

Research Paper**THE CONTRIBUTION OF INDUSTRIAL MINERALS TO
SOLVING ENVIRONMENTAL ISSUES**

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Complutense of Madrid, c/José Antonio Novais 2, 28040 Madrid, Spainjpcalvo@ucm.es**Abstract**

Mitigation of environmental issues and decontamination of land by using a variety of industrial minerals mainly immobilizes contaminants in solution, whether in polluted water or contaminated soils and sediments. That is because a variety of minerals, in particular carbonates, clays and zeolites, have a significant capacity to adsorb harmful ions and to react to form precipitates. Phosphates, iron hydroxides, some silica minerals and lime-derived products can also be used to solve environmental issues. This paper focuses on the amendment of soils and sediments affected by the impact of mining or by waste landfills, with some reference to the use of minerals in cultural heritage conservation. An example of actions leading to the amelioration of contaminated land is provided after describing some current pilot experiences on highly polluted wastes derived from mining in SE Spain.

Keywords: *Environment, pollutants immobilization, sorption, industrial minerals, cultural heritage*

Περίληψη

Η χρήση ποικίλων βιομηχανικών ορυκτών για τον μετριασμό των περιβαλλοντικών ζητημάτων και της απορρύπανσης της χέρσου οδηγεί στην αδρανοποίηση των ρυπαντών εν διαλύσει, είτε βρίσκονται σε μολυσμένο νερό,

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είτε σε ρυπασμένο έδαφος. Αυτό οφείλεται στο ότι κάποιες ποικιλίες ορυκτών, ιδιαίτερα των ανθρακικών, αργίλων και ζεολίθων, έχουν την σημαντική ικανότητα να προσροφούν / απορροφούν επιβλαβή ιόντα και να αντιδρούν σχηματίζοντας ιζήματα. Φωσφορικές ενώσεις, υδροξείδια του σιδήρου, μερικά πυριτικά ορυκτά και προϊόντα προερχόμενα από την κατεργασία ασβέστου, μπορούν επίσης να χρησιμοποιηθούν για την επίλυση ορισμένων περιβαλλοντικών ζητημάτων. Αυτή η εργασία επικεντρώνεται κυρίως στη βελτίωση εδαφών και ιζημάτων τα οποία επηρεάζονται από τις επιπτώσεις των εξορυκτικών δραστηριοτήτων ή των χώρων διάθεσης απορριμμάτων και δευτερευόντως στη χρήση διαφόρων ορυκτών για την διατήρηση της πολιτιστικής κληρονομιάς. Δίνεται ένα παράδειγμα τέτοιων ενεργειών που οδήγησαν στη βελτίωση ρυπασμένης γης περιγράφοντας τις παρούσες πιλοτικές εμπειρίες σε εξαιρετικά ρυπασμένα απόβλητα προερχόμενα από την μεταλλευτική δραστηριότητα στη ΝΑ Ισπανία.

Λέξεις κλειδιά: Περιβάλλον, αδρανοποίηση ρυπαντών, προσρόφηση, βιομηχανικά ορυκτά, πολιτιστική κληρονομιά

1. Introduction

Mitigation and/or solution of environmental issues by using industrial minerals can be undertaken in various ways depending on the problem to be solved, for example: (a) improving water quality, (b) treatment of residual waters (urban, industry, mining and irrigation), (c) reduction of impacts of pollutants from industrial contamination, (d) agricultural and livestock pollution, (e) waste disposal facilities. In addition, a number of industrial minerals are used in civil engineering projects relevant to the aforementioned issues.

Ingestion of several industrial minerals helps to either prevent human disease or contribute to improved health. The discipline of Medical Geology (Selinus, 2004) and Environmental Mineralogy are expanding areas of research (Carretero and Pozo, 2007; Vaughan and Wogelius, 2013). A complementary aspect concerns the use of industrial minerals as critical materials for developing green technologies, crucial to reduce CO₂ emissions, as well as to some commodities.

A not yet fully explored field concerns some industrial minerals behaving as nanoparticles. This shows increasing application in the field of cultural heritage conservation.

The most significant properties of industrial minerals as environmental mitigation agents relate to deal ion exchange capacity, adsorption/absorption capacity, hydraulic and thermal conductivity, ionic diffusivity, mechanical strength, behaviour at high temperature and pressure conditions, and resistance to chemical and biological agents.

Keeping in mind these properties that are important for dealing with certain environmental issues, industrial minerals can be grouped as follows:

- 1) Some minerals, e.g. carbonates, can behave as high solubility pollutant hosts, allowing the release of the pollutants.
- 2) In contrast, other minerals like phosphates show low solubility after hosting pollutants, i.e. after forming metal phosphates.
- 3) A number of industrial minerals are composed of particles with large surface areas, which is an important feature controlling the release or uptake of pollutants.
- 4) Minerals exhibiting layered crystal structure, e.g. some types of clays are relevant because of their ability to intercalate pollutants between the layers.
- 5) Industrial minerals such as zeolites have open structures that may act as molecular sieves and trap a range of pollutants.

2. Sources for contaminants in water, soils and sediments

A number of inorganic pollutants, e.g. cadmium, zinc, lead, arsenic, etc, are commonly present in soils and sediments. Both organic and inorganic pollutants of various origins can accumulate and/or be transported in surface and groundwater, can be immobilized in contaminated soils and sediments, or can blow as atmospheric aerosol particles (dust and finer particles). Table 1 shows sources of inorganic pollutants that are usually found in contaminated land.

ELEMENT	MAJOR USES	SOURCES
Arsenic	Pesticides, desiccants, animal feed additives, detergents	Coal, petroleum, mining debris, mineral processing, atmospheric deposition
Cadmium	Paint pigments, plastic manufacturing, batteries	atmospheric deposition, metal processing, chemical industry
Chromium	Stainless steel, paint pigment, brick manufacture	Manufacturing of metals, domestic wastewater, sewage sludge
Copper	Plumbing, electric wires, antifouling paint, bronze	Metal manufacturing, sewage sludge, atmospheric deposition, metal processing,
Lead	Batteries, metal products, pigments, chemicals, combustion of oil, coal and gasoline	Atmospheric fallout, metal manufacturing, sewage sludge
Mercury	Manufacturing of plastics and electrical equipment, production of chemicals, pesticides	Coal-burning power plants, atmospheric fallout
Nickel	Metal alloys, chemical production, batteries, combustion of oil, gas and coal	Domestic wastewater, metal processing, sewage sludge, atmospheric fallout
Zinc	Coatings on metals, batteries, rubber manufacturing	Metal manufacturing, domestic wastewater, atmospheric fallout

Table 1: Common uses of some elements that are inorganic pollutants, with indication of their sources in an industrial environment (modified from Blatt, 1997).

