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Geochemical constraints in slag valorisation: the case of oxyanions and nanoparticles

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Abstract

Treatment of slags and alkaline solid wastes is generally not successful at reducing leaching oxyanion forming elements (As, Cr, Se, Mo, Sb, V, W), although detailed knowledge of the leaching mechanisms of these elements is in some cases available. Nanoparticles are emerging contaminants of which the fate in slags has not yet been studied. An overview is therefore presented of the geochemical mechanisms that control leaching of oxyanions and nanoparticles and some examples are given of how this knowledge may be applied in slag valorisation and waste treatment technology to ensure environmentally safe deposition and recycling or to give way for new hydrometallurgical applications of nanotechnology.

Introduction

One of the challenges in slag valorisation and waste management is developing materials that have both beneficial physical properties, *e.g.* for recycling as construction material, as well as beneficial chemical properties in terms of trace element leaching. The knowledge base on geochemistry of metal leaching in alkaline matrices has increased considerably in the last few decades, which has given way to advanced treatment technologies to reduce trace element leaching. Particular emphasis has been put on metals such as Pb, Zn, Cd, Ni and Cu, because these metals often occur in relatively high concentrations in slags and alkaline wastes alike and the potential exposure of the environment to these metals has been severely regulated for several decades.¹

Ecotoxicological investigations on the environmental effects of Se, Mo, Sb, V and W generally are more recent compared to other metals and metalloids, which explains why leaching of Se, Mo, Sb, V and W has only recently been regulated (*e.g.*, European

Council Decision 2003/33/EC for landfilling of hazardous and non-hazardous waste). Like As and Cr, that have been regulated for much longer, Se, Mo, Sb, V and W form oxyanions, negatively charged species containing oxygen. Considerable concentrations of oxyanion forming elements may occur in slags and alkaline wastes² and leaching regularly exceeds legal limit values.^{1,3-7} Moreover, it will be shown in this review that treatment technologies that are developed to reduce leaching of metals such as Pb, Zn, Cd, Ni and Cu, are generally unsuccessful at improving the leaching behaviour of oxyanion forming elements. The knowledge gaps in the geochemistry of oxyanion forming elements in alkaline has gradually been addressed in the last decade and it will be shown that the lack of success of slag and waste treatment technologies to reduce oxyanion leaching can be explained on the basis of oxyanion geochemistry.

Engineered nanoparticles are emerging contaminants in environmental research. The specific material properties that emerge when the dimensions of materials are reduced to several nanometers have inspired new slag treatment technologies.⁸⁻¹⁰ However, these newly discovered properties have also inspired caution, because ecotoxicological research indicates that the properties specific to some nanoparticles may cause deleterious health and environmental effects (*e.g.* Ref.¹¹). The expected future production increase in consumer products that contain nanotechnology has been projected to increase the nanoparticle concentration in municipal solid waste, which is incinerated in many countries.¹² Depending on the fate of nanoparticles during incineration, which to date has not yet been studied, the concentration of nanoparticles may therefore increase in residues of municipal solid waste incinerators (MSWI) such as bottom ash and Air Pollution Control residues.¹² Moreover, carbonaceous nanoparticles are neo-formed during incineration and can thus be found in fly ash and Air Pollution Control residues.¹³ Understanding the fate of nanoparticles in slag and waste porewaters can therefore aid new hydrometallurgical waste treatment technologies that apply nanoparticles as well as risk assessments of nanoparticles.

The leaching mechanisms of oxyanions are summarised in this review and it is shown that similar leaching trends can be expected in most alkaline residues, despite their diversity in terms of origin and composition. This knowledge is then applied to understand the failure of treatment technologies and to suggest improvements. The geochemistry of nanoparticles is also summarised because it may be expected that interest in the behaviour of nanoparticles in slags will increase, both with respect to risk assessment of slags and to develop slag valorisation techniques using nanotechnology.

