In situ resource recovery from waste repositories: exploring the potential for mobilisation and capture of metals from anthropogenic ores

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Abstract

This paper addresses the potential to achieve technospheric mining through in situ leaching. Candidate waste streams are identified and analogue leaching systems from the mining industry (e.g. heap leaching) and contaminated land (e.g. soil flushing) are discussed to demonstrate that many aspects of existing technologies are readily transferable to technospheric mining. The intensity of processing via in situ technology is necessarily low and consequently the benefits and disbenefits of this with regard to metal recovery, economics and the environment need to be considered. As such in situ recovery of metals from anthropogenic ores is a novel technology area that links new sustainable remediation approaches for contaminated materials and technospheric mining for closing materials loops.

Introduction

Waste repositories can be considered the ore deposits of the 'anthropocene'. Having historically disposed of vast quantities of industrial, municipal, metallurgical and mining waste into the ground, societies have put into geological storage an enormous amount of resources in a range of materials of value such as metals and energy (in the form of biomass and polymers). Therefore, instead of considering these waste repositories to be a legacy waste issue and a long-term liability, a paradigm shift is required to view these installations as 'resource hubs' for future recovery. This has to some extent been recognised with commensurate but small scale landfill mining occurring internationally[1], and the concept of mining materials from the 'technosphere' (rather than the lithosphere) is gaining ground. Following the definition of Johansson et al.[2], the 'technosphere' is defined as material stocks established by human agency, which originates from technological processes, in contrast to stocks in

the lithosphere established by slow, primary geological processes. The technosphere can be distinguished from the lithosphere which is where historically humans have derived all of their metal resources. Three major technospheric stocks have been defined[2]: metals tailings ponds (i.e. mining wastes), slag heaps (e.g. metallurgical wastes) and landfills as 'controlled inactive stock' which are amenable to 'landfill' or 'secondary' mining.

In situ recovery

This paper discusses the potential and some of the concepts that underpin in situ technologies as a means to achieve technospheric mining. The meaning of in situ requires clarification. Many modern waste repositories have a well engineered liner system to prevent contaminants escaping from the repository to the subsurface environment and thus in situ technologies that enhance leaching could be applied directly to the waste repository without fear of exacerbating pollution. However some wastes (especially older sites which predate environmental legislation) may not be lined and thus either an in situ barrier / liner systems needs to be created e.g. a cut-off trench or the waste need to be moved on to a lined leach pad before leaching can be applied. Thus in the latter circumstance the leaching is not sensu stricto 'in situ' but 'ex situ'. However since the leaching mechanisms applied would be the same – i.e. a stationary solid phase is flushed by an extractant, or the biogeochemical environment around the solid phase is manipulated in situ, thus for the purposes of this paper leaching wastes on leach pads is also regarded as 'in situ' technology.

The recovery of resources from waste repositories has not been widely adopted, beyond the limited extraction of landfill gas for energy generation. In this paper, parallels are drawn with conventional mining and contaminated land remediation technology. The aim of the paper is to examine analogue leaching systems so as to highlight the potential role of in situ processes in the new field of technospheric mining. Can resource (elements of value-tech elements and energy) be recovered by leaching and other treatments whilst the material lies in situ, thus avoiding the need to actively mine the material or at least minimise earth works and thereby minimise ecological and environmental impacts? The fundamental geoscience that underpins this is: is it possible to engineer the in situ biogeochemistry of the waste within the system to mobilise, transport and capture metals?

Elements of particular interest in recovery from waste repositories are the so called "E-tech" elements (Co, Te, Se, Nd, In, Ga, HREEs) whose security of supply is an issue in addition to them being essential to green technologies. Furthermore there are the 'EU-14' supply threatened elements including platinum group metals (Pt, Nb, W, Ta, Ga, Ge, Sb, Mg) and elements of value including precious and base metals: Au, Pd, Ag, Cu, Pb, Zn, Co, Ni, Sn and Cr. Many of these elements are found in significant

concentrations in common wastes (e.g. tailings and metallurgical wastes). Furthermore there are predicted shortages in geological reserves for many metals, and exploitation of more complex deposits including anthropogenic deposits is a natural extension of this developing trend.