The concentration of toxic substances in the environment is in sometimes the result of natural processes but they are in mostly derived from human activities, particularly industrial operations and mining (Fig. 1).

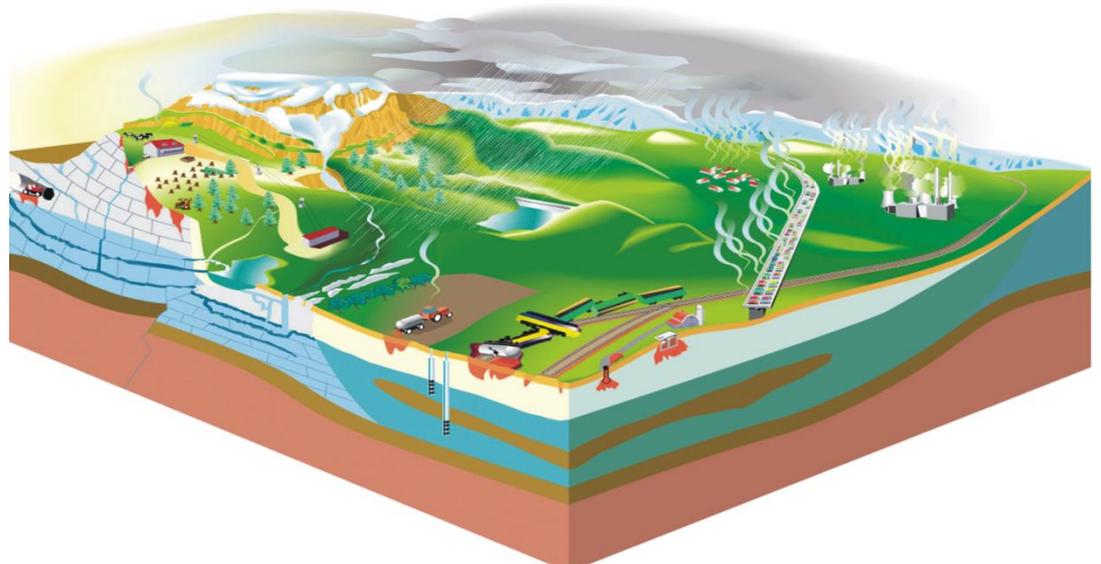


Fig. 1: Sketch showing the varied sources of pollution in the man environment, with emphasis in industrial activities, traffic and local underground structures.

Pollutants can be classified in several ways based on their physical and chemical properties, abundance, persistence in the environment, effect on ecosystems, or toxicity. A common subdivision distinguishes the following groups (Van der Peck, 2006):

- *solid phase constituents* (based on their chemical composition, these can be subdivided into inorganic minerals and organic compounds)
- *major dissolved phase constituents* (these include substances that are abundant as dissolved ions in natural waters, namely calcium, magnesium, sodium, potassium, iron, manganese, carbonate species, chloride and sulfate)
- *nutrients* (raw materials that are assimilated by living organisms to sustain life, and promote growth, development, and reproduction)
- *heavy metals* (these include metals and metalloids of high atomic mass associated with contamination and potential toxicity or ecotoxicity)
- *radionuclides* (elements having unstable nuclei which spontaneously disintegrate emitting ionizing radiation)
- *organic pollutants* (made up mainly of carbon, hydrogen and oxygen, with a few other elements).

Based on the major phase present (gas, liquid, or solid phase), three environmental “compartments” can be distinguished: soil/sediment, water and air. Water is usually further classified in surface waters, which are in contact with the free atmosphere, and subsurface waters (groundwater).

Issues derived from atmospheric pollution are beyond the scope of this work so discussion on these environmental compartments is restricted to soil/sediments, groundwater and surface water.

Soil and sediments

Soil can be defined as “a centimeter or thicker unconsolidated layer of fine-grained mineral and/or organic material, with or without coarse elements and cemented portions, lying at or near the surface of planets, moons, and asteroids,

which shows clear evidence of chemical weathering” (Certini and Ugolini, 2013). Sediments are defined as “all kinds of deposits of solid material that has settled down from a state of suspension in a liquid, and refers to essentially unconsolidated materials on the Earth surface” (Bates and Jackson, 1980).

The input of pollutants into soil and sediments can occur *via* a wide range of pathways:

Municipal, industrial, or mine wastes can contain a large variety of contaminants, including metals, cyanide, polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), asbestos, methane, ammonia and hydrogen sulfide. Dispersal of pollutants from waste disposal sites is usually restricted by sustainable isolation of the site but there are many dump sites where isolation is not efficient or is absent (Fig. 2). In addition, release of industrial pollutants to soils and sediments may occur accidentally.

