWs to design aftercare measures of the landfill to protect the environment. Kim et al. (2018) and Lee et al. (2017) reported that column leaching experiments are able to replicate the natural percolation of rainwater and therefore provide insights about the concentration of metals in leachate with respect to cumulative liquid to solid ratio for tens of years. However, ensuring the long-term performance of the landfill containment systems is a considerable challenge and if it fails, the leachate from these deposits escapes to the environment, creating several risks to human and ecological receptors. For example, leaching of inorganic compounds (such as ammonium, nitrate and nitrite, bicarbonates, carbonates, sulphates and chloride), xenobiotic organic compounds, aromatic hydrocarbons, chlorinated aliphatic, phenols, pesticides and pollutants like dioxins and furans from waste is of major concern as they are not only contaminating sub-surface and groundwater but are also linked to several serious health impacts in human beings (Soliman and Moustafa, 2020; Luo et al. 2019; Sharma et al., 2022).

On the other hand, the shortage of supply for aggregates, critical metals and metalloids (henceforth designated as metals) is increasing worldwide. The critical metals are defined as metals of high importance for national growth but having significant shortage in supply (i.e. rare earth elements). The extraction of minerals from natural ore is often environmental harmful and non-sustainable due to (i) requirement of excavation and generation of dust, wastewater and post-mining residues, (ii) hazard for the miners and surrounding built environments and (iii) requirement of heavy machinery, with commensurate fossil fuel usage and explosives for blasting, and fill materials for mine closure (Laurent et al., 2019). IMMW can host several critical metals, which if extracted might be an alternative source. For example, fly ash is a source of precious metals (Fe, Cu, Zn, Al, Cd, Cr, Ni) and inert oxides of silica, iron, alumina, calcium and iron, which has potential applications as road subbase, adsorbent media, replacing mineral aggregate in ceramic industries, cement and concrete, stabilizing agents and source of nutrients in agriculture (Bruno et al., 2021; Luo et al., 2019). Hence, it may be advantageous to engineer waste storage facilities in such a way so as to allow the extraction of previously untapped resources from the IMMWs to achieve the circular economy concept.

Accelerated supergene processes in repository engineering (designated as ASPIRE) is proposed by utilising the concept of ‘store, contain, clean and concentrate’ to create future ore reserves and provide critical metals (Sapsford et al., 2023). The proposed concept is basically to consider the ASPIRE as temporary storage of IMMWs with the primary objective to extract metals from IMMWs (i.e. combustion ashes, alkaline industrial waste, mine wastes and dredging) by using nature-based intervention and giving residual clean material (i.e. fulfilling the criteria of permissible limit of metal leaching concentration) that may have several uses e.g. as aggregates, agriculture and infrastructure. As opposed to geological ore formation which takes millions of years, ASPIRE storage tends to concentrate ore within an anthropogenically significant timescale (i.e. few years). It has several advantages over the conventional mining processes in terms of mine safety, reversing environmental degradation, energy friendly, carbon neutrality and sustainability as depicted in Figure 1.