Candidate wastes / waste repositories

The candidate materials generally fall under the classification of "controlled inactive stocks"[2] and are usually the result of current waste management practices. The following are candidate wastes which may be amenable to in situ recovery of metals. This consideration is based on the following reasoning (i) because they are extremely large mass arisings of these wastes, with (ii) significant concentrations of metals of interest in them, (iii) there is evidence of hydrometallurgical research work being done on recovering metals from these materials, and (iv) they have suitable physico-chemical characteristics (e.g. mineralogy, particle size etc). It is not an exhaustive list but highlights some of the key arisings which may suit in situ leaching. Another key criterion for in situ techniques is a hydraulic conductivity conducive to the flow of leachates, many of the waste do not meet this criterion but there are technological solutions existing for this such as agglomeration or electrokinetics.

Red Mud

Red mud is a by-product of the Bayer process, the process by which aluminium is produced from bauxite ore. For every tonne of alumina produced, between 1 and 2 tonnes (dry weight) of red mud residues are produced[3]. The global annual arisings are 120 million tonnes and 2.7 billion tonnes of this material has been stockpiled[4]. It is composed primarily of fine particles of silica aluminium, iron, calcium and titanium oxides and hydroxides. Due to its high sodium hydroxide, elevated pH, and metal(loid) content (Al, As, Cr, Cu, Ni, Mo, V and Zn)[5] red mud is viewed as hazardous waste. These elements might also be considered a resource, red mud also contains the rare-earth elements (REEs) and scandium[6,7].

Coal Fly ash and bottom ash

Whilst the UK usage of coal for power generation is rapidly decreasing as old coal fired power stations are decommissioned and not replaced, the global consumption of coal for power has, for various economic reasons, actually increased and as such coal will likely continue to play a role in the global energy mix for many years. Waste arisings from coal-combustion, principally fly ash and furnace bottom ash have been variously utilised in applications such as a cement component in concrete, grout and road bases but supply outstrips demand with only 25 % being utilisation globally[8,9] and the

remainder is stockpiled. Example figures for the EU arisings of coal-combustion for energy generation residues for 2010 were 100 Mt[10]. Arisings are circa 6 Mt in the UK of which approximately 50% are utilised and an estimated 53 Mt of fly ash lies in UK repositories[11]. It is recognised that and there is a pressing need for more applications [12] but most actual applications and research publications concern fly ash utilisation especially in civil engineering applications. In terms of resource recovery, coal fly ash contains REEs[13] and there has been interest in coal ash as a resource of REEs (e.g. Franus et al[14]), especially La, Ce and Y but there may also be potential for in situ flushing of potentially contaminating species such as Cr(VI), V and B where they occur at high enough concentrations to hinder ex situ reuse (particularly in unbound forms).

Mine wastes

With annual extraction of ores and coal running to billions of tonnes there is a commensurate and larger production of mining wastes. Typical mine wastes include piles of overburden, waste rock, marginal ore and tailings. For materials that are excavated the classification of the materials as 'waste' is contingent on factors such as the value of the target metals at the time, their ease of extraction from the materials and the extraction process used for the particular site. Thus what at some times is considered a 'waste' is at other times an 'ore'. Tailings are the waste resulting from the beneficiation of mined materials to produce an ore concentrate for further processing, the tailings are thus concentrated in gangue (non-economic) minerals but no beneficiation process is completely efficient and technologies are variously effective at separating ore from gangue minerals, so that a proportion of the target metals will report to the tailings. It is also the case that historic beneficiation processes were typically less efficient, and with changes in metal prices and technology the remining of old tailings, or other mine wastes has occurred. For example, historic Pb-Zn mines in Wales were originally mined for Pb in the late 19th century and the Zn minerals discarded, these wastes were later reworked for Zn when Zn prices rose in the early 20th century. There is also the possibility that metals that were not originally the target metals for mining, but have since become economically important (e.g. the EU critical metals), maybe be enriched in the waste and become the valuable target (e.g. Dehain and Fillipov[15]). In terms of physical characterisation, mine wastes tend to have a larger and wider particle size distribution (PSD) than tailings which are typically fine (< 60 μm), thus hydraulic conductivity of the materials for in situ leaching is an important consideration.