General properties of slags and alkaline wastes

Slags and alkaline wastes are generally residues of industrial high temperature processes such as waste incineration, fossil fuel combustion (FFC) or metal smelting. Despite the widely varying composition of slags and alkaline wastes caused by their variety of sources, there are many similarities. Acidic gases such as CO_2 , SO_2 , NO_x and HCl are volatilised during incineration or metal smelting and leave behind oxides such as CaO , Al_2O_3 , SiO_2 and Fe_2O_3 , while the acidic gases are absorbed during Air Pollution Control by excess lime (CaO) or limestone (CaCO_3). The mineralogy of slags and alkaline wastes varies widely, but because CaO , Al_2O_3 and SiO_2 can be found in most residues, a limited set of hydrated, calcium containing minerals will emerge: portlandite ($\text{Ca}(\text{OH})_2$), calcium silicate hydrate (CSH), minerals of the AFt family of which ettringite ($\text{Ca}_6\text{Al}_2(\text{SO}_4)_3(\text{OH})_{12}\cdot 32\text{H}_2\text{O}$) is the most common one, calcite (CaCO_3) and various minerals of the AFm family of which monosulphate ($\text{Ca}_4\text{Al}_2\text{SO}_4(\text{OH})_{12}\cdot 26\text{H}_2\text{O}$) and monocarboaluminate ($\text{Ca}_4\text{Al}_2\text{SO}_4(\text{OH})\cdot 26\text{H}_2\text{O}$) are the most important ones (Table 1). The quantity and nature of other minerals varies widely. Municipal solid waste incinerator (MSWI) bottom ash, blast furnace slags and steel slags contain, for instance, much more silicates and iron oxides because partitioning of SiO_2 and Fe_2O_3 to flue gases is limited.

Hydrated calcium containing minerals are relatively soluble compared to the other minerals in Table 1 and therefore control the porewater pH, which varies between 10 and 13 in many slags and alkaline wastes.¹⁴ The quantity of calcium containing minerals varies considerably, which is reflected by the acid neutralisation capacity (ANC), the amount of acid that needs to be added to achieve a porewater pH round 7. Hydrated cement pastes, for instance, are nearly exclusively composed of such minerals and thus have a high ANC. Cement is therefore included in Table 1, also because cement solidification is an important slag treatment as will be discussed further.

Leaching mechanisms of oxyanions in slags

Figure 1 summarises the different possible leaching mechanisms that may control oxyanion leaching in slags and alkaline wastes. The upper limit of a contaminant's activity (M)_{aq} in waste pore waters is determined by the activity of matrix ions that form an amorphous precipitate with the contaminant (process A in Figure 1). The crystalline analogue generates a lower activity (M)_{crystalline}, (process B in Figure 1), but the formation of this compound is often kinetically impaired. Surface adsorption (process D) can reduce oxyanion activity below pure-phase saturation levels as long as the density of surface sites is not exceeded. Finally, a structural anion of a matrix

Table 1: ANC and experimentally detected mineralogy for important types of slags, and alkaline wastes and cement pastes

	MSWI bottom ash ^{15,16}	FFC fly ash	Blast furnace slags ¹⁷	Steel slag ^{18,19}	Cement pastes ^{20,21}
ANC (eq kg ⁻¹)	0.5-1.2 ²²⁻²⁴	0.1-5.5 ^{25,26}	0.01 ²⁷	1.8 ²⁸	20 ²⁹
Silicates	Quartz	Quartz	Quartz	Ca-silicates	CSH
	Si-Al-glass	Si-Al-glass	Si-Al glass	Ca-Fe	
	Ca-silicates	Hematite	Ca-silicates	silicates	
	Ca-Al silicates	Mullite			
Iron and aluminium oxides	Hematite	Magnetite	Magnetite	Hematite	
	Gibbsite	Anhydrite	Chromite		
	Goethite				
Carbonates	Calcite			Calcite	Calcite
					Monocarbo-aluminate
Metals		Al ⁰	Fe ⁰		
Sulphur-containing minerals	Ettringite	Ettringite	Sulphides	Ettringite	Ettringite
	Anhydrite				Gypsum
					Monosulphate
Other	Portlandite	Lime		Portlandite	Portlandite
					Hydrotalcite

mineral (e.g., SO₄²⁻ or CO₃²⁻) is replaced by an oxyanion during solid solution formation (process E), which may also reduce the activity of oxyanions below pure-phase solubility levels.