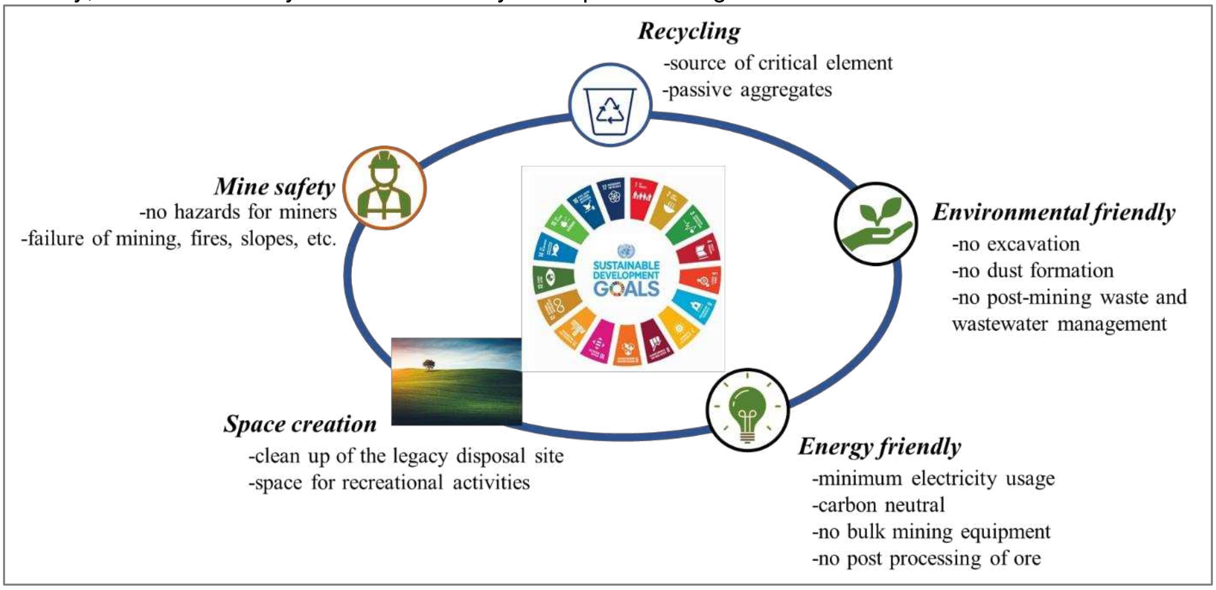


Figure 1. *Benefits of ASPIRE concept of anthropogenic ore storage compared to conventional mining activity*

Overall extraction of metals from the waste and creation of 'anthropogenic ore' within an ASPIRE storage would rely on the mobilisation, transport and trapping of the metals, which in turn depends on the various geochemical processes (i.e. dissolution, precipitation, sorption, ion exchange and complexation) and hydraulic phenomena. Most of the metals in IMMW exist at metastable state under atmospheric conditions; hence when they interact with a lixiviant (i.e. rainwater), geochemical reactions take place, leading to leaching of metals. Estimation of the concentration of leachable metals from waste is the first step in evaluating the potential for temporary storage of wastes in ASPIRE storage. However, the laboratory test results (based on EU/CEN standards) and mathematical models (Kim et al. 2018; Lee et al. 2017) used to evaluate long-term leaching of metals from waste mass suffer to directly implemented in ASPIRE due to complexities associated with mobilisation and its dependency on several parameters. Therefore, a detailed analysis of the crucial processes associated with mobilisation only, including effect of parameters, such as properties of (i) IMMWs (age, morphology, pore structure, saturation state, zeta potential, specific surface area, cation exchange capacity, redox state and chemical composition) and (ii) lixiviant (pH, flowrate, temperature, organic content) has been performed.

2. ASPIRE CONCEPT OF ANTHROPOGENIC ORE STORAGE

The ASPIRE storage is conceptualized as three zones of different attributes and purposes. As depicted in Figure 2, these zones are illustrated as layers for sake of representation. The top cover consists of a vegetation-based layer which is a source of root exudate containing low molecular organic acids and has the capability to form metal complexes. The development of vegetative cover on the surface of waste deposits provides not only a physical protective layer but may also have other effects on the material because plants release organic compounds through their roots (Potysz et al. 2017). Root exudates consist largely of a range of low-molecular-weight organic compounds that are freely and passively released by the roots of living plants (Canarini et al. 2019; Adeleke et al. 2020). Current theories link root exudation to functions such as stimulation of beneficial micro-organisms, promoting nutrient acquisition, sensing nutrient availability in the surrounding environment and enabling recognition between self-roots and neighbour-roots (Canarini et al. 2019). Below this layer, IMMWs is placed, which need to decontaminate (i.e. metal leaching concentration below permissible limits) and after passivation, they will be used for engineering applications. Once the metal is mobilised and dissolved in leachate coming out of waste, it will pass through a trap zone, where metal will be captured and concentrated for future use. A reasonable number of active and passive treatment technologies to sequestrate metals and decontaminate water, wastewater and municipal solid waste leachate are available already (Sapsford et al. 2023). In ASPIRE concept, indigenous microorganisms present in hydrous ferric oxides and organic matter rich waste materials (i.e. water treatment sludge) can be utilised for trapping of metals in the matrix by resorting to change in redox or pH, (co)precipitation, sorption and chelation depending on the nature of metals.

Natural infiltration (i.e. rainfall) will facilitate the migration of root exudates and will help in the mobilisation of metals from ASPIRE over a period of time (also can be represented as L/S ratio). Therefore, the recovery of valuable metals from this repository relies on the three major processes, i.e.,