Steel-making dusts

There are a range of wastes arising from the multitude of metallurgical processes and potential to recover resources from them with a range of hydro- and pyrometallurgical

techniques. Steel-making dusts including blast furnace (BF), basic oxygen steel (BOS), and electric arc furnace (EAF) dusts are considered here as they constitute a large metallurgical waste stream. The BOS process involves introduction of oxygen into the crucible of molten pig iron in order to reduce its carbon content. This creates waste dust up to 0.02 t/t of steel. These dusts cannot be recycled into the steel-making process for the iron content because of the presence of Zn (circa 10%)[16] as a contaminant which has an adverse effect on the process performance and eventual quality of steel[17]. Zn is present because galvanised scrap is often used as an additional charge to the process and the Zn is volatilised into the furnace off-gas where it cools and forms zinc oxides and zinc ferrites (e.g. franklinite) in the dusts. The Zn in the dusts is amenable to acidic hydrometallurgical extraction e.g. Havlik et al[18] as well as pyrometallurgical extraction e.g. Jaafar et al[19] but poor separation between Fe and Zn extraction means further processing is often required. A major route for recycling scrap is the use of electric arc furnaces. EAFs dusts from this process are also very rich in zinc content (>20%) with franklinite a major phase in the dust. Manganese, cobalt, nickel, chromium also occurs isomorphously substitutes for Zn in the franklinite. Fe is present, except of franklinite, mostly as magnetite, Fe_3O_4.[20, 21]

Metallurgical dusts are a more likely target than metallurgical slags from a mobilisation/dissolution perspective – although the dusts are composed of recalcitrant Fe and Zn oxides; they have a very small particle size, thus limitations of solubility are somewhat mitigated. Again with this comes the penalty of the reduced hydraulic conductivity for an in situ leaching process.

Phosphogypsum

Phosphogypsum is the main by-product of the production of phosphoric acid by sulphuric acid digestion of a concentrated slurry of pulverised phosphate ores[22]. Phosphate ores are often naturally enriched in REEs and the REEs report significantly to the process residues and can be recovered with acidic leaching (e.g. Preston et al[23]). Example figures for REE content are given by Binnemans et al[24].

Dredged Sediments

Annually, approximately 40 million wet tonnes of sediment are disposed of in approximately 150 licensed disposal sites around the coast of England[25]. The main reasons for dredging include navigation; maintenance of operational shipping depth; flood control and construction and reclamation and mining for infill materials. Reuse options for dredged sediments include conditioning of agricultural land and fill applications. However, a considerable proportion of dredged materials are contaminated which precludes reuse in many (especially unbound) applications. Of the approximately 300 million/m³ of sediments dredged to deepen harbours and shipping

lanes in US, 3–12 million/m^3 are considered highly contaminated[26]. Metal removal from contaminated sediments would have the dual role of recovering metals and potentially allowing reuse of the decontaminated sediment.

Analogue leaching/recovery systems

Acid Rock Drainage and heap (bio)leaching

Metals bound as suphides, when exposed to the subaerial weathering environment, will be released as the sulphides spontaneously oxidise. The rate of weathering and release of metals from sulphides is kinetically controlled and influenced by microbes, including bacteria, archaea and eukarya (see for example Schippers et al[27]) with the ecosystem being driven by metabolic energy derived fom the free energy available upon the oxidation of the ferrous and sulphur moeity of the sulphide minerals. This spontaneous breakdown of sulphide minerals is advantageous with regard to metals extraction (see heap leaching section below) but disadvantageous from an environmental perspective as it causes acid mine drainage and metaliferous metal leaching (AMD-ML) from mines, AMD-ML as is one of the biggest causes of metal pollution worldwide.

Many heap leaching systems take advantage of this natural breakdown in heap (or 'dump') leaching where lixiviants (sulphuric acid and/or recycled lixiviant) are introduced at the top of the heap and allowed to trickled down through ore material (or agglomerated material). Heap leaching of sulphide ores is well established for Cu ores and exploits and enhances the AMD-ML biogeochemistry leading to mobilisation and recovery of Cu. The metals are then extracted from the pregnant liquor which is collected from the base of the heap using approaches such as ion exchange/solvent extraction before electrowinning from the concentrated solution. Not all heap leaching takes advantage of microbial mediated reactions, but complexation reactions instead. For example, heap leaching of gold/silver and some non-sulphide Cu ores is accomplished with a cyanide lixiviant and some uranium ores use sodium bicarbonate as a lixiviant.