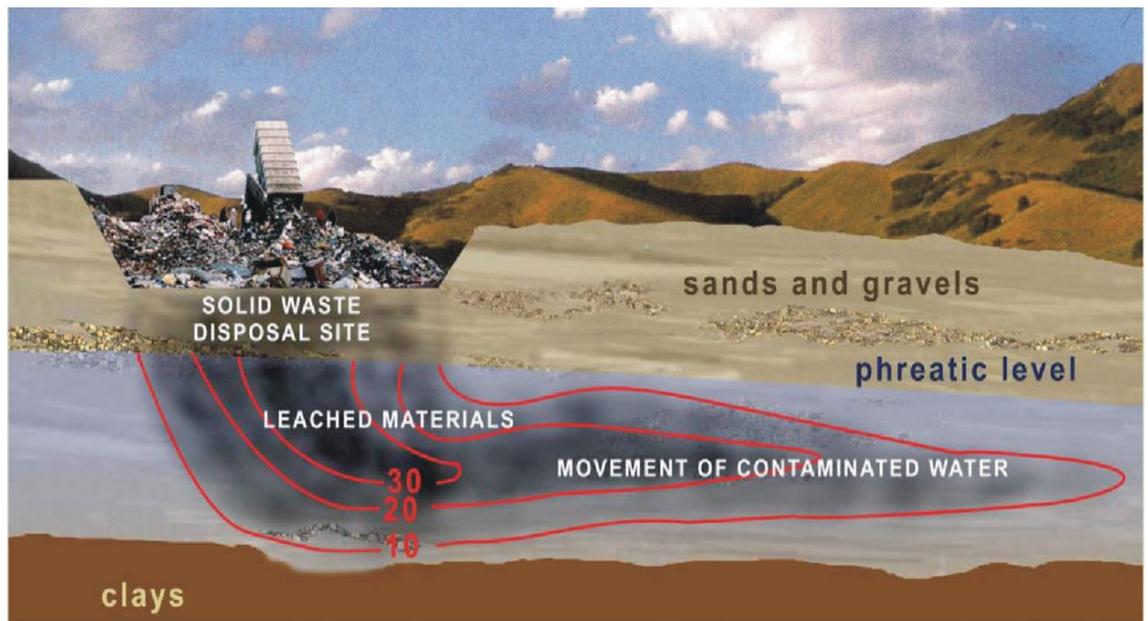


Fig. 2: Contaminant plume in a waste disposal site undergoing leaking of leached materials. Red numbered lines correspond to isolines of ammonium (NH_4^+) in mg/L (from López-Geta et al, 2006).

In *agricultural areas*, application of pesticides and fertilizers is an important source of pollutants in soils. Pesticides include a variety of organic compounds that can contain heavy metals whereas fertilizers promote plant growth by enhancing supply of essential nutrients, such as nitrogen, phosphorus and

potassium. These nutrients are included in organic fertilizers (manure, compost and sewage sludge) or in inorganic artificial fertilizers. But, like pesticides, fertilizers often contain heavy metals. The application of fertilizers and pesticides has resulted in slight but widespread contamination of most agricultural soils.

Radionuclides exist in the environment either naturally or artificially. It has been estimated that, on average, 79% of the radiation to which humans are exposed is from natural sources, 19% from medical application and the remaining 2% from fallout of weapons testing and the nuclear power industry (Wild, 1993). However, most of the public concern over radiation from radionuclides has been focused on global fallout from atmospheric nuclear weapons testing and the operation of nuclear facilities. Both of these activities have introduced a substantial amount of man-made radionuclides into the environment and have caused radionuclide contamination of large areas of land worldwide (Zhu and Shaw, 2000). Radionuclides in the environment can eventually be passed on to human beings through food chains and, so, may be an environmental threat to the health of impacted populations.

Roads and railways are a potential source of soil contaminants, such as metals and hydrocarbons, originated from a wide range of non-point sources including wet and dry deposition, vehicle exhausts, and vehicle and road wear, de-icing operations, accidents, abrasion of construction materials and soil erosion.

Groundwater

Groundwater is defined as the water present in the saturated zone beneath the water table.

The main sources of groundwater pollution are similar to those of soil and sediment pollution and include landfills, accidental spills, agriculture, septic tanks and atmospheric deposition. Dissolved pollutants can move with the pore water while organic liquid pollutants may reach the groundwater directly. In addition, in areas where surface water infiltrates into groundwater, surface water pollution is a potential source of groundwater contamination. Another source of

pollutants in groundwater is the artificial input of contaminated water by deep well injection.

Surface water

Surface water includes all water on the surface of the Earth found in rivers, streams, canals, ditches, ponds, lakes, marshes, wetlands, coastal and marine waters, and as ice and snow. Because much of the surface water has previously passed through the soil (surface or profile) or groundwater, many of the sources of soil pollution and groundwater pollution may be sources of surface pollution as well.

Urban runoff in particular contains increased levels of contaminants including nitrogen, phosphorus, heavy metals, and organic compounds. Direct point source releases of pollutants include *drainage from mine areas* (Fig. 3) and effluent discharges of *untreated or treated industrial and municipal wastewater*. Sewage water is particularly rich in pathogenic bacteria and viruses, organic matter, and nutrients, but may also contain increased levels of heavy metals and dissolved salts.

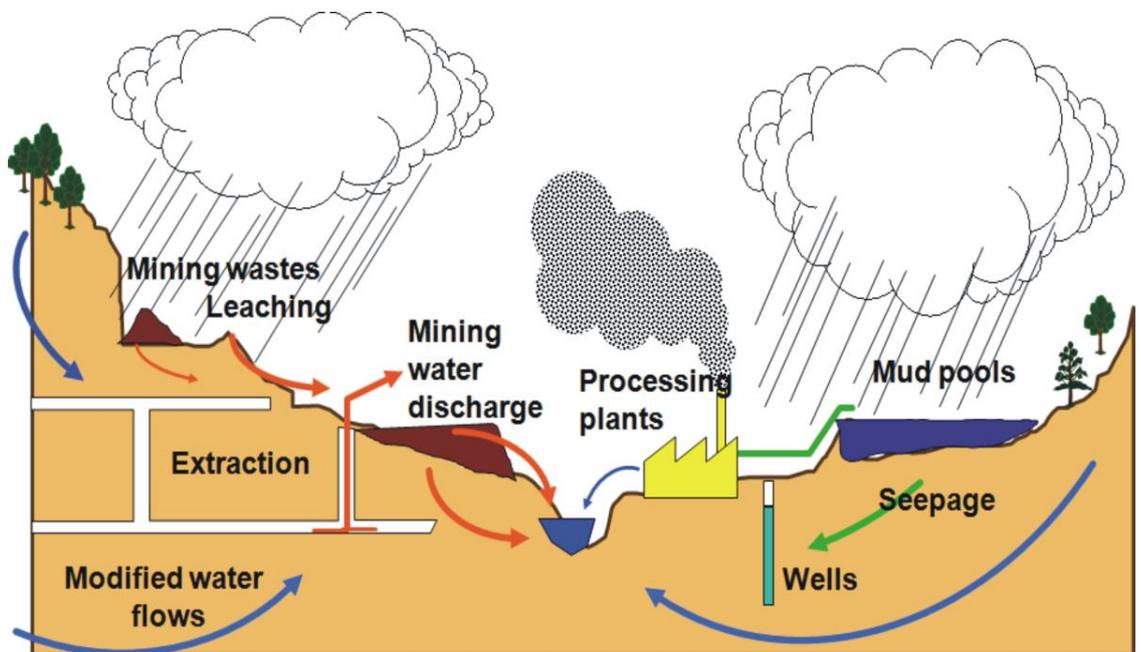


Fig. 3.: General sketch showing the environmental impact mainly related to the surface water and groundwater flows in mining operations.

Accidental spills can cause severe pollution of surface water. They may occur, for example, in leaks from chemical processing or products from industrial installations, release of contaminated firefighting water during fire abatement, or failures of tailing dams of mine reservoirs.

3. Mechanisms for neutralizing pollutants

The use of reactive or stabilizing materials for remediation of metal and organic contaminants in soils has been widely studied and is gaining broader acceptance as a remediation approach (O'Day and Vlassopoulos, 2010).

Two strategies can be used to remediate contaminated soils (Adriano, Wenzel, Vangronsveld and Bolan, 2004). One is *in situ* stabilization (Sun et al., 2015) (e.g. immobilization by chemical amendments and phytostabilization), and another is *ex situ* extraction or separation of metals from contaminated soils (e.g. washing and flotation). The use of stabilization/solidification in the treatment and remediation of contaminated soils has been gaining prominence because of its cost-effectiveness and rapid implementation as well as its appearance as a potentially valuable alternative technique for a wide range of polluted sites.

Over the past few decades many remediation strategies have been applied worldwide to deal with contaminated soils and waters. Among these techniques, chemical immobilization by means of soil amendments has been investigated as a technique for a wide range of contaminated sites (Scanferla et al, 2009). A number of natural or synthetic materials, such as phosphate rocks (Mignardi, Corami and Ferrini, 2012), zeolites (Kosobucki, Kruk and Buszewski, 2008; Shi et al., 2009), municipal biosolids (Madrid and Florido, 2010), red mud (Garau et al., 2007; Liu, Naidu and Ming, 2011) or carbonates (Pérez-Sirvent et al, 2011) have been tested to evaluate their ability to immobilize pollutants.

The aim of *in situ* amendment technologies is to sequester and stabilize contaminants in soils in order to reduce their ability to partition to water or biota, and thus their potential for transport and toxicity. Soil amendments have been employed to treat both organic and inorganic contaminants, although the selection of amendment treatment and the mechanism of hazard reduction

necessarily differed widely depending on the target contaminant, or mixtures of contaminants, at a given site.

Immobilization mechanisms

Sequestration mechanisms associated with mineral-based amendments to soils fall into two broad categories (Table 2), but in complex mixtures of amendments and soil, both mechanisms may occur and change with time.

ABSORPTION	Internal structural sorption	interlayer spaces and structural channels uptake of hydrated cations and other molecules
SURFACE ADSORPTION	Adsorption	inner-sphere: direct bonding of an ion to atoms on the mineral surface, outer-sphere: presence of water or hydroxyl ligands between the metal center and the surface
	Ion exchange	exchange of cations in clay mineral interlayers with species in solution
	Surface oxidation/reduction	either microbial biodegradation of organic compounds coupled to mineral reduction, or the oxidation/reduction of adsorbed inorganic contaminants
STRUCTURAL INCORPORATION	Coprecipitation	Precipitation of new phases involving the formation of amorphous (coprecipitation) or crystalline solids (solid solution) and contaminant substitution, or the micro-encapsulation precipitates containing contaminants into new phases.
	Solid solution	
	Micro-encapsulation	

Table 2: Main processes dealing with sequestration mechanisms associated with mineral-based amendments to soils.

4. Properties of industrial minerals

The use of industrial minerals in environmental management is highly dependent on their interactive characteristics. Mineral stability is dependent on both the nature of the mineral itself and the nature of, and interactions with, the surrounding environment. A number of industrial minerals show properties that contribute to eliminate, neutralize, sequestering and/or immobilizing harmful

substances. In the field of mineralogy and environmental management, the most significant properties (Cotter-Howells et al., 2000) are given in the following sections.

Adsorption/absorption capacity

The adsorption capacity of solid materials (adsorbents) is defined by the adhesion of atoms, ions or molecules from a gas, liquid or dissolved solid to a surface of the adsorbent material. This can be a mineral, e.g. zeolite, or a treated and synthetic material such as silica gel, activated carbon, Fe oxyhydroxides, etc. The adsorption capacity of these materials is directly related to their specific surface area (SSA), which is usually expressed as the total surface area of a material per unit of mass (m^2/g).

The adsorption capacity is a property linked to a surface-based process which differs from absorption. The latter phenomenon implies that a fluid permeates or is dissolved by a liquid or solid, in this case an absorbent. Many industrial minerals show high absorption capacity, for instance diatomite and some clay minerals; common absorbent clays show high inter-lamina spaces (smectite clays) or structural channels (fibrous clays such as palygorskite and sepiolite) which can uptake hydrated cations and other molecules within the clay structure. Very often, adsorption and absorption capacities of minerals or in general solids cannot be properly separated. In these cases the term ‘sorption’ can be used to define properties.

Ion exchange capacity

Ion exchange capacity is a measure of the ability of an insoluble material to undergo displacement of ions previously attached and loosely incorporated into its structure by oppositely charged ions present in the surrounding solution. This property is characteristic, for instance, of zeolite minerals, which are used in water softening. Most zeolite minerals have a large capacity to exchange Na^+ for Ca^{2+} of hard water.

High cation-exchange capacities are also characteristic of several clay minerals because of their layered crystal structure. Cation exchange capacity can be estimated by measuring the number of exchangeable cations per dry weight that a soil and/or sediment is capable of holding, at a given pH value, and are available for exchange with the soil water solution. It is expressed as milliequivalent of hydrogen per 100 g of dry soil.

Structural incorporation

Some amendments react with soil water and minerals to alter composition, pH, or Eh of the system, causing dissolution of solids and precipitation of new phases that can structurally incorporate contaminants. Among these, microencapsulation can localize each particle in a stable matrix. Silica and cement-based amendments are examples of reducing contaminant partitioning into pore-water and also may also result in permeability reduction, decreasing the flux of water through treated soil and potential for leaching of stabilized contaminants.

This class of sequestration mechanisms has the potential for more permanent immobilization, compared to surface adsorption or ion exchange, since mineral dissolution is required to partition the contaminant into water.

Mechanical properties

Physical strength, plasticity, density and swelling behavior, diffusion resistance, and permeability are mechanical properties of industrial minerals that are relevant to waste management. Clay or clayey soils are used as barriers primarily because their particle size is small enough to limit the flow of fluids (i.e., relative impermeability). The physical strength of some clay minerals allows their use in compacted clay liners. Swelling of some clay minerals (especially those of the smectite group, with montmorillonite as the best known mineral of that group) may be also a suitable for engineering. Swelling refers to change in clay volume by adsorption of water or other polar solvents. Two types of swelling, osmotic and inner crystalline, are observed (Hermanns Stengele and Plötze, 2013). Whatever the type, swelling is closely related to ion exchange capacity and, thus,

the physical-chemical properties of the clay minerals. A similar comment can be made regarding the diffusion resistance of clays.

5. Minerals and other substances

As mentioned previously, a number of mineral-based materials can be used as amendments for remediation of contaminated soils and sediments, geotechnical works related to waste management, treatment of waters, etc. Table 3 shows a list of industrial minerals that are usually used in solving environmental issues.

In summary:

AMENDMENT TYPE	SOURCE MATERIAL	STABILIZATION MECHANISM
Carbonate Lime Portland-type cements	Calcite, dolomite, magnesite, siderite, Lime, portlandite Mixture of Ca-silicate, Ca-aluminate and Ca-aluminoferrite	Adsorption, Solid solution and encapsulation
Clay	Layered silicates	Adsorption/ion exchange
Zeolites	Framework aluminosilicates	Adsorption/ion exchange
Sulfates	Gypsum, ferrous sulfate, aluminum sulfate	Solid solution
Silica minerals	Soluble alkali silicate salts	Adsorption, encapsulation
Phosphates	Apatite group minerals and soluble phosphate	Solid solution

Table 3: Summary of common mineral-based and related amendments.

Carbonates

The most common carbonate minerals include calcite, aragonite, dolomite, magnesite and sodium carbonates such as trona and natron. In addition, lime or quicklime, a product of thermal decomposition of limestone, and Portland-type cements are considered to be industrial minerals. All of these mineral-based substances have important environmental applications because of their high acid-neutralization capacity. A major application of that property is in solving issues related to acid mine drainage, which is critical in sulfide mining areas. This is good in dealing with modern mining operations but also in ancient works

that, in many cases, have left huge amounts of problematic residual wastes. Similarly, through formation of leachates in landfill situations, problems can be dealt with. Moreover the consolidation of hazardous wastes with carbonate cement is useful because of the physical strength of the resulting concrete. Some other uses of carbonates to solve environmental problems are desulfuration in metallurgical processes and decontamination of soil and sediments.

Pulverized limestone and/or quicklime and Portland-type cements can be used as neutralizers to treat river and lake water pollution caused by acid rain and industrial and mining waste. Calcitic products milled below 75 μm are the most efficient (Chang, 2002). However, whereas limestone has a sluggish rate of reaction and cannot neutralize a strong acid much over pH 6.0, quicklime reacts faster and reaches higher neutralization values. Whichever is the case, the limestone products are by far the lowest-cost acid neutralizers per unit of basicity. Moreover, they are widely available in almost every country.

Hydrotalcite, a type of layered doubled hydroxide (LDH), occurs as a natural mineral and can be synthesized by reacting dilute aqueous solutions of magnesium and aluminium chlorides with sodium carbonate (Mills et al, 2012). The interlayer anions of hydrotalcite, most commonly carbonate, can be exchanged with a wide range of inorganic and organic anions. The removal of organic species from discharged wastewater to be able to reuse the water is an important environmental issue.

Although the conservation of cultural heritage is not strictly an environmental issue, preservation of monumental works by using industrial minerals, in particular limestone is worth writing about. The use of new forms of precipitated calcium carbonate (PCC) in mortars has strongly contributed to the improvement of deteriorated constructions elsewhere (Maravelaki-Kalaitzaki et al., 2005; Cizer et al., 2012). Nowadays, progress in nanotechnology provides a new frontier as nanomaterials display properties that are modified by the reduction in size. Thus, use of lime nanoparticles increases the penetration of the stone treatment as well as minimizing water absorption and colonization by micro-organisms. This results in higher durability and resilience of cultural heritage against deterioration (López-Arce et al., 2009; Giorgi et al., 2010).

Clay minerals

These include a large variety of mineral structures corresponding to a diversity of uses according to the specific type of clay. Regarding mitigation/solution of environmental issues, the most common practice is infilling of voids and cavities, e.g. those related to mining, immobilization of urban and/or industrial waste, and creation of impermeable screens for waste management (Fig. 4). *Containment* is a fundamentally important concept in environmental and civil engineering. Preparation of synthetic membranes together with clays is an example of environmental screening. Other uses of clay minerals include sealing of radioactive storage sites, decontamination of radioactive and non-radioactive waters, and depuration of gas emissions.

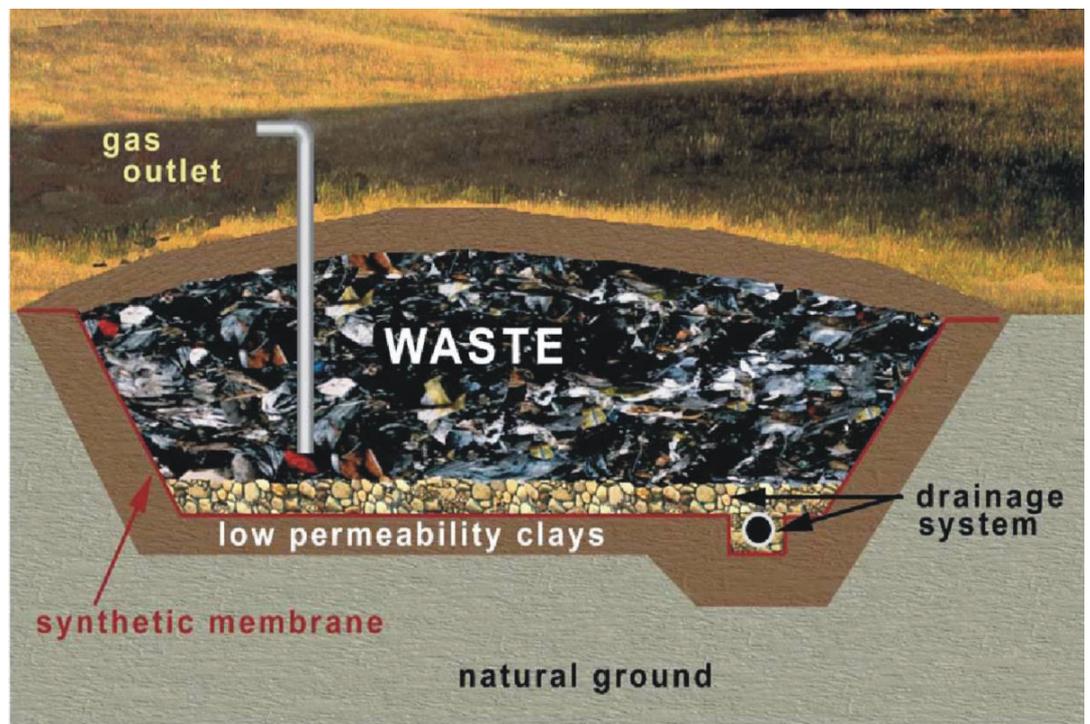


Fig. 4: Schematic cross-section of a secure waste-disposal site showing the distribution of clay barriers and geo-membranes (from López-Geta et al, 2006).

In the aforementioned uses, the most important clay minerals belong to those grouped as bentonites (several types of smectites) and fibrous clays (sepiolite and palygorskite), which show high cation exchange capacity, swelling capacity, high plasticity, low permeability and resistance to diffusion. Kaolinite is used occasionally for depuration of residual gases.

Illite, kaolinite and smectite rank among the most common species in terms of barrier clays, often due as much to their ready availability as to their desirable properties (Trauger, 2006). Smectite clays, specifically montmorillonite-bearing bentonite, are commonly used as a mixed with existing soils in barrier applications. Because of its water absorption and volumetric swelling properties, a small percentage of bentonite can significantly decrease the hydraulic conductivity of a porous soil or sediment. Bentonite and attapulgite are applied less conventionally in containment barriers.

Zeolites

Zeolites are hydrated aluminosilicates with a three-dimensional framework-type structures that have cavities and channels of molecular dimensions. This open structure allows the movement of large ions during cation exchange and of water molecules during reversible de-hydration, and makes zeolites chemically active in absorption, ion exchange and catalysis (Chang, 2002). The most common zeolite minerals, including both natural and synthetic forms, include analcime, chabazite, clinoptilolite, mordenite, erionite, natrolite and heulandite.

Properties related to the specific structure of the zeolites are varied including (a) a high degree of hydration, (b) low density and large void volume when dehydrated, (c) large cation exchange capacity, (d) uniform molecular-sized channels in the dehydrated crystals, (e) stability of crystal structures when dehydrated, (f) ionic electrical conductivity, (g) adsorption of gases, and (h) catalytic properties. These properties make the zeolites particularly interesting in industries dealing with resolution of environmental issues. The ion exchange capacity of zeolites is used in the treatment of radioactive waste. For instance, chabazite-erionite products were used in the clean-up operation at the Three Mile Island nuclear power plant site.

Clinoptilolite ion exchange processes are used to remove ammonium ions from sewage and agricultural effluent. Natural mordenite and clinoptilolite are capable of selectively adsorbing SO_2 , thus allowing high-sulfur coal to be used in the production of electric power. Similarly, certain zeolites are used in the

purification of natural gas by selective adsorption of CO₂, H₂S and H₂O. They are also used in methane-recovery and purification. They are also used for decontamination of soils.

Phosphates

Most phosphate minerals, in particular some hydrated phosphates of the crandallite group, are used in remediation of contaminated land because of their potential to immobilize toxic metals, e.g. Hg, Zn, Pb, Cd (Monteagudo et al, 2005). The most common use in remediation of metal-contaminated soils is by conversion of the polluting metals into metal phosphates that commonly have low solubility. As concluded from several investigations, e.g. Hodson et al (2000), the formation of Pb phosphates has the potential to be a sustainable, economic method for the remediation of metal-contaminated land.

Fe-oxyhydroxides

Although usually classified as metallic minerals, Fe-oxyhydroxides (goethite, hematite, ferrihydrite) show some properties that make these minerals to be useful in the mitigation of environmental problems. A principal interesting property is their capacity to absorb some harmful chemical elements and/or compounds on their structure as is the case, for instance, for uranium and its ions, Sr and Sb. Other oxides and hydroxides of Al (gibbsite), Mn (pirolussite, manganite) and Mg (brucite) show similar adsorption capacities. Silica gels can also be used. Special interest is shown in hydrotalcite, a layered double hydroxide, and some minerals included in that group which, though rare in nature, are easy and inexpensive to synthesize.

Other mineral-based materials

In addition to the industrial minerals described above, diatomite, gypsum and other sulfates, olivine, silica compounds, etcetera, all have applications in dealing with environmental problems. Some minerals contribute to developing green technologies, e.g. lithium salts, REE minerals. The latter minerals include more than 150 species of which monazite, xenotime and bastänite are of major

economic interest. These are the main source of the rare earths that have industrial uses in catalysts and other applications integrated in the so-called ‘Green Technologies’ (see below).

6. Neutralization of potentially toxic elements by limestone filler – case study from SE Spain

As mentioned before, limestones are used as fillers in a large number of industrial applications. One of the relevant uses of limestones concerns remediation of soils and/or sediments containing harmful components as a result of continued impacts of mining over time. A case study on the suitability of limestone-based technosols for decreasing the toxicity of the leachates in sites contaminated by potentially toxic elements in an area affected by mining activities in SE Spain illustrates this.

Study area

The Sierra Minera of Cartagena-La Unión is one of the most important polymetallic mining districts of the SE Iberian Peninsula, known to ancient Mediterranean cultures some 3,000 years ago. Mining activities originally (from the 7th century B.C.) focused on Ag and Pb, with a renewed interest in Zn and Fe throughout the past two centuries.

Portman Bay is located close to the La Unión mining region. From 1957 to 1991, it was the site of ore concentration (the “Lavadero Roberto” plant). The ore was ground and passed through flotation circuits for the separation of sulfides (galena, sphalerite and pyrite). The resulting waste materials were discharged directly into the sea, originally in the inner part of the bay; later, the wastes were discharged farther offshore. The composition of the waste deposits shows two distinct mineral associations: (1) chlorite, sulfides, siderite and silicates, (2) greenalite, magnetite, sulfides and silicates. Magnetite was initially recovered but that process ceased after 1967. Wastes in Portman Bay show significantly high contents of trace elements and iron oxides (magnetite, goethite and hematite).

As a result of dumping, the whole bay was filled with wastes. The coast line advanced about 800 m, gaining 70 ha of land from the sea (Fig. 5). Coastal dynamics transported fine particles offshore while the sand fraction filled the bay. As a result, the bay contains largely unaltered mine wastes; only a small proportion of the infilling materials underwent weathering. Locally, the waste materials were accumulated under reducing conditions.

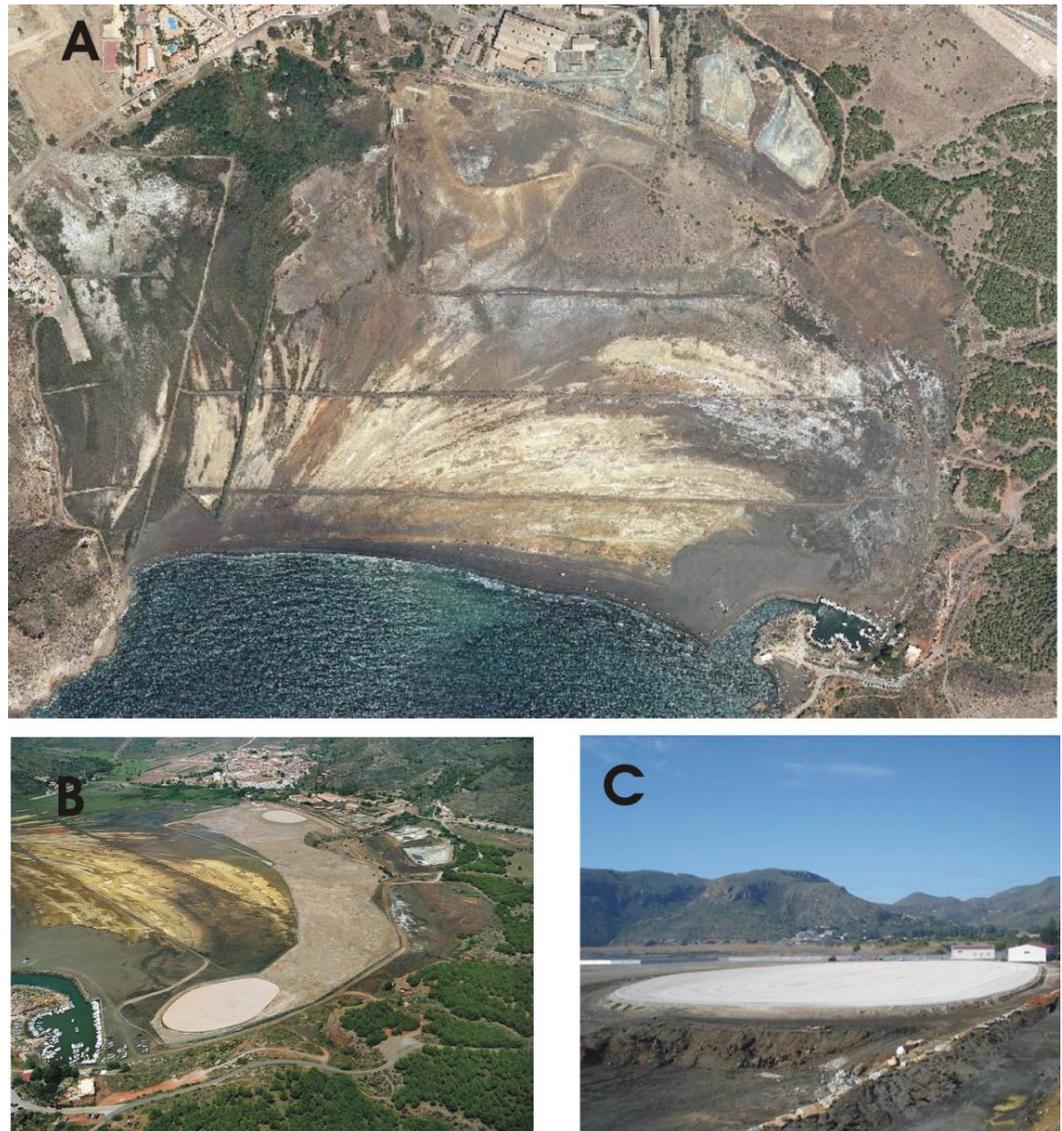


Fig. 5: Portman Bay. A) Pre-operational stage; B) Aerial view of the experimental plots; C) Detail of an experimental plot.

Experimental design

The stabilization approach was based on the use of limestone filler, a by-product of the marble cutting industry in the region, because of its low permeability, low solubility and high degree of physical-chemical stability. Moreover, the limestone filler is a non-toxic material with a high finely divided calcium carbonate content (Martínez-Sánchez, et al., 2014).

Four soil samples showing differences in pH (from 4.0 to 7.1) were collected and a stabilization approach was simulated by mixing with limestone filler mainly composed of calcite (86%). For this purpose, 0.5 m³ of soil samples were mixed with different proportions - 10%, 20% and 30% - of limestone filler. The stabilized samples were stored in containers for a year and moistened twice (60 L each episode) simulating rainfall. The percolates obtained were collected in polyethylene bottles and stored at 4°C until analysis.

Results

When polluted soil samples were mixed with filler limestone (10-30%), the heavy metal concentration decreased as the carbonate content increased. The stabilized samples were characterized by a near-neutral pH, low heavy metal concentration and high calcite percentage. The immobilization experiment confirmed that if polluted soil samples are mixed with filler limestone in a variable proportion from 20-30%, the resulting stabilised soils show similar behaviour to soils in which natural attenuation took place.

In addition, rainfall simulation cycles were carried out in order to evaluate heavy metal leachability (Fig. 6). Two rainfall episodes of 60 L were applied in one year, with a period of five months for drying between the two episodes. After the first rain episode the percolates from acid soils had an acidic pH, high electrical conductivity and high trace element content. When these soils were mixed with 10, 20 and 30% of limestone filler, the pH was neutral and the soluble heavy metal content strongly decreased, being under the detection limit when limestone percentage was 20% and 30%.

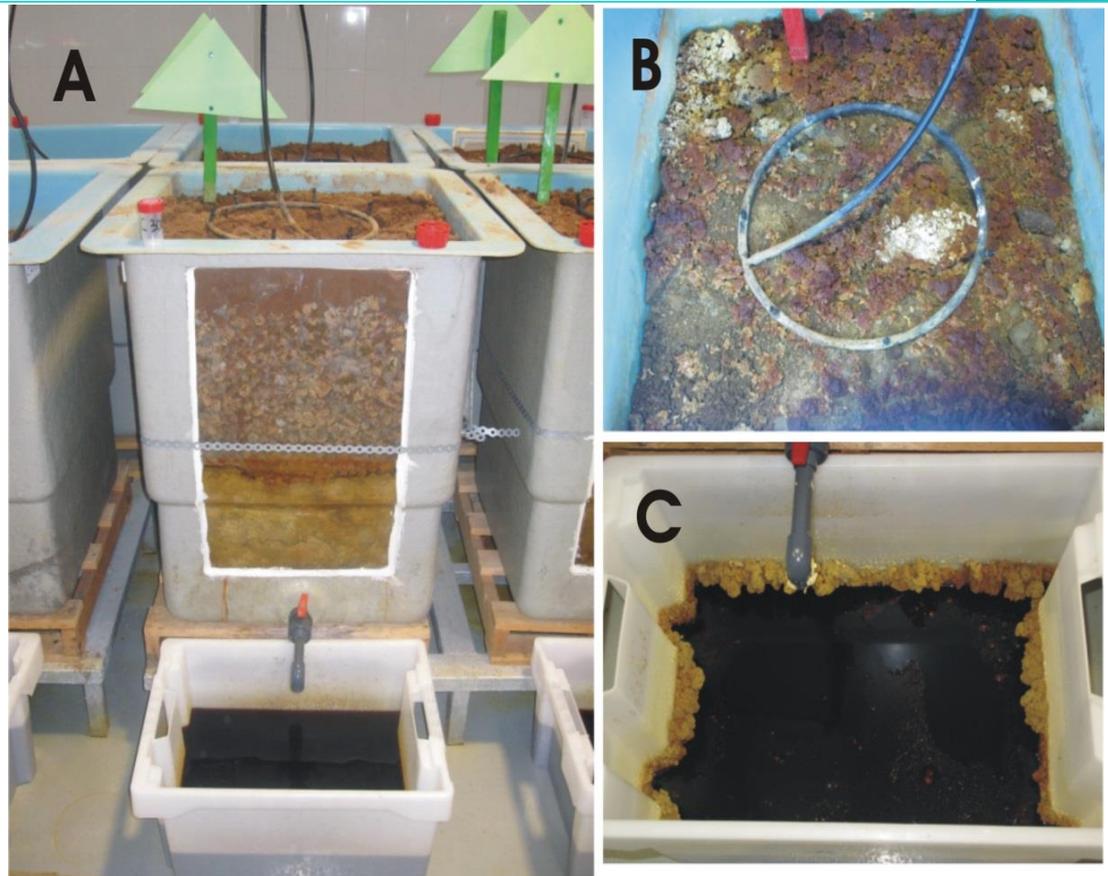


Fig. 6: Percolation assay (Portman Bay case study). A) Experimental container with created technosols; B) Rainfall simulation procedure; C) Collected leachate.

When the second rain episode was simulated, the results obtained were similar: percolates from acid soils were characterized by acidic pH and very high soluble heavy metal concentrations while in the soils mixed with limestone filler, the pH increased to neutrality and the soluble heavy metal content diminished. Accordingly, the addition of limestone filler to soils polluted by heavy metals is a useful and low impact strategy for reducing the soluble fractions of As, Cd, Cu, Fe, Pb and Zn. This amendment can be recommended for treating similar mining wastes elsewhere.

7. Green technologies

Green technologies, also named ‘environmental or clean technologies’, embrace both future and existing systems that conserve energy and natural resources curbing the negative impacts of human involvement. They include alternative power (wind turbines, solar energy), hybrid and electric cars, batteries, magnets,

as well as several technologies dealing with water purification, desalination, and carbon capture and storage.

Industrial minerals used in the field of green technologies are varied including many elements, but especially lithium, cobalt, gallium, yttrium, indium, tellurium and, in particular, most of rare-earth minerals such as Ce, Pr, Nd, Pm, Sm, and Eu (Chang, 2002). For example, gallium, indium and tellurium are common components of solar cells; praseodymium, neodymium and samarium are necessary for the fabrication of magnets of wind turbines and vehicles; and cobalt, lithium, lanthanum, cerium, and others are used in batteries.

The “green” industrial minerals have the potential to be critically important in these essential uses and, consequently are subject to concerns about security of supply.

8. Concluding remarks

A variety of industrial minerals, in particular carbonates, clays and zeolites, has a significant capacity to adsorb harmful ions and to react to form precipitates. Carbonate products (limestone, quicklime) have important environmental applications because of their high acid-neutralization capacity, which is particularly useful in dealing with acid mine drainage. Clays are mainly used for infilling of voids and cavities, e.g. those related to mining, immobilization of urban and/or industrial waste, and creation of impermeable screens for waste management. The open structure of zeolites allows the movement of large ions during cation exchange and of water molecules during reversible de-hydration, and makes zeolites chemically active in absorption, ion exchange and catalysis. Therefore, most significant properties of industrial minerals in their role of environmental mitigation agents deal with ion exchange capacity, adsorption/absorption capacity, hydraulic and thermal conductivity, ionic diffusivity, mechanical strength, behaviour under high temperature and pressure conditions, and resistance to chemical and biological agents. Scarce minerals are essential for use in “green technologies” giving rise to concerns about future security of supply.

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