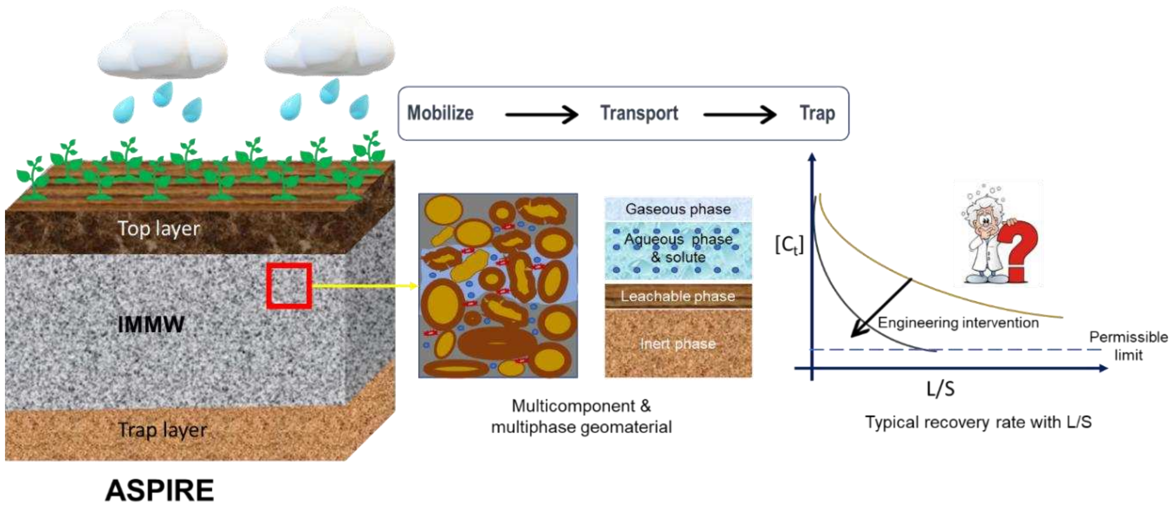
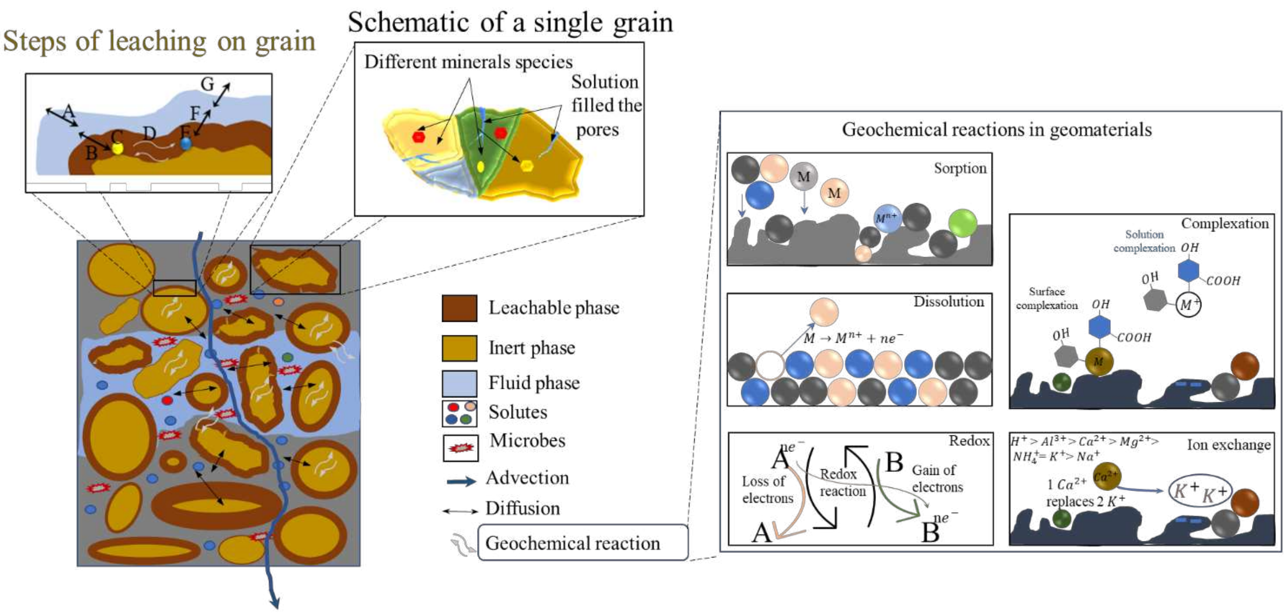


Figure 2. *Conceptual diagram of ASPIRE concept of anthropogenic ore storage*

mobilise, transport and trap. Mobilisation of metals from waste is the first step in evaluating the potential for temporary storage of wastes in ASPIRE storage, and major challenge is how it can be accelerated.