There are not many surfaces to which oxyanions can be adsorbed in slags and alkaline wastes (process D). The silicates are relatively inert¹⁵ and published iso-electric points (IEP) of iron and aluminium oxides in Table 1 are generally lower than pH = 8,³⁰ which suggest that the surfaces of these oxides in alkaline porewaters are predominantly negatively charged.³¹ The surface of hydrated calcium containing minerals is also negatively charged at high pH, but CSH and portlandite can accumulate dissolved Ca²⁺ near their surface and can thus develop a positive zeta potential at high pH and dissolved Ca²⁺ concentrations, where anions can subsequently be adsorbed.^{32,33} However, the oxyanions of As, Cr, Se, Mo, Sb, V and W that occur in porewaters of slags and alkaline wastes have to compete with ubiquitous dissolved matrix anions such as hydroxide, sulphate, carbonate, and

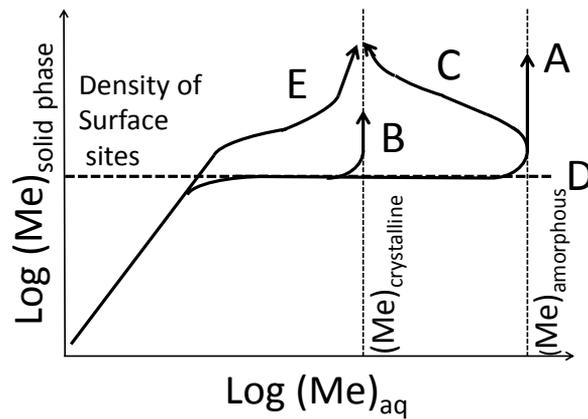


Figure 1: Possible trends in sorption isotherms of oxyanions: A. (surface) precipitation of an amorphous phase. B. (surface) precipitation of a thermodynamically stable solid phase. C. Same as B., but the metastable phase evolves to a stable phase. D. Surface adsorption only. E. Adsorption and (ideal) solid solution formation (Adapted from Ref.³⁷)

silicate for these anion adsorption sites. Moreover, detailed investigations of some of the possible solid solutions in slags that are formed by the oxyanions of As, Cr, Se, and Sb show that these solid solutions are non-ideal.³⁴⁻³⁶ This means that only partial mixing is possible and reaction B rather than reaction E of Figure 1 will occur, also because there is again competition with other oxyanions such as hydroxide, sulphate, and carbonate.

It is thus not surprising that the leaching of oxyanions in slags and alkaline wastes is predominantly solubility-controlled. Table 2 summarises leaching mechanisms of oxyanion forming elements in slags and alkaline wastes that have been established through the combined efforts of geochemical modelling or advanced synchrotron-based techniques. Note that most of the oxyanion forming elements are redox sensitive and several oxidation states of the same element can be found together in porewaters, each controlled by different leaching mechanisms.² Table 2 is biased by the overwhelming experimental evidence gathered from leaching studies of cement pastes and MSWI bottom ash,² but despite large differences in slag composition, it appears that leaching of most of the higher and some of the lower oxidation states of oxyanion forming elements are solubility-limited by forming calcium metalates (mechanisms A and B in Figure 1). Calcium metalate precipitation is more likely than *e.g.*, iron or barium metalate precipitation, because barium and iron oxides are much less soluble than matrix minerals containing calcium at high pH. As a general rule, reduced oxidation states are less soluble than oxidised states, which explains why leaching from blast furnace slag slags is generally low, because the oxyanion forming elements are in their elemental state or contained in sparingly soluble compounds such as spinels.²

Table 2: Dominant leaching mechanisms of the most important oxyanion forming metals and metalloids in alkaline matrices

