Metal Pollution and Mining in the Iberian Pyrite Belt: New Remediation Technologies to Improve the Ecosystem Services of the River Basins

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Abstract: The highly metal-contaminated Odiel-Tinto River basin, located in the Iberian Pyrite Belt (IPB), has been the focus of many environmental studies as a natural lab for biodiversity and environmentally catastrophic scenarios and as a reference site for mining places with similar conditions. This study demonstrates the feasibility and effectiveness of two different technologies to recover ecosystems affected by acid mine drainage (AMD) in the area of IPB. The current study compiles results of two newest technologies for AMD remediation: passive remediation (dispersed alkaline substrate—DAS) and a new disruptive technology (Adiabatic Sonic Evaporation and Crystallization—ASE&C) that purifies the contaminated water, obtaining two by-products (high-quality water and metal conglomerates) that improve the general quality of the ecosystem including biodiversity by eliminating more than 90% of the contaminants from AMD and mining waters. The removal of contaminants, enhancement of AMD treatment efficiency, and offset operating costs were compared and analyzed for the different uses of the decontaminated effluents, including an old tailing pond failure, the Aznalcóllar mining spill. The efficiency of the removal of elements from the contaminated water is significant using both technologies, although the passive DAS does not still reach the international benchmark for some compounds (such as Fe, sulfates, and Mn); whereas ASE&C obtains distilled water fulfilling all the international benchmarks with conductivity values lower than 120 μS cm^{-1} or metal concentrations lower than μg/L. Both technologies are eco-friendly and cost-effective as a result of the generation of valuable by-products such as fresh water and metal conglomerates as potentially commercial products while remediating aquatic ecosystems impacted by mining activities.

Keywords: acid mine drainage; circular economy; water challenge; ecosystem services; Odiel-Tinto basin

1. Introduction

The case of the Iberian Pyrite Belt (IPB) is known worldwide because of its historical mining activity and the metal(loid) contamination of its watersheds. This volcano-sedimentary unit, which hosts massive sulfate deposits with reserves estimated at 1700 million tons [1], has been historically exploited [2]. Natural processes and mining promoted the formation of acid mine drainage (AMD—highly acid lixiviate with metal (loid) and sulphate contents), which assumes the main environmental problems associated with the fluvial courses of the IPB [3] and associated accidental mining spills (e.g., [4–7]).

According to [8], in Andalusia there are currently six active operational mines (Riotinto Mine, Aguas Teñidas Mine, Magdalena Mine and Sotiel Mine-Huelva-, Cobre Las Cruces-Seville, and Minas de Alquife-Granade-), one in the opening process (Minera Los Frailes-

Seville) and numerous exploration permits (e.g., Tharsis, La Zarza, San Telmo, Escacena, Paterna, El Berrocal, among others in Huelva and Seville; Los Pedroches-Cordobe, and Linares in Jaén). Therefore, the existing operational mines, the historical residues, and the reopening of mines suppose that changes in the environment cause impacts on living organisms (Figure 1). Ref. [9] reviewed the impact of mining operation, considering the mine dumps as responsible for the risk of contaminated soil, air, and water; and [10] scavenged the relationship between mining and biodiversity through diverse pathways and spatial scales (from habitat loss/fragmentation, waste discharge, invasive species, climate change, etc.).
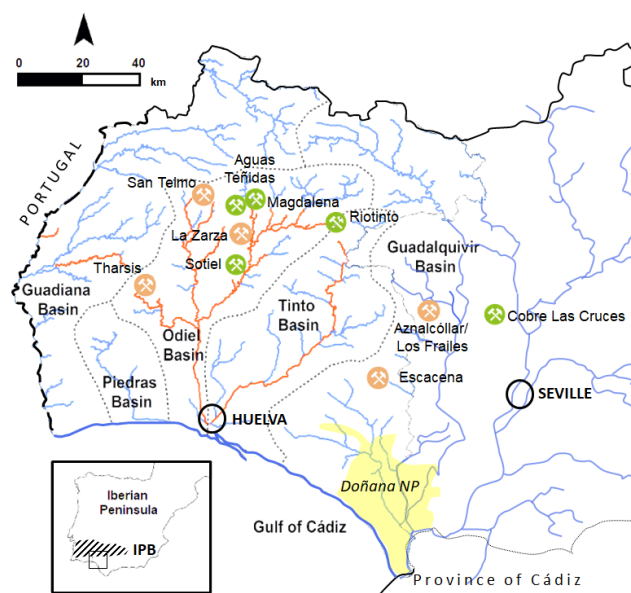