3. MOBILISATION OF METALS IN AN ASPIRE STORAGE

Mobilisation of metals takes place by several mechanisms as depicted in Figure 3. Before wastes are disposed, they are mainly screened for environmental risk by determining the leaching concentration of heavy metals. Leaching tests have been mainly classified as static and dynamic tests, such as column leaching and batch leaching, respectively. Rosende et al. (2008) stated that batch leaching studies are time consuming due to the various steps involved in sample preparation and maintaining steady state conditions, which is not representative of the in-situ conditions. Also, the redistribution of elements amongst different phases, already existing or newly created might lead to erroneous results. To overcome these issues, continuous flow, sequential injection and flow injection assemblies are used, wherein different delivery of the extracts, such as forward flow, bidirectional flow, multi-bidirectional flow and intermittent flow can also be used (Rosende et al. 2008). The suitability of the leaching tests depends on the physical and chemical properties of the waste, composition of source, age of the waste and climate conditions (Tiwari et al. 2015). However, the relative performance (viz., time of the process, reagent, and biotic agents) of these treatments decides the type of methods adopted for the commercial application. Though laboratory studies can help to the make estimation of leaching from the wastes, as pointed out by Garrabrants et al. (2021) prediction of in-situ mobilisation of metal from IMMWs is a major challenge due to different saturation states, redox conditions, microbial actions, heterogeneity, overburden, mineralogical alteration and weather condition. LeachXS™[1], a data management and visualisation tool, originally developed by the Energy Research Centre of the Netherlands (Petten, The Netherlands), DHI (Horsholm, Denmark) and Vanderbilt University, to provide data on leaching of metals from wastes, soils, cements, etc. at different pH and liquid solid (L/S) ratio is a potentially useful tool to make an initial assessment of mobilisation.



A. Diffusion of lixiviant through liquid boundary layer
B. Diffusion of lixiviant through leachable layer
C. Adsorption of lixiviate on the grain surface
D. Geochemical reaction on grain surface
E. Desorption of adsorbed products generated during geochemical reaction
F. Diffusion of product through leachable layer
G. Diffusion of product through liquid boundary layer

Figure 3. *Mobilization processes in IMMW [modified from Laurent et al. (2019)]*

[1] https://www.vanderbilt.edu/leaching/leach-xs-lite/

An ASPIRE storage will largely consist of a multiphase geomaterial, with inert and leachable solid phases and a pore volume filled with gas and liquid phases, which carry various metals, organic acids and microbes (see Figure 2). Presently available laboratory-based tests do not consider this state of material and consequently, it becomes difficult to predict the in-situ long-term mobilisation of metals.

For instance, in field IMMWs is present under variably saturated state, whereas the column leaching studies are performed under saturated condition (USEPA-1314, 2017), hence, it does not emulate in-situ conditions. Therefore, the complexity of mobilisation process in ASPIRE storage must be understood by discussing its controlling parameters.

4. PARAMETERS EFFECTING MOBILISATION IN ASPIRE STORAGE

The different geochemical processes related to mobilisation of metals depend on the various attributes including properties of metal, lixiviant and IMMW matrix, as depicted in Figure 4. Wang et al. (2021) have reported that the leaching of heavy metals depends on the waste contents, properties of lixiviant (i.e., pH, COD, Cl^- content and alkalinity). Shahbaz (2022) reported that pH, temperature, time, leaching agent type and its concentration, pulp density and pretreatment that increase or decreases the leaching, are responsible for the extraction efficiency of rare earth metals from secondary sources. Based on a review conducted on the leaching of MSWI ash (i.e. fly ash and bottom ash), Luo et al. (2019) have stated that leaching is primarily affected by pH, L/S ratio, age, contact time, solubility of metal oxides, sorption on solid surface of hydroxides and ash properties.