Heap leaching is typically employed where ore grades are not sufficiently high to justify more intensive hydrometallurgical/pyrometallurgical options. This illustrates the continuum of options between process intensity (cost) versus recovery and rate of recovery and highlights that in situ techniques are applicable for materials with lower concentrations. Where the particle sizes or ores are prohibitively small in terms of insuring hydraulic conductivity for the lixiviant then agglomeration techniques (using water and/or binders) have been applied to fines to improve lixiviant contact and flow in the heap leach, resulting in good recoveries even for fine grained materials. This technological development is clearly of relevance to many of the candidate wastes highlighted in this paper.

Contaminated land remediation technologies

Heap leaching in mining and removal of contaminants from contaminated land can be considered as reciprocal approaches: in land remediation the aim is recovery of the material (soil/sediment) with leaching resulting in purification/decontamination of target soil, rather than in heap leaching (above) where the target is the leached metal. However these processes can be seen as a the same processes with simply a difference of perspective, where remediation recovers the soil material/value. The following are common examples of decontamination processes which have been applied to contaminated materials.

Soil flushing

Both in situ soil flushing and ex situ soil flushing have been investigated for the removal of metals from contaminated soils[28]. In situ recovery requires that the material to be flushed overlies an impermeable stratum such that a pump and treat system can be applied to the soil capturing the extractant downstream in collection borehole(s) without polluting aquifers. A further variation of this approach is to excavate the material and place on a liner (as in heap leaching in mining), applying an extractant, collecting the pregnant liquor, removing the metals and then recycling the extractant. Chelates are typically used to enhance metals removal but whilst metal recoveries are dramatically improved with chelating compounds, the metal are also then conversely difficult to extract from the chelates without resort to expense oxidation methods. Several studies have examined soil flushing and/or heap leaching for decontamination of dredgings [26,29,30,31,32]) in the latter study[32] 62% of the metals were leached in a 120 day percolation leaching test.

Phytoremediation

Phytoremediation is an established in situ technology (although still requires periodic harvesting) and is a very low intensity 'land farming' technique for metal contamination remediation. Much recent research has been directed at chelate enhanced phytoremediation (especially biodegradable chelates) to overcome the fact that many metals are not readily available for plants, and or have no natural tendency to hyperaccumualte in any plant species. Desirable plant species are those that are fast-growing, have a high biomass and can be easily harvested[28].

In situ deactivation and accelerated stabilisation technologies

In situ technologies for resource recovery / landfill mining do already exist and have developed for application to MSW landfill where the concept of the value recovery is not in the metals leached from the system but in (i) the value of the land (ii) the energy

recovery (methane combustion) see for example Jones et al[33] and (iii) facilitating subsequent ex situ mining for land, soil, materials and energy recovery. Metals have not historically been a target for recovery from MSW landfills as the leachates do contain economically recoverable amounts of metals. Kjeldsen et al.[34] report that leached metals may account for less than 0.02% of the total present. The majority the metals mass resides within the landfill in largely insoluble components. Whilst there is scope to increase this substantially, this may not be viable compared to ex situ recovery of those materials.

The in situ enhanced recovery of energy via the "anaerobic bioreactor" concept is a relatively mature field, especially in the US, Germany, Australia and the Netherlands. The aim is to increase the total amount and production rate of methane from the biodegradable component of the landfill. This has been achieved via leachate recirculation and/or through temperature, pH control[35,36] and more recent research is examining enzyme addition e.g.[37]. Another related in situ concept is the "aerobic bioreactor" and the "sustainable landfill" concepts (see for example [38,39,40]) which rely on the the rapid biological stabilisation of landfills in order to bring about stable conditions as soon as possible to allow ex situ mining of the biologically stabilised (i.e. not actively gassing) landfill for materials and land recovery such that landfills become simply "temporary storage"[33]. There are also hybrids systems between the anaearobic/aerobic reactor concepts.