Figure 1. Location of active mines (green) and mines with exploration permission (orange) in Huelva and Seville provinces; and AMD-affected courses in the Odiel-Tinto basin and location of Doñana National Park (yellow).

Due to the peculiar composition of the soil and the extreme conditions characterized by highly acidified environments with high concentrations of metal(loid)s, the biosphere hosting the IPB has peculiar characteristics with organism–environment adaptive particularities. The best studied organisms of the IPB are microorganisms, especially extremophile microorganisms, which were demonstrated to have a stretch gas–water–rock interaction [11,12]. The Iberian Pyrite Belt Subsurface Life Detection Project characterized the subsurface biosphere of the Tinto River in terms of biodiversity and distribution, but also the energy source services available for life [13,14]. However, there are some other projects focused on the study of the biological and ecosystem services of the IPB (e.g., Faja Project [15], or [16]), which seek directly or indirectly the preservation of the ecological diversity, the protection of threatened species, or the regeneration of degraded vegetation for greater soil protection.

Despite the environmental conditions, a secondary effect of mining aggravated the scenario. In other words, mining accidents that occurred in the IPB, such as Aznalcóllar [4–7], resulted in migratory contamination and the consequences of metal contamination reached the coastal areas. Mobility and bioavailability of elements provoked toxicity in water and sediments (lethal [5] and sublethal effects [6]), with a latent presence of contamination till nowadays.

Cutting off the AMD formation would be the formation of this lixiviate; this is usually achieved with the isolation of residues from oxidizing conditions (tailing restoration, technosols). However, due to the split and the massive dispersion of the mining residues, this seems unviable. A second choice implies avoiding migration from sources; however, mines, tailings, and residues are located close to streams flowing to the main course.

Preventive results are impossible due to the longevity of AMD formation, the mismanagement of the spreading residues, and the situation of abandoned mines. Therefore, the current AMD practices focus on remediation (in mining sites, significant sludge production and efficacy varies by mining site conditions and AMD load), and reuse and resource recovery as sustainable AMD practices (reduction of residues, increased treatment efficiency, and offsetting of operating cost recovery) [17]. In the case of the IPB, the main resource recoveries are sulfuric acid, metal(loid)s, and rare earth elements (REEs). The last ones are included in the technology critical metals group (TCMs) and the European Critical Raw Materials (CRMs), and they suppose a marked advantage due to their scarcity and current market prize. Today, it has been estimated that around 5.8 t of REEs, 1.3 t of Y, 248 kg of Sc, 139 kg of Ga, and 138 kg of Tl are annually delivered to the Atlantic Ocean by the Tinto River [18]. Additionally, the estimation of the contribution of the Tinto-Odiel River as dissolved metal(loid)s are annually 7900 t of Fe, 5800 t of Al, 3500 t of Zn, 1700 t of Cu, and 1600 t Mn [19]. The application of two new technologies (Figure 2): A passive approach named Dispersed Alkaline Substrate (DAS) and an active technology defined as Adiabatic Sonic Evaporation and Crystallization (ASE&C). Both located in contaminated courses in the IPB (and other contaminated places), they will allow recovering the aquatic ecosystems and obtaining two by-products, freshwater and conglomerates of metal(loid)s and other raw materials with commercial importance. This will provoke a revolution in the circular economy of the mining processes and in the remediation of impacted aquatic ecosystems.
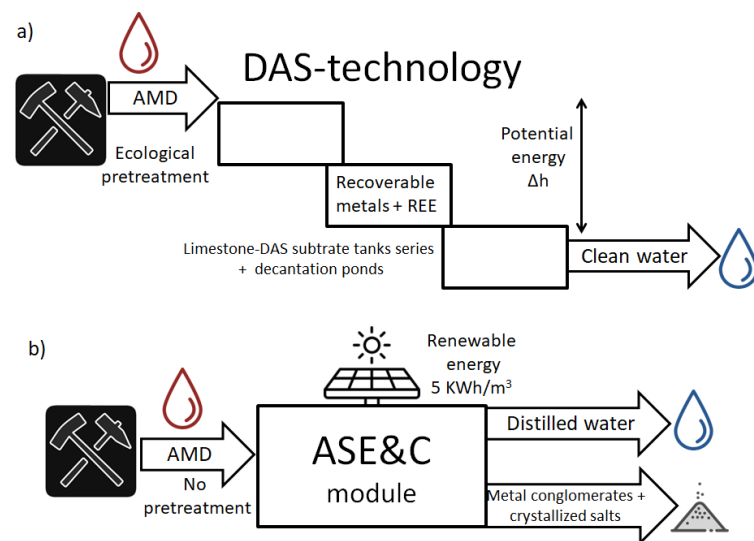

Figure 2. Working scheme of DAS technology (**a**) and ASE&C technology (**b**).

For the first time, the current work presents results of two innovative remediation systems that are currently available for AMD treatment, with the aim of biodiversity protection and general quality improvement in aquatic ecosystems, as well as studying their potential use in the recovery of CRMs for commercial purposes. The analysis of the results obtained after AMD treatment of samples from the IPB using these two technologies demonstrates for the first time a zero-liquid discharge in the treatment of contaminated mining waters, producing two commercially feasible by-products. Furthermore, for comparative purposes, their potential use in an old mining spill (Aznalcóllar, Mina Los Frailes, 1995) to clean the contaminated waters is also discussed. The comparison of both technologies' basis and results will highlight the advantages and disadvantages versus other remediation systems with the aim of obtaining zero pollution in aquatic ecosystems and the commercialization of two by-products, freshwater and commercial raw materials. The economic implications for the reutilization of mining by-products such as metal(loid)s and REEs after the application of these technologies will be evaluated.

The success of these objectives will address future research work on protecting the biodiversity of river basins affected by contaminated mining waters from, e.g., AMD and the opportunity from the treatment of these contaminated waters to obtain commercial by-products such as metal(loid)s and raw materials under a circular economy approach.

2. Materials and Methods

The current study focuses on two AMD remediation technologies that have achieved the pilot scale for superficial water treatment. They are in different development phases and present different advantages and treatment strategies (chemical and physical). These innovative systems (Figure 2) have demonstrated AMD treatment efficiency and can be used, for example, for other AMD-polluted watersheds and, in the case of ASE&C, for general contaminated mining samples [20–22].

2.1. DAS-Passive Treatment

An innovative long-term and eco-friendly passive treatment system known as Dispersed Alkaline Substrate (DAS) was designed to reduce acidity and metal (loid) loads in highly polluted AMD (Figure 2a). It consists of a multi-step alkaline passive treatment system [23,24] with an oxidizing pretreatment [25] and limestone-DAS reactive substrate tanks connected in series with decantation ponds that employs the natural energy (potential energy) to transform AMD into a neutralized effluent. This system decreases the sulfate concentration (schwertmannite and basaluminite) and promotes the adsorption and co-precipitation of elements by dissolving the limestone [25–27].

2.2. ASE&C Disruptive Technology

Adiabatic Sonic Evaporation and Crystallization (ASE&C) is a disruptive technology that has been designed and patented (World International Patent Organization: EP3135635) for contaminated fluid purification using a physical approach by distillation for the separation of dissolved solids and liquids by promoting adiabatic changes and acceleration of themselves (Figure 2b). It is eco-friendly because, although it consumes energy, this could be obtained from thermo-solar panels or other renewable energies. In addition, this technology does not need electricity and can use residual heat or other sources of energy wasted by industrial processes that are often carried out in the industrial and mining areas.

The technology has been used in the treatment of different contaminated fluids under a high concentration of metals and acidic conditions [20–22,28], as will be discussed in the next sections. The process obtains two by-products after the purification: distilled water and dry solids, crystallized salts and metal conglomerates in the case of AMD.

2.3. Sample Analyses

The AMD samples were collected in different areas of the IPB and treated with two different technologies (NADs and ASE&C). Aliquots of the samples were collected before the treatment of both technologies from the input (non-treated) and after the treatment output (treated) from both technologies. Subsamples of the collected water were filtered (0.45 mm Whatman) and acidified (pH < 2) for metal(loid)s analysis and transported in dark and cold conditions to the laboratory. Elemental concentrations were determined by means of Inductively Coupled Plasma-Mass Spectroscopy (ICP-MS, Thermo Electron Corporation©, X-series II). Detection limits were 0.1 mg/L for all elements. Conventional analysis of parameters such as pH, electrical conductivity, and dissolved oxygen were conducted as outlined by [20–22,28].

The results of the efficiency of acidity neutralization and metal(loid) removal are further studied and already published for DAS by [23–27], and the contamination removal associated with ASE&C using different contaminated fluids such as mining waters, swine slurries, textile industrial waters, and radioactive waters are outlined by different reports [20–22,28]. DAS system effluents were also ecologically tested in [29–31].

3. Results and Discussion

Results of the AMD characterization samples before and after treatment are presented in Table 1. The EC of AMD (3293–4730 µS cm^{-1}) was reduced after both treatments (105–341 µS cm^{-1}), and the pH rose from 2.7 up to 6. In the case of AMD treated with DAS, the removal efficiency was almost complete for most of the elements (e.g., Al, As, Cd, Co, Cr, Cu, Ni, Mo, Pb, Tl, and U, among others); however, sulfate, iron, and manganese varied slightly and even increased as calcium, respectively. Ref. [28] recently reported that all elements analyzed after the treatment of DAS met the limit values recommended by the Food and Agriculture Organization of the United Nations (FAO) for irrigation waters [28], by the World Health Organization (WHO) for drinking water, as well as the Canadian Environmental Quality Guidelines (CEQGs) for the Canadian Environment Council [32,33], except for sulfates, manganese, and iron.

Table 1. Effluent characterization samples in the input (sample) and output (AMD treated) with the DAS and ASE&C technologies.

| | | *DAS* | | *ASE&C* | | | | | |
| | | **AMD** | | **AMD1** | | **AMD2** | | **AMD3** | |
	Units	input	output	input	output	Input	output	input	output
EC	µS cm^{-1}	3293	341	4450	120	4340	110	4730	105
T	°C	14.8	11.2	25.2	25.1	25.7	25.2	24.9	24.8
pH		2.72	6.51	2.7	5.9	2.8	6.1	2.7	6.4
HCO$_3$	mg L^{-1}			<25	n.d.	<25	n.d.	<25	n.d.
CN	µg L^{-1}			<12	n.d.	<12	n.d.	<12	n.d.
DO	mg L^{-1}	2.9	3.1	7.7	7.9	6.1	8.1	6.9	7.9
Al	µg L^{-1}	111,790	106	157,900	n.d.	142,400	n.d.	129,300	n.d.
Sb	µg L^{-1}			<5.0	n.d.	<10	n.d.	<10	n.d.
As	µg L^{-1}	350	76	99	n.d.	159	n.d.	63	n.d.
Ba	µg L^{-1}			<50	n.d.	<100	n.d.	<100	n.d.
Be	µg L^{-1}			17	n.d.	17	n.d.	18	n.d.
Cd	µg L^{-1}	63.02	<1	120	n.d.	221	n.d.	230	n.d.
Ca	mg L^{-1}	133[a]	551 [a]	182	n.d.	185	n.d.	201	n.d.
Cl	mg L^{-1}			13	n.d.	14	n.d.	14	n.d.
Co	µg L^{-1}	417	5.94	927	1.1	907	n.d.	1003	n.d.
Cu	µg L^{-1}	13,509	17.2	19,810	1.6	25,220	4.2	25,600	3.2
Cr	µg L^{-1}	17.14	<1	21	n.d.	22	n.d.	20	n.d.
PO$_4$	mg L^{-1}			0.19	n.d.	0.29	n.d.	0.14	n.d.
Fe	µg L^{-1}	348,663	220	180,200	12.5	232,600	15.1	213,000	21.2
Mg	mg L^{-1}			455	n.d.	465	n.d.	526	n.d.
Mn	µg L^{-1}	3171	3769	37,090	1.6	38,950	2.1	41,540	2.4
Hg	µg L^{-1}			0.023	n.d.	0.04	n.d.	0.03	n.d.
Mo	µg L^{-1}	6.3 [a]	0.2 [a]	2.2	n.d.	4.3	n.d.	2.0	n.d.
Ni	µg L^{-1}	126.7	2.81	480	n.d.	476	n.d.	521	n.d.
Ag	µg L^{-1}			<50	n.d.	<100	n.d.	<100	n.d.
Pb	µg L^{-1}	19.07	<1	62	n.d.	61	n.d.	60	n.d.
K	mg L^{-1}			1.5	n.d.	1.4	n.d.	1.7	n.d.
Se	µg L^{-1}	3.319	<1	22	n.d.	21	n.d.	22	n.d.
Na	mg L^{-1}			17	n.d.	17	n.d.	20	n.d.
SO$_4$	mg L^{-1}	2872 [a]	2061 [a]	5502	n.d.	6066	n.d.	6648	n.d.
Tl	µg L^{-1}	0.06 [a]	0.00	<50	n.d.	<100	n.d.	<100	n.d.
U	µg L^{-1}	10.21	<2	20	n.d.	20	n.d.	21	n.d.
V	µg L^{-1}	70.8 [a]	0.4 [a]	1.7	n.d.	5.3	n.d.	1.8	n.d.
Zn	µg L^{-1}	11,650	31.91	67,320	n.d.	70,200	n.d.	72,210	n.d.

Notes: n.d.: not detected, the detection limit was in the order of the unit considered for each element;.<: below the detection limit; [a] [27].

On the other hand, AMD samples treated with ASE&C obtained complete removal of all analyzed elements (Table 1), including sulfates, manganese, and iron, fulfilling in all cases the mentioned international regulations (FAO, WHO, CEQG) and probably all international regulations in this matter, based on the production of distilled water.

Both technologies have shown strength enough to significantly improve ecosystems services in the Odiel-Tinto River basin by decontaminating the water and producing clean water that can be reused or disposed of freely in the river. In this sense, the quality of the disposed water is significantly better than the existing one, which improves the general quality of the water and the associated ecosystems and their services in the river basin. [31,34] demonstrated that by decreasing these contaminants' values after AMD treatment, the biologically adverse effects have been significantly decreased and, in most cases, it produced a recovery in the general quality of the ecosystem, including biodiversity.

3.1. Advantages of DAS and ASE&C Technologies

(i) Both treatments produce cost-effective quality water and significant improvement in the ecosystem services in the Odiel-Tinto river basin. For the DAS system, by using low-cost and long-lasting materials, effluent water increases pH to 6.5, and removal of 99% of Al, As, Cd, Co, Cr, Cu, Mo, Pb, Tl, Sb, Z, V, and REEs, up to 97% of Ni, U, and Se, 90% of Fe, and 86% of Sc, with optimal cost-effectiveness [27]. Furthermore, it uses low-cost materials such as reagents and recycled wood chips from neighboring forestry waste [35]. The ASE&C does not require pre-treatment of the samples, and neither uses chemical reagents for the depuration process. The output effluent of treated AMD increases to 5.9–6.4, and achieves the removal of 100% of most elements (Table 1).

(ii) The DAS system is a passive system that consumes the potential energy and requires a sloped terrain with extension enough for the lagoon, tanks, and ponds construction. Meanwhile, the ASE&C system is an active technology that uses renewable energy (low-cost thermo-solar energy of 5 kWh m^{-3}) coupled to the module as panels. Moreover, ASE&C is a versatile technology that can be adapted to energy supply from different origins, taking into account that it needs heat or electricity for the operation, for example, photovoltaic, residual heat, biomass, etc.

(iii) One of the main advantages of both calcite-DAS and ASE&C systems is the final result of two potential commercial by-products (clean water and valorized solids) as a promising secondary source that might potentially offset the operational costs. In the DAS system installed in the 'Esperanza mine' (SW, Spain), around 100 t of recoverable metals were retained in the tanks (in 28 months, equivalent to 56.000 m^3 of mine water treated) [27]. The total amount of the percentage of clean water recovery was not specified by these authors, although it could be assumed that different processes such as evaporation (residence time was reported between 4–5 days) could affect the final production of clean water. The ASE&C system produces 100% of distilled water from an input of contaminated water without any rejection. Volumes of 100 m^3 per day have been treated and tested under controlled conditions in the pilot plant for several weeks, demonstrating the production of 100 m^3 per day of distilled water. The system occupies a 40 feet standard container and can be transported to any place needed. Additionally, it is ready to scale up to the treatment of 600 m^3 per day occupying the same space. Furthermore, ASE&C can be scalable to as many m^3 as necessary. Recently, a plant of 1500 m^3 daily has been installed to treat other kinds of fluid. Regarding the production of salts and metal conglomerates, it obtains between 90–99% of the total solutes included in the original input water (or fluid). An extrapolation from the results obtained could be calculated from the initial concentration of metals or salts and the treated volume to estimate the total production of metal conglomerates. For example, in the case of Cd for water AMD3 (230 µg L^{-1}, Table 1) and maintaining a treatment of 600 m^3 per day during one year, it is expected to obtain 138 kg per day and more than 50 t per year. Similar calculations could be performed for the rest of the interesting elements. In any case, it should be mentioned that unless specific treatments are applied to the initial fluids, the final by-product will be a conglomerate of

all the elements dissolved in the AMD. Compared to the DAS approach, the ASE&C will obtain the dissolved solids in the AMD, avoiding interferences with clays or other minerals not dissolved in it.

Today, China dominates worldwide REE production (90%) [36]; however, these two technologies would work as suitable REE (and Y) sources with an estimated production of between 70 and 100 t of annual REE reserves for the entire IPB. Ref. [37] calculated the economic potential of the DAS-treatment. Thus, elements of interest contained in AMD that may be retained in the treatment sludge would have a total annual valuation of 24.1 M\$, of which Al and REEs would account for 43.6 and 22.6% of the total, respectively. However, some technical and economic limitations would impose a more realistic value between 4.2 and 10.3 M\$ yr^{-1}. Regarding the ASE&C estimations for these compounds, it should be the same and probably higher taking into account the interferences with other material (clays, minerals, etc.) and the kinetics of the process that in the case of ASE&C is sped up, being estimated to recover between 90 and 100% of the REEs dissolved in the AMD in the form of conglomerates. Furthermore, the application of ASE&C to the active mines and their rejected and operating fluids will significantly increase the economic potential of their use for the valorization of leachates produced in the day-to-day operation of the active mine.

Taking into account that today there are six fully operating mines in the IBP ([8] (Figure 1), these estimated numbers could be increased by at least one or two orders of magnitude. Furthermore, it will avoid the impact and contamination associated with leachates produced in the working procedures of the mines, producing distilled water that can be used in the different processes during mine exploitation as well as improving the general quality of the Odiel-Tinto river basin and its ecosystem services.

(iv) The CO_2 footprint of the DAS technology is estimated at 1.86 kg CO_2 eq m^{-3} of treated AMD [35]. Annual CO_2 emissions for ASE&C technology would be estimated at approximately 0.2 tons for a daily production of 600 m^3 with energy consumption of 5 kW m^{-3}; so that these emissions would be approximately null in case of replacement by thermo-solar panels as a source of energy. Thus, taking into account a consumption of 5 kW of electric energy would emit 0.5 kg CO_2 eq m^{-3}.

(v) Both technologies can be installed and adapted to the AMD characteristics for a proper efficient process. The DAS system requires some specific design in the landfill because it needs a gravity potential difference and a significant extension of space for a proper installation and functioning, and also it should be close to the AMD source. The ASE&C is a portable module occupying the space of a 40 feet standard container and can be located anywhere. Additional space could be needed for using hermos-solar energy for a final scale of 600 m^3 per day. The ASE&C dimensions, such as the DAS system, are designed to the volume of input treatment, although treatments between 10 to 600 m^3 per day of input and output water use the same extension. Thus, ASE&C will need a significant less area and space extension, and it can be installed in situ or ex situ without any terrain requirement.

(vi) Both technologies have been shown to be efficient in improving of the ecosystem services in the Odiel-Tinto river basin, being in compliance with the legislation of the EU Water Framework Directive [38,39] to achieve a 'good ecological status of superficial water'. The DAS technology accomplishes (with the exception of Fe, Mn, and sulfate) the FAO standards for irrigation, and the WHO for drinking water [27]. However, the effluent of DAS technology, once dumped into the watercourse, reaches environmental quality standards (EQS) of the EU WFD [29–31]. The ASE&C obtains distilled water that can be re-used for different purposes: due to the proximity to mines, the better choice would be to reinvest this water for mineral/metallurgical processes; it could be injected in wells, and used to fill up and purify aquifers; basic remineralization costs for drinking purposes is also possible; mixture with aquifer water could be used for irrigation and also it could be dumped to superficial water, achieving a good ecological status (EU Water Framework Directive).

These advantadges are summarized for comparative proposes in Table 2.

Table 2. Comparative advantages of the AMD treatment technologies: DAS and ASE&C.

	DAS technology	**ASE&C technology**
Treatment type	Passive	Active
Treatment capacity	0.8 L s^{-1} [a]	Unlimited *
CAPEX	196100 € [a]	Under development
OPEX	8428 € [a]	Under development
Installation	In situ built with significant extension and sloped terrain	Small portable module
Energy consumption	No (potential energy)	5 kWh m^{-3} (renewable energy)
Chemicals	Limestone-DAS, pine wood chips, limestone sand	None
Valorization of residues as secondary sources	Water + re-valuable residue	Distilled water + metallic conglomerates
CO$_2$ footprint	1.86 kg CO$_2$ eq m^{-3}	0.5 kg CO$_2$ eq m^{-3}.
Compliance legislation/improvement ecosystem services	Yes (except SO$_4^-$,Mn, Fe)	Yes (all elements)

Notes: Operational expenditures (OPEX); capital expenditures (CAPEX); [a]: [27]; * the amount of treatment is decided by the user taking into account the volume to treat. If more than 600 m^3 per day is needed, a different number of containers will be needed as multiples of this number. For example, for the production of 9000 m^3 per day of distilled water (or the treatment of 9000 m^3 of contaminated water), 15 containers will be needed.

3.2. Some Other Recent Technologies Used for AMD Remediation and Improvement of Ecosystem Services

AMD remediation has been historically classified as active or passive treatment approaches [40,41]. In recent years, there have been some AMD treatments that combine different processes. Many chemical, physical, and biological remediation approaches are mainly focused on the oxidation process (which is also a catalyzer key of AMD formation). This naturally occurs in nature, i.e., in the Odiel-Tinto River basin, the increase of pH causes the precipitation of amorphous (poorly) crystalline reddish orange iron-oxy-hydroxides and other metals [42].

The combination of AMD drainage with buffer materials has been explored for potential beneficiation and valorization to minimize their environmental impacts and footprints. One of the recent studies in this matter [43] applied basic oxygen furnace and submerged arc furnace slags for the treatment of AMD, obtaining an increase of pH up to 9.2, 99% removal efficacy for Fe, Al, and Mn, and less than 50% for SO$_2^{4-}$. Other passive system treatments using limestone concentrated >90% REEs using lime (three times more than active systems) [44].

One of the latest physical remediation technologies is based on ultrafiltration membranes that combine reverse osmosis and/or nanofiltration (this is further reviewed by [17]. These are working as pilot scale [45–47], achieving more than half of the water recovery, but require pretreatment of AMD and involve high operational costs (membrane fouling and chemical cleaning).

Hydrogels have become more popular for AMD remediation. These are 3D networks combined with polymers capable of adsorbing contaminants from liquid solutions. The polymers can be natural (bio-based) from animal or vegetable waste materials, or artificial or synthetic in nature. Both determine the efficiency of the hydrogel by selecting functional groups and targeting specific element ions. For example, the suitability of an eco-friendly natural hydrogel made of carboxymethylcellulose cross-linked with functionalized magnetite (Fe$_3$O$_4$) nanoparticles has been tested for the remediation of AMD-affected streams [48].

Ref. [49] recently reviewed the biological remediation of AMD for the permanent removal of sulfate and metals, the generation of less-hazardous water and the greater ability to recover valuable metals through: (i) active systems such as sulfidogenic bioreactors with sulfate-reducing bacteria (SRB) (such as δ-subclass of proteobacteria, Gram-positive bacteria (*Desulfotomaculum, Desulfosporosinus*), or branches formed by *Thermodesulfobacterium* and *Thermodesulfovibrio*); (ii) passive biological treatment such as permeable reactive barriers, algal bioremediation, packed bed bioreactors, and aerobic/anaerobic wetlands. However, the biological action in the AMD treatment has been demonstrated to be a strong ally in the remediation process. A recent study ([50]) was able to obtain a 99% sulfate removal using biofilm reactors with *Sulfurospirillum* spp. as a catalyzer. Living algae species (*Posidonia oceanica*, [51]; *Gracilaria gracilis*, [52]) can remove between 60–70% of REEs.

Other treatment systems have been designed based on biogeochemical technology, such as the study of AMD treatment by [53], which consisted of a five-unit linear treatment for iron removal, sulfate reduction (SRB), sulfur recovery (sulfur oxidizing bacteria, SOB), manganese removal (mineral adsorption with modified attapulgite) and purification. They obtained an effluent with a pH of 8.6 (from the initial 2.70), a 99% removal efficiency for Fe, Cu^{2+}, Mn^{2+}, and 33% for SO_4^{2-}. Adsorption processes to remove REEs from mine water by biosorbents were reviewed by [54]; however, precipitation processes demonstrated a greater REE removal.

3.3. Using DAS and ASE&C in an Old Mining Spill (Los Frailes Mine, 1995), an Approach to the Improvement of Ecosystem Services in the River Basin of the Iberian Pyrite Belt

After the failure of the tailing dam that stored the waste from the "Los Frailes" mining exploitation, located in Aznalcóllar (Seville, Figure 1), in April 1998, there were different impacts on environmental health and human health. It was known as the Aznalcóllar mining spill, and a significant number of publications covered the impact (e.g., [4–7]). The accident produced a spillage of water and sludge, which contained high concentrations of various metals and metalloids; the highest concentrations were associated with Fe, Zn, Pb, and Cu with strong acute and chronic effects in different river basins of the IPB and in the estuary of the Guadalquivir River [55].

Table 3 shows the concentration of the main metals present in the water and sludge inside the dam and that were spilled to the environment [56] and an estimate of the effectiveness of using DAS and ASE&C in this situation.

Table 3. Average chemical characterization of water (W) and sludge (S