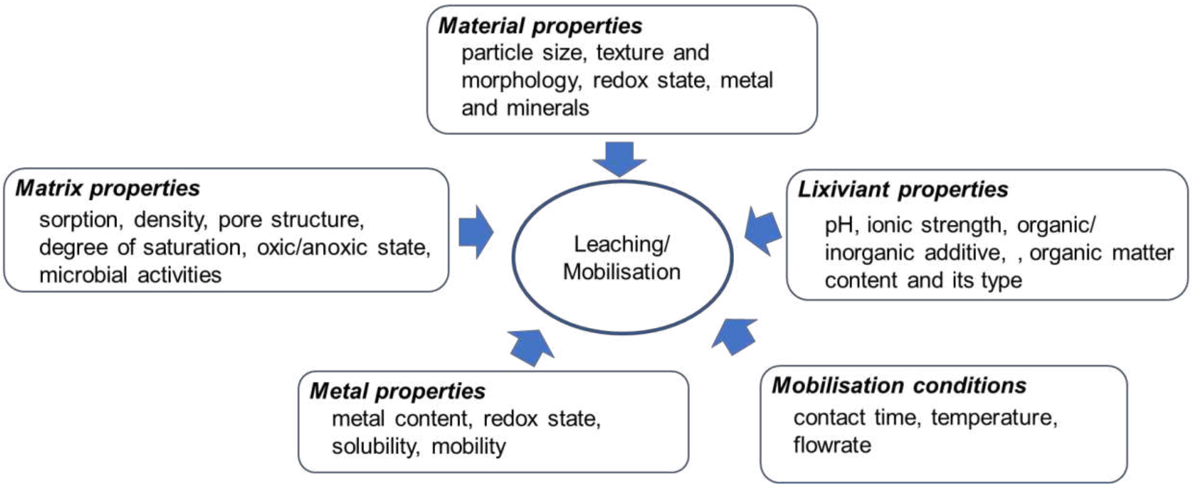


Figure 4. *Parameters influencing the mobilisation in ASPIRE repository*

4.1. pH

The pH has a crucial influence on elemental leaching from IMMW as depicted in Figure 5(a), developed by using the data of samples of coal power plant fly ash obtained from LeachXS Lite. The leaching of cationic elements (such as Ca, Cu, Mn, Zn, Cd and Pb) increases as pH decreases, whereas amphoteric element (Al and As) exhibits maximum leaching either at low or high pH (i.e., highly acidic and basic conditions). Therefore, due to huge variations in leaching concentration of metals with pH change, pH-dependent leaching tests are crucial to determine the effect of external factors on leaching (van der Sloot et al. 2001). Gonzalez et al. (2019) have studied the sequential leaching of trace elements (i.e. Cr, Pb, Sb, Zn and Ni) from MSWI BA and geochemical modelling and observed that Cr is well stabilised (as residual form) whereas Ni leached at low pH. However, Pb and Zn leached at a wide range of pH, except for neutral, where they exhibited a partial amphoteric nature. Patel and Devatha (2019) studied the leaching behaviour of the metals (Hg, Se, As, Fe, Cd, Zn, Pb, Ca, Co, Ni, Cr and Cu) by varying the pH (=3, 5, 7, 9 and 11) and noticed that the highest concentration of Hg (9.3 mg/L), Se (2.4 mg/L) and As (9.7 mg/L) took place at pH=11.

4.2. Liquid to solid ratio

Liquid to solid ratio plays an important role in mobilisation of metals from waste (Raschman et al., 2019). Keeping this in view the database of LeachXS Lite for coal power plant fly ash has been used to plot

Figure 5(b) and it can be noticed that L/S ratio has a very little effect in leaching for almost all investigated metals. Xie et al. (2022) observed that L/S has an insignificant effect on the immediate release of heavy metals (where the rate of reaction inhibits release) but significantly affects the cumulative release over time. Cao et al. (2018) observed that rare earth extraction from coal fly ash increases from 40 to 60% when L/S is increased from 5 to 10, and after that, there was no further improvement in extraction efficiency. In simple terms, higher L/S indicates more contact with solid surface and H^+ ions, which leads to more dissolution of minerals and increases the leaching. The leaching of Ba, Pb, Sb, Zn and V increases when L/S increases as their leachability are solubility controlled. Therefore, at low L/S the dissolution of mineral is incomplete due to low proton concentration.

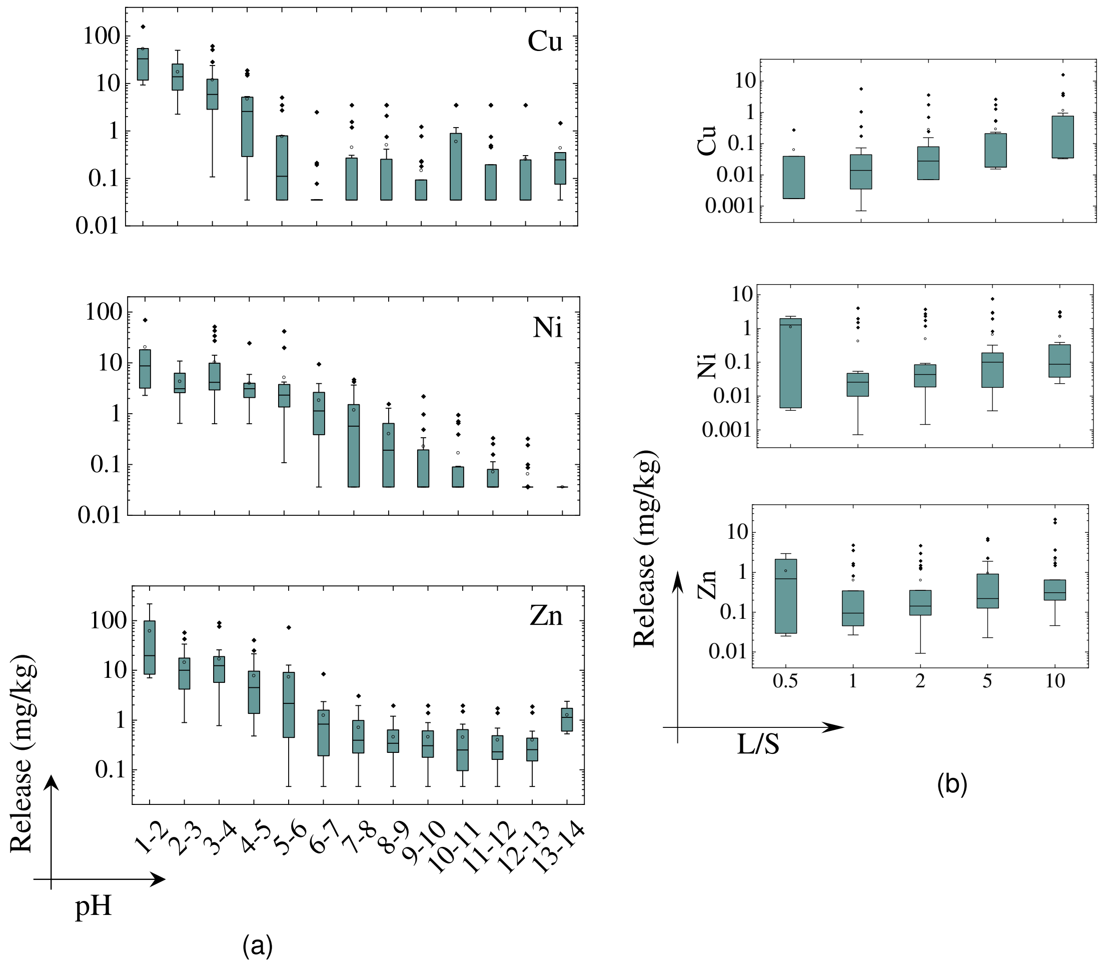


Figure 5*. Release content of selected metals from different fly ash at different (a) pH and (b) L/S ratio (LeachXS)*

4.3. Minerals and nature of metals

The mineral phases and lixiviant chemistry affect the leaching of metals. For example, portlandite [$Ca(OH)_2$], anhydrite, ettringite and calcite are readily dissolved in acidic conditions, leading to high Ca leaching at low pH (Gonzalez et al., 2019). Also, Sjöstedt et al. (2022) have studied the effect of koritnigte ($ZnHAsO_4.H_2O$) mineral on the speciation of As. They found that koritnigte reduces the solubility of As(V) by 2 folds at pH>5. Wang et al. (2022) have found that leaching of redox-sensitive elements (like As, Se, Sb and V) from coal ash surface impoundments are not always simulated in laboratory condition, which clearly demonstrated the effect of redox condition existing in-situ. The redox state in the field is different due to presence of biotic and abiotic conditions, such as reductive dissolution of hydrous ferric oxide, microbial sulfate reduction and direct microbial oxidation. The redox conditions at site can result in elements having different mobilities to those determined in the laboratory. For instance, Arsenite [As(III)] oxidized to As(V) which has a higher attraction towards iron oxides, which reduces its mobility. On the other hand, under reduced condition, Se was immobilized through formation of insoluble precipitate Se(0) of FeSe. As partitioning was affected by a series of reactions, such as a change in As speciation, reduction in adsorption due to the dissolution and recrystallization of As-Sulfide minerals.

4.4. Leaching fluid and leaching conditions

Shahbaz (2022) reported a wide range of lixiviants such as the KOH, NaOH, HCl and H_2SO_4, out of them alkaline solvents are environmentally benign, whereas acidic solutions are corrosive. Fedje et al. (2010) have studied the leaching of metals from incinerated ash by using different leaching agents, such as EDTA, organic acids, ammonium nitrate and ammonium chloride. The EDTA and mineral acids were very effective for the leaching of several metals, whereas organic acids were not effective in leaching. Yuan et al. (2022) reviewed the use of deep eutectic solvents (decanoic acid, 1-propyle alcohol, ethylene glycol, glycerol), a family of neoteric solvent, for metal extractions from a variety of sources, including industrial waste, e-wastes, etc. as they are easy to prepare, non-toxic to the environment. The metal extraction by using deep eutectic solvents depends on their physico-chemical properties, namely density, viscosity, conductivity, water affinity and pH, which can be modulated as per the application requirements.

4.5. Other parameters

Particle size has an important impact on the leaching of metals regardless of whether they are surface-associated (when particle size will affect the sorption/desorption characteristics, cation exchange capacity and metal retention capacity) or distributed within the particles (when the rate of metal release by both diffusion and dissolution are controlled by particle size). The data obtained from the review by Ajorloo et al. (2022) were plotted in Figure 6 to understand the effect of particle size on leachability of Cd, Cr, Cu, Pb and Zn from MSWI fly ash (at L/S=20 with acetic acid) from different locations of China, Thailand, Italy, Spain, France and Japan. From this figure, it looks like the leaching is solubility controlled and it varies with particle size and ash type, which is a function of combustion technology, bulk waste composition, particle size distribution and chemical speciation (Luo et al., 2019). Based on the lysimeter analysis, Stegemann et al. (1995) opined that alkaline pretreatment increases the recovery of the metals (Cd, Cu, Cr, Ni, Zn, Pb), producing recoveries of ≈0.05 to 1.1%, compared to ≈ 0.02-0.48% with DI water alone. Pretreatments have been given by Li et al. (2022) by water washing associated with microwave and ultrasonic treatment, which could remove 85% Cl and other water soluble salts and subsequently augment the efficiency. Chen et al. (2022) reported that about 83% of the initial sulfate could be removed from MSWI bottom ash after 20 min of washing with wastewater from concrete batching plant (pH=11.58±0.52) at a L/S of 10.

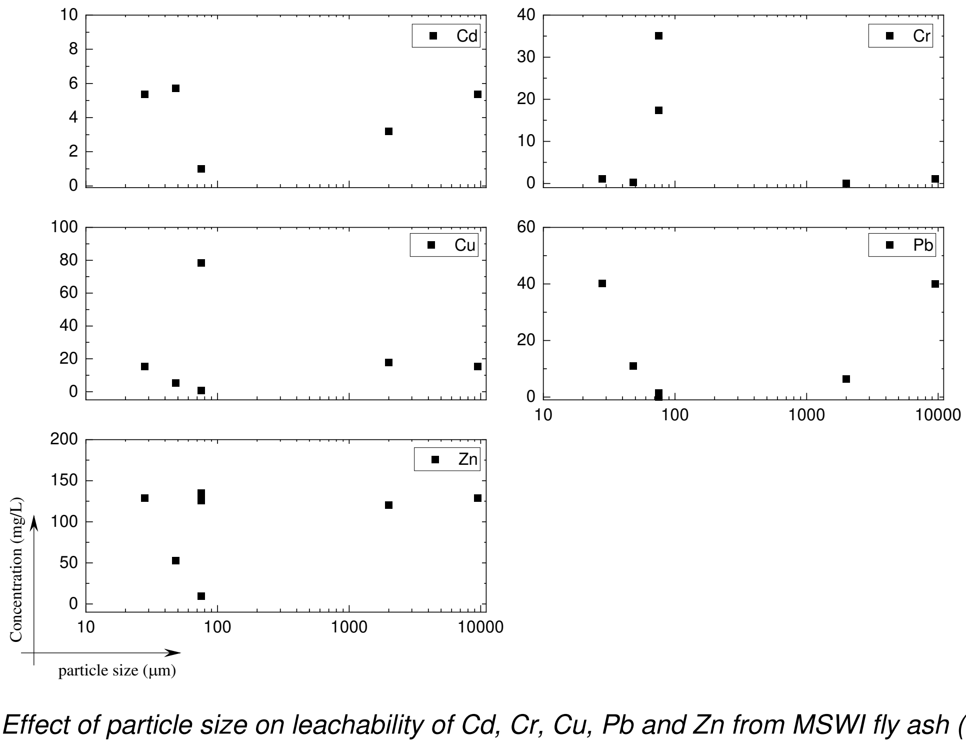


***Figure 6**. Effect of particle size on leachability of Cd, Cr, Cu, Pb and Zn from MSWI fly ash (from Ajorloo et al. (2022))*

The presence of calcium and iron ions in this washing liquid was essential as they controlled the leaching of As, Cd, and Sb from MSWI bottom ash due to the formation of stable crystalline pharmacosiderite, cadmium hydroxide sulfate, and hydromeite. Luo et al. (2019) highlighted that ageing leads to alteration of properties by hydrolysis of Na, K, Al and Ca, precipitation/dissolution of hydroxides and salts, carbonation, neutralization of pH, oxidation/reduction and formation of clay-like minerals, which change the chemical characteristics (i.e. cation exchange capacity, sorption) of secondary products, pH, surface area and consequently impact the leaching. Furthermore, dissolved organic matter plays a crucial role due to its ability to form metal complex and alter the leaching. For instant, Cu leaching behavior is largely governed by the complexation with organic matter (van der Sloot et al., 2001). In ASPIRE storage, dissolved organic matter will enter into IMMW pile from top vegetative layer, which is a crucial factor that governs the mobilisation as discussed in next section.

5. ROOT EXUDATES FOR MOBILISATION OF METALS

Root exudates are composed of a variety of complex compounds, such as enzymes, simple and complex sugars, amino acids, phenolics, vitamins, purines, nucleosides, proteins, flavinoids and organic acids (Adeleke et al. 2020). Though primary metabolites, namely sugars, amino acids and organic acids, generally have higher concentrations, depending on the plant species and their age as well as the soil type and environmental conditions their concentration are highly variable (Potysz et al. 2017; Adeleke et al. 2020). In a scenario such as that of the ASPIRE storage, where plants would be grown on IMMW, rather than a well-developed soil layer, microbial cycling and other mechanisms of retention in the topsoil would be reduced, potentially allowing for a greater proportion of exudates to leach downwards into the waste repository. Increased leaching (i.e. removal from the thin rhizosphere zone) may consequently encourage further exudation, by contributing to generating a concentration gradient close to the roots (Canarini et al. 2019). Another aspect of the ASPIRE concept that may encourage an increase in root exudation, is the stress conditions generated by the waste material on the plants. Root exudation is largely influenced by different biotic and abiotic stresses in the soil, such as mechanical interference, drought, metal toxicity and nutrient deficiency (Canarini et al. 2019, Adeleke et al. 2017). For example, the production rate of organic acids in the rhizosphere is significantly influenced by the presence of insoluble forms of mineral nutrients such as phosphate (Canarini et al. 2019, Adeleke et al. 2017). Similarly, a lack of nitrogen may cause a stronger concentration gradient and increase the flux of exudates to the rhizosphere (Canarini et al. 2019). It has also been observed that in response to metal stress (e.g. Al concentrations), some plant species release higher quantities of citric, oxalic and maleic acid (Canarini et al. 2019, Adeleke et al. 2017). This not only is an advantage in terms of larger exudate fluxes, but also in terms of the potential for increasing mobilization of heavy metals in waste within an ASPIRE storage. It has been observed that in particular organic acids have the potential to change metal speciation and enhance metal mobility in soil profiles both by reducing soil pH (acidification) and forming soluble complexes with heavy metals (e.g. chelation with citric, oxalic and malic acids) (Adeleke et al. 2017; Potysz et al. 2017; Alasmary et al. 2020). Proton released from the organic functional groups (e.g. COOH) also creates negatively charged sites and thus binding sites exhibiting a high complexation affinity towards cations (Potysz et al. 2017). This can lead to mineral dissolution and reduce metal sorption, enhancing bioavailability and mobilising heavy metals (Potysz et al. 2017, Adeleke et al. 2017, Alasmary et al. 2020). In ASPIRE storage, indigenous grassland species have repeatedly been found to be early colonisers in the process of primary succession at waste sites due to their tolerance to metal stress and capacity to develop a dense and strong root system (Gomes et al. 2016; Tischew et al. 2014; Kiehl et al. 2010; Kucharski et al. 2005; Hashimoto et al. 2008; Wasilkowski et al. 2014). Therefore, these species are thought to be suitable for both phytostabilization and leaching of metals from IMMW via root exudation.

6. CONCLUSION

It is likely that, without significant changes to the approaches taken, landfilling will continue to be the approach adopted to dispose of industrial, mining and mineral wastes despite having their potential to be utilised. The ASPIRE storage concept aims to utilise the time of storage in landfills (i.e. temporary storage) and nature-based intervention to extract resources from IMMWs and create future ore reserves to provide critical metals by emulating the natural ore making process but within significantly shorter timescales. In this repository, mobilisation of metals from wastes plays a decisive role in design of trap zone and final recovery of metals. Based on the analysed data, it has been noticed that leaching concentration of metals from fly ash varies drastically. This can be attributed to the variation in physico-chemical properties of ash, which depend on combustion technology, bulk waste composition, particle size distribution, chemical speciation and grade of feedstock. Also, their leaching concentration is reduced by several Log orders (i.e. 3 to 4 for Cu, Ni and Zn) when pH changes from acidic to basic condition. However, leaching concentration of these metals either remained constant or slightly increased as L/S ratio increases up to 10. Though plant root exudates show potential to accelerate the mobilisation of metals, no conclusive decisions can be taken based on limited studies reported in literature. It can be opined that mobilisation of metals in ASPIRE storage would depend on several parameters, which have not been addressed in laboratory-based tests, making a prediction of long-term mobilisation of metals by applying root exudates challenging.

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