Krook et al[41] point out that soil from landfills systems have been a major target of previous landfill mining efforts. Kartineen at al[42] describes the fine fraction of landfill "may comprise up to soil materials used for e.g. landfill intermediate covers. Appearing in such large mass fractions, up to 74% of the landfill body, the fate of the fine fraction may be crucial for the economics of a landfill mining project". Landfill fines (fraction <75 μm) have been found to contain up to 30% metals, and high concentrations of Zn, Cu, Cr and Pb in particular have been reported[43]. And it is interesting to note that soil flushing (see above) would be an ideal decontamination/metal recovery technique which may render this large amount of soil a higher value application. Thus an in situ leaching approach might be applicable to materials recovered post ex situ mining.

In addition to in situ approaches to biological stabilisation of landfills, other in situ stabilisation or decontamination techniques are relevant to other wastes. For example, Fedje et al[44] discuss methods for leaching metals from MSW incineration fly ash so as to render the fly ash classfiable as non-hazardous waste – which also also facilitates reuse options. Further examples include the weathering /carbonation of blast furnace slags to remove problematic lime content ahead of its use as a product in aggregate applications and the accelerated carbonation of alkaline wastes e.g. Van Gervn et al[45]. These materials also contain heavy metals such as Cu, Pb, Zn, Cr, As, etc.

Process Intensity: economic and environmental perspectives

Target wastes for in situ recovery of metals will be lower in the concentration of target metals compared to lithospheric ores, as is the case with the application of heap leaching versus more intensive beneficiation the decision is based largely on economics. The same reasoning has been applied to remediation of contaminated land (Cundy et al, 2013). Leaching is a hydrometallurgical approach ranging from aggressive reagents such as acid or alkaline leaching at elevated temperature/presssure to induce solubilisation within the confines of reactor vessels. These chemicals and conditions cannot be used in the environment. Thus the reactor gives way to an a lined heap, the processes happen at ambient environmental, temperature and pressure and reagent consumption minimised as much as possible. But how far should and how far can the reduction in process intensity be taken? The ultimate recovery and the recovery rate of the target species are clearly important. If the driver for the in situ leaching is economic recovery of metals alone then the process needs to have a high and fast recovery rate, whilst if the driver is land decontamination (albeit with economic recovery of metals to offset remediation) then the intensity might be very low.

The following simple examples illustrate some hypothetical choices regarding the implementation of different intensity processing of mine wastes:

(i) High metal value determined in mining waste→ In situ approach not used: A mine waste becomes highly valuable for target metal. A process to excavate, grind and leach the mine waste in strong acid is devised with commensurate high intensity metal recovery (solvent exchange and electrowinning).

(ii) Intermediate metal value determined in mine waste→ In situ approach applicable. A mine waste is identified as containing moderate value of metals and is processed by heap leching. The material is loaded on to a leach pad. Dilute acid reagent is applied (intermediate reagent costs) and recirculated, the heap is leached over the course of 2 years, intermediate intensity metal capture system is utiised.

(iii) Low level of metal value in mine waste (decontamination of waste is also an aim) → in situ approach applicable. Environmentally benign and inexpensive lixiviant applied to accelerate natural AMD-ML processes with a passive treatment systems which captures and recovers metals in an economically viable form.

From the examples above it is easy to see the continuum of options. Furthermore the decisions are determined by the geochemistry, mineralogy and particle size of the waste and how these influence the lixiviant choice etc which dictates the practicality of the in situ leaching approach. i.e. what concentrations of metals do they contain and how soluble are they, and/or how quickly can they be recovered using various reagents?

The solubility of wastes in water is dependent on such factors as their mineralogy, particle size and crystallinity. The example above of sulphide minerals reacting with

rain water leads to appreciable metal release if the acid mine drainage process begins. If the valuable species is within the sulphides then this will be released as they breakdown, but furthermore as the reaction produces sulphuric acid then this may tend to solubilise other components of interest. Thus wastes containing sulphides will be amenable to self-extraction if engineered appropriately (as is known with heap leaching) thus sulphidic tailings and mine wastes are a target for in situ leaching. Wheres other wastes such as smelter slag whilst metal-rich may be vitreous and very insoluble in rainwater (plus the constraints of occlusion of the bulk within the interior further restricts mass transfer to the dissolved phase.