Element	Oxidation state	Mechanism ^a
As	V	calcium arsenate precipitation
	III	calcium arsenite precipitation ^{38,39}
Cr	VI	solid solution formation with AFt phases
	III	Ca ₂ Cr ₂ O ₅ precipitation
Mo	VI	CaMoO ₄ precipitation, solid solution formation with AFm phases
Se	VI	solid solution formation with AFt phases ^{40,41}
	IV	CaSeO ₃ precipitation ^{38,40} adsorption to CSH ^{42,43}
Sb	V	calcium antimonate precipitation ⁴⁴
	III	Sb ₂ O ₃ precipitation, adsorption to oxides, spinels ^b
V	V	Pb ₂ (VO ₄) ₃ or Ca ₃ (VO ₄) ₂ precipitation
	III	V(OH) ₃ precipitation or contained in spinels ^b
W	VI	CaWO ₄ precipitation
	III	contained in spinels ^b

^a unless otherwise stated, the mechanisms were based on Ref. ² and references therein

^b spinels are sparingly soluble oxides such as magnetite (Fe^{II}O.Fe^{III}₂O₃) where cations of different valencies can occur simultaneously

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Table 2 shows that only chromate and selenate leaching are controlled by mechanisms other than calcium metalate precipitation, which is probably due to the relatively high solubility of calcium chromate (Cr^{VI}) and calcium selenate (Se^{VI}).² The solid solutions formed in slags by these oxyanions are non-ideal and relatively high leaching concentrations of Cr and Se can thus be found when these elements occur in their highest oxidation states.²

Geochemistry of nanoparticles

Nanomaterials are currently used in various applications such as bactericidal agents, catalysts, for drug delivery, and in sunscreens, and comprise such diverse materials as metallic (*e.g.* Ag^0), metal oxide (*e.g.* TiO_2 , ZnO , CeO_2) nanomaterials, but also carbon-based particles such as fullerenes (C_{60}) or carbon nanotubes (CNT).¹¹ This large diversity is increased by the range of different coating materials that is applied to commercially available nanomaterials. The operational nanoparticle definition “having at least one dimension smaller than 100 nm”¹¹ refers to specific “nanoproperties” that cannot be explained by the mere increase in specific surface area.⁴⁵

Powerful models predicting the colloidal transport in natural media with high accuracy have not yet been developed despite years of research on the fate of colloids in natural systems. Environmental modelling of engineered nanoparticles in solid matrices has currently only predictive powers in well-defined, saturated soil columns (*e.g.* sand columns^{46,47}), despite huge interest in the improvement of zero-valent iron applications to remediate soils contaminated with *e.g.* chromate or polyhalogens.^{48,49}

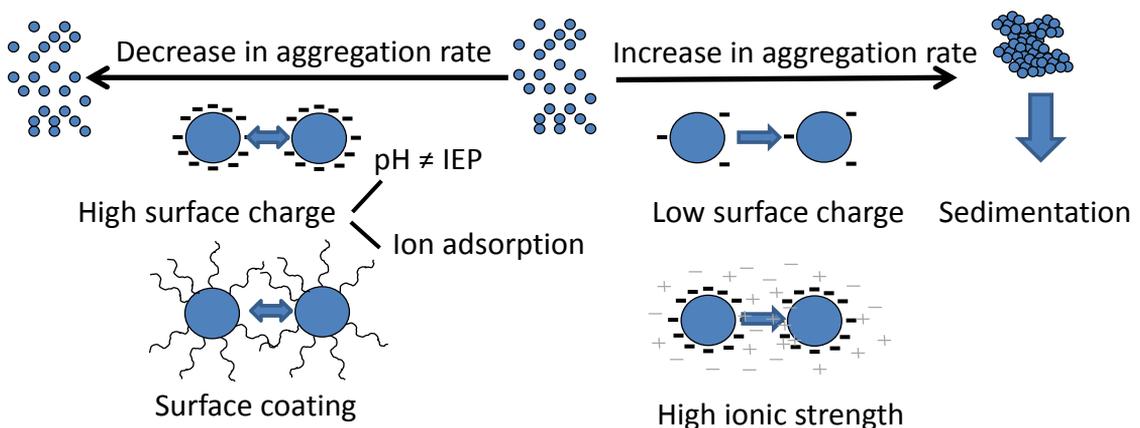


Figure 2: Factors determining the aggregation rate of nanoparticles: surface charge as determined by pH and ion adsorption, commercially applied or adsorbed surface coatings and ionic strength

Difficulties to develop predictive models for the nanoparticle fate may be related to the complexity of colloidal behaviour in non-idealised systems. Because of their small size, single nanoparticles will not sediment, because Brownian motion counteracts gravitational settling. However, as time proceeds, Van der Waals forces can cause an irreversible attachment of nanoparticles called aggregation. The collision efficiency, *i.e.* the probability that a collision between two particles leads to an attachment, determines the aggregation rate, which can vary widely as a function of particle properties and environmental parameters (Figure 2). The aggregation rate is reduced if the particles possess surface charge, causing electrostatic repulsion, or if the particles have an organic coating, causing steric repulsion.⁵⁰ The surface charge of nanoparticles increases if the porewater pH differs much from the IEP of the (possibly coated) nanoparticle surface or if ions or dissolved organic compounds adsorb to the surface of nanoparticles. Electrostatic repulsion decreases with increasing ionic strength, because dissolved electrolytes shield the surface charge, leading to increased aggregation.

Figure 3 summarises the fate-determining properties of nanoparticles in solid matrices. With time, growing aggregates sediment (Process 1 in Figure 3), because they have become too large for Brownian motion to counteract gravitational forces, but by that time, the nanoparticles may have travelled some distance (process 2 in Figure 3). The travelling time in solid matrices is likely smaller than in aqueous systems, because nanoparticles can be deposited on the many solid surfaces (process

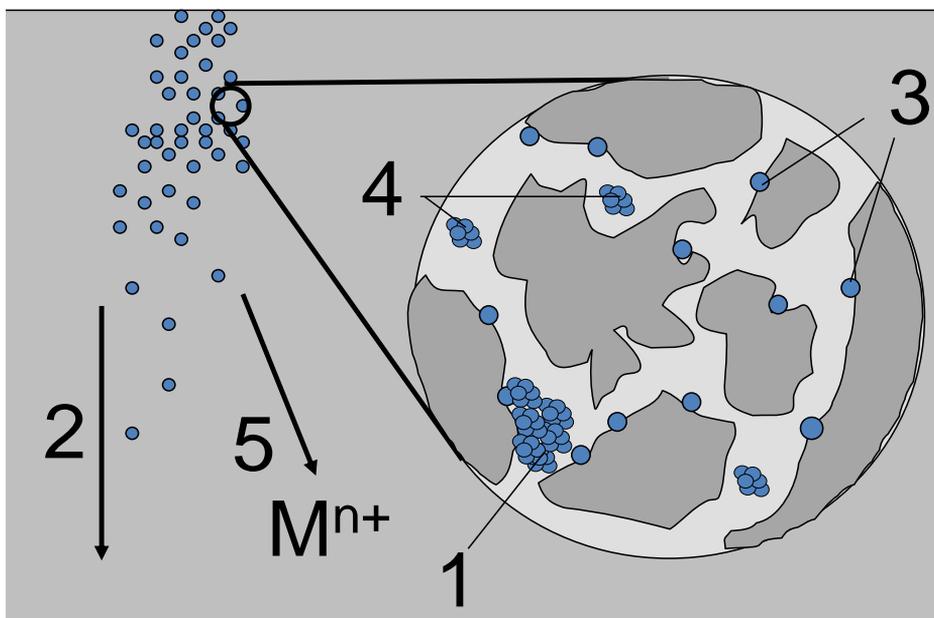


Figure 3: Possible fate-determining processes of nanoparticles in solid matrices: 1. Sedimentation, 2. Transport, 3. Deposition, 4. Aggregation, 5. Dissolution

3 in Figure 3), again depending on the surface properties of both the nanoparticle and the solid surface. Limited aggregation (process 4 in Figure 3) does not always reduce transport of nanoparticles. Exclusion of aggregates from micropores can even accelerate nanoparticle transport, because their movement is restricted to larger, less tortuous pores and because larger aggregates diffuse less and therefore interact less with solid surfaces.⁵¹ Metallic or metal oxide nanoparticles such as Ag or ZnO can also dissolve (Process 5 in Figure 3). The dissolution rate of nanoparticles is generally higher than more coarsely grained powders, because of the much higher surface energy of nanoparticles.^{52,53}

It is thus clear that the fate of nanoparticles is determined by many non-equilibrium processes, which is challenging for risk assessments that traditionally rely on partitioning coefficients (K_d values) that assume equilibrium. Dissolved contaminants are retarded during transport through pores, depending on their K_d value, whereas nanoparticles are not retarded, but filtered while travelling through pores (Figure 4).

Slag and waste valorisation and oxyanion leaching

Many successful valorisation techniques have been put forward of which only a limited number are described below. However, most of the commonly used valorisation techniques have been developed to decrease leaching of metals such as Zn, Pb, Ni, Cd and Cu that do not form oxyanions in solution or only at high pH values

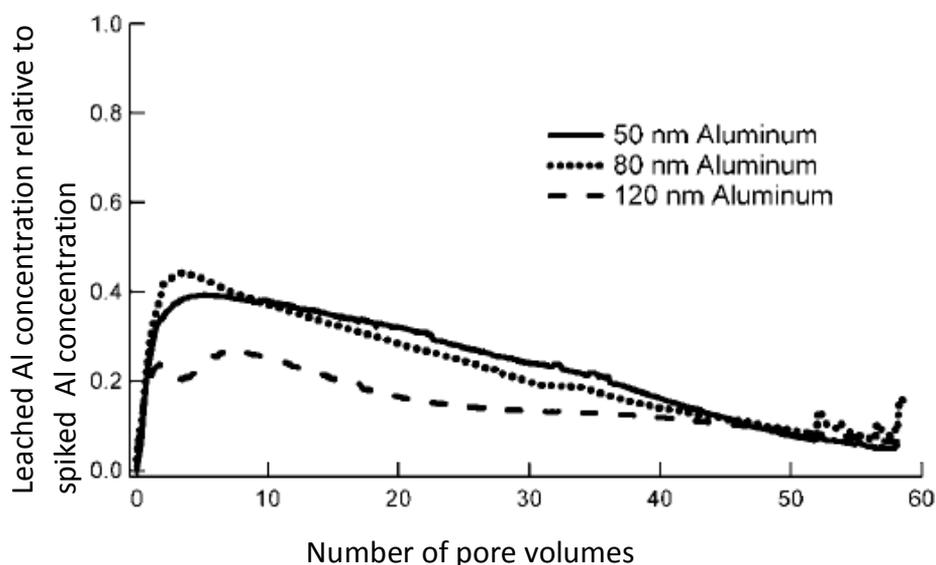


Figure 4: Transport of three differently sized aluminium nanoparticles through a soil column expressed as the aluminium concentration measured at the column as a function of the number of pore volumes that passed through the column. (Taken from⁵⁴)

in the case of Zn and Pb. Specific treatment technologies for oxyanion forming elements are probably scarce, because until recently, there were no legal incentives to limit leaching of oxyanions other than As and Cr.²

Phosphate addition

Phosphates are generally sparingly soluble compounds and addition of phosphates is thus successful to reduce leaching of metals such as Pb, Cd and Ni.⁵⁵ Effects on oxyanion leaching are generally not reported, but it can be expected that formation of calcium phosphate ($\text{Ca}_3(\text{PO}_4)_2$) will increase competition for precipitation with Ca^{2+} and thus increase dissolution of other metalates.

Cement solidification/stabilisation

Solidification/stabilisation with cement generally results in very beneficial oxyanion leaching characteristics, as solubility of some metalates such as *e.g.* $\text{Ca}_4(\text{AsO}_4)_2(\text{OH})_2 \cdot 4\text{H}_2\text{O}$ ⁵⁶ or $\text{Ca}_{1.13}\text{Sb}_2\text{O}_6(\text{OH})_{0.26} \cdot 0.47\text{H}_2\text{O}$ ⁴⁴ is particularly low at the high pH values in cement pores (pH ~ 13) and cement pastes are almost exclusively composed of hydrated calcium containing minerals (Table 1). However, not all cement formulations are sufficient to stabilise oxyanions in cement. A higher sulphate concentration, for instance, promotes ettringite formation and hence better fixation of chromate and selenate,^{36,40,57} and possibly also molybdate (Table 2). Fixation of most other oxyanions will most likely rely on high pH and calcium concentration and the latter is suppressed by sulphate and carbonate addition, which then results in *e.g.* higher arsenate leaching.^{58,59}

Vitrification

The mineralogy of slags is altered significantly during vitrification,^{55,60} because the slags are heated to $T > 1500^\circ\text{C}$ in a plasma which generally results in a material with beneficial physical and leaching properties for most trace elements including oxyanions that are occluded in the vitreous matrix.⁵⁵ The leaching of oxyanions can be improved even further if iron ore is added during the process.⁶¹ However, vitrification is very energy-intensive and produces Air Pollution Control residues that need separate treatment.⁶² Moreover, the long-term leaching characteristics have not yet been investigated in detail.

The ferrox procedure

Heating slags and wastes after addition of ferrous sulphate results in the formation of poorly crystalline ferrihydrites that can adsorb trace elements.¹⁰ The ferrox procedure is generally not successful in reducing oxyanion leaching,^{4,55,63} probably because the pH value is not reduced to values that are favourable for oxyanion adsorption to the neofomed ferrihydrite. Especially Cr leaching increases, because

Cr^{III} that occurs in sparingly soluble compounds is partly oxidised to the much more soluble Cr^{VI}.

Accelerated carbonation

Accelerated carbonation, the reaction with CO₂ at pressures higher than atmospheric, has been inspired by observations that natural carbonation, the reaction with atmospheric CO₂ often results in lower metal leaching from slags and wastes.²³ However, accelerated carbonation increases leaching of most oxyanions.^{55,64-66} The introduced CO₃²⁻ competes with oxyanions for calcium metalate formation and reduction of pH increases the solubility of some metalates.^{44,56} In addition, most of the hydrated calcium containing minerals dissolves during carbonation as calcite becomes thermodynamically more stable.

Possible improvements of slag valorisation techniques

With the exception of cement solidification, most of the aforementioned techniques do not significantly decrease leaching of oxyanion forming elements in slags and wastes, which calls for improvements, especially in the case of slags and wastes that contain relatively high concentrations of oxyanion forming elements such as steel slag, Air Pollution Control residues and fly ash.²

Accelerated carbonation also results in neof ormation of iron- and aluminium oxides, which, together with the pH-decrease that makes anion adsorption to these oxides more favourable, may explain why some authors observe a moderate reduction in oxyanion leaching during accelerated carbonation.⁶⁷ Accelerated carbonation may therefore be combined with the ferrox procedure to increase the amount of neof ormed oxides.

An underused aspect of the geochemical behaviour of oxyanion forming elements is that their lower valence states are generally less soluble (Table 2). Blast furnace slags often comply with leaching standards despite relatively high total concentrations of oxyanion forming elements, in particular V and Cr.² Cr and V can form trivalent non-oxyanionic oxidation states Cr^{III} and V^{III} that often occur in sparingly soluble spinels, whereas the higher oxidation states chromate (Cr^{VI}) and vanadate (V^V) are relatively soluble. However, whereas blast furnace slags contain many elemental metals and sulphides that can maintain V and Cr in their reduced state, the reductive capacity of other slags is much more quickly depleted.² Moreover, it is not desirable to reduce As^V, because As^{III} is much more toxic and Mo and W are generally not considered to be redox sensitive, except possibly in metallurgical slags (Table 2).

Rapid quenching of slags generally results in higher leaching of trace elements, because metastable phases are formed with smaller crystal sizes.⁶⁸ Smaller crystals are more soluble than large crystals because of a higher surface energy and the kinetics constraints for dissolution are also lower.⁶⁹ Sparingly soluble spinels, for instance, are more likely to form if quenching conditions allow cooling to be slower, which explains lower leaching of Cr and V, because these metals are often contained in spinels (Table 2).⁶⁸ Slower cooling also reduces Mo leaching, possibly because it occurs as a solid solution in slowly crystallised silicates.⁶⁸

Nanoparticles in slags

Maximizing transport (process 2 in Figure 3) and thus minimizing aggregation and deposition (processes 3 and 4 in Figure 3) is beneficial in the case that nanoparticles are added voluntarily to treat slags, whereas maximizing transport increases the risk that possibly harmful nanoparticles can leach from the slag.

Transport studies in sand columns suggested that the transport of nanoparticles is increased in the case that the porewater properties decrease the aggregation or deposition rate of nanoparticles, *i.e.* the pH differs from IEP, ionic strength is low, and the concentrations of adsorbing ions or dissolved organic compounds that increase the surface charge of nanoparticles is relatively high.^{54,70,71} However, more recent studies suggest that the presence of oppositely charged particles in the porewaters may lead to a process called heterocoagulation, where dissimilar particles are attracted to each other, despite low ionic strength.^{52,72}

The high pH of slags and alkaline wastes will induce a high negative charge on nanoparticles, whereas few minerals in slags can develop a positive charge (except portlandite and CSH). Dissolved organic carbon concentration in slags and alkaline wastes is much lower than in natural systems, except in MSWI bottom ash.² Finally, nanoparticle dissolution is generally below detection limits at pH > 9,^{52,72} except possibly in the case of ZnO and Al nanoparticles that may dissolve as $\text{Zn}(\text{OH})_4^{2-}$ and $\text{Al}(\text{OH})_4^-$. The mobility of nanoparticles thus likely depends predominantly on the ionic strength. The ionic strength in slag and waste porewaters is generally higher than porewaters of soils. Bottom ash porewaters, for instance have ionic strengths similar to seawater (70 – 200 mM)⁷³. Aggregation experiments in seawater at pH = 8⁷⁴ show that aggregation rates of nanoparticles are moderate despite the relatively high ionic strength, because nanoparticles acquire a high surface charge at pH = 8. Coating with natural organic matter increases stability further in seawater, because it provides steric stabilisation, in addition to electrostatic stabilisation (Figure 2). Nanoparticles might thus travel considerable distances in slags and alkaline wastes, especially if they are coated prior to application.

Applications of nanotechnology in slag valorisation are to date limited, but appear promising, especially in the improvement of physical properties of building materials.^{75,76} The high reactivity of CNT, TiO₂, SiO₂ and Cr₂O₃ nanoparticles are, for instance, used to develop high-strength concrete with blast furnace slag as a binder.^{9,76-79} The leaching properties of slags were dramatically improved by applying a thin film of TiO₂ and SiO₂ nanoparticles. A better understanding of the fate of nanomaterials in alkaline matrices could aid to assess the long-term stability of these applications and possible environmental implications.⁷⁶

Conclusions

Current slag and waste treatment often do not succeed in reducing oxyanion leaching below legal limit values. There is, hence, much scope for improvements, despite advancements in understanding the geochemistry of oxyanions in slags and alkaline wastes. The fate of nanoparticles in solid matrices with a high pH has not yet been investigated, but such investigations may be required depending on future evolutions in regulation of nanoparticle leaching and they may also assist the application of nanotechnology in slag valorisation and waste treatment.

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