Whilst some wastes are not sufficiently soluble in water alone, a lixiviant can be selected which significantly enhances solubility through pH change (e.g. sulphuric acid) or through chelation, or by converting the recalcitrant phase in to a more water soluble or environmentally reactive phase. Chelates have been applied in the case of soil flushing for contaminatned land but there are also a range of microbially produced chelates that might be applied to enhance solubilisaton of target metals. Other approaches might involve physicochemical alteration of the phases in situ through electrical or microbially-induced oxidation or reduction. Biogeochemical and biohydrometallurical approaches are being researched, for example in the study by Hocheng et al[47] Acidithiobacillus thiooxidans and fungi Aspergillus niger were tested for application to the leaching of steel slag. Cheng et al[48] looked at bioleaching from Pb/Zn smelter slags.

The Sustainable remediation context: Resource recovery, gentle remediation and ecosystems services

An important consideration not taken into account in most cost / benefit calculation (including the exmples above) is ecosystems service benefits / disbenefits as well as effects on other wider environmental components such as social and cultural heritage. Many waste repositories provide ecosystems services with respect to wildlife habitat and can be amongst other things important educational and heritage features of the landscape. Thus when considering recovery of metals from waste repositories these factors need to be taken considered in the accounting. The lower the intensity of the process the lower impact (probably) on potential ecosystems services that the site provides and thus lower intensity approaches to resource recovery may add (if apportioned significant weighting in the decision-making) considerably to the benefits in the cost / benefit analysis. Parallels can be drawn from contaminated land risk management which has evolved from a focus on containment, cover and removal to landfill through to in situ and ex situ treatment technologies and more recently to the concept of Gentle Remediation Options (GRO) where soil functionality is retained (and thus the ecosystems services of that soil preserved) in addition to risk management[46]. These technologies use plant, fungal and microbiologically-based methods, with or

without chemical additives, for reducing contaminant transfer to local receptors by in situ stabilisation or extraction of contaminants and are considered as part of a new suite of sustainable remediation technologies. In situ recovery of metals from waste repositories where the dual purpose of decontamination and site reclaimation is achieved also fits into this classification.

Metals Capture Technology

The intensity of processing also dictates the intensity of metal capture from the aqueous stream once metals have been mobilised and recovered from the waste. The decision about process intensity will be based (as discussed above) on the various cost/benefits which inform metal recovery and decontamination of wastes. Inevitably factors such as less intensive leaching systems using non-aggressive, environmentally benign lixiviants and limitation of recovery by heterogeneous flow means that the intensity of in situ processing of wastes will be much lower and the timescales possibly be counted in years. Thus the technology used to capture the metals leached from the system has to be of commensurate intensity. For example in high value process intensive systems such as gold processing the gold is captured by the 'carbon in pulp' method and the carbon stripped from gold. Whereas lower intensity leaching systems might use ion exchange resins over longer periods.

Low intensity capture analogues are being developed for the "passive" treatment of metalliferous mine waters. Such systems use a variety of (bio)geochemical engineering approaches to achieve immobilisation of metals. Variously processes of precipitation, adsorption, microbiological reduction and or oxidation and manipulation of pH to achieve the sequestration of metals. Thus these technologies offer a readily transferable options for low intensity harvesting of metals which achieve (i) eventual decontamination of the mine waste, (ii) protection of the environment from metal pollution and (iii) recovery of the metals. Similarly, phytoremediation represents a very low intensity process for metals removal and is being widely investigated as an in situ technique for both decontamination and metal recovery.

Future research directions

There is much scope for the development of the in situ apporach to technospheric mining, fruitful avenues for future research include: (i) In situ conversion of wastes to more valuable product (ii) The application of new metallurgical approaches that are highly selective to the target metals. (iii) Novel technologies for the manipulation of biogeochemical environments within waste repositories to achieve dissolution of target species (iv) Novel technologies for controlling flow in materials of low hydraulic conductivity.

Conclusions

The in situ recovery of metals has been applied variously in mining and contaminated land environments although with different objectives. However, many aspects of both of these exisitng technology are readily transferable to technospheric mining. This paper has outlined some of the key wastes where in situ leaching could be applicable, outlined the similarities with existing processes and their geochemistry and sought to outline the continuum of concepts between remediation and metals recovery and how this fits in with concepts of sustainable remediation. In situ recovery of metals involves mobilisation, transport and capture of the target metals in a concentrated form – the challenge is to devise various physical, chemical, biological and biogeochemcial engineering technologies to achieve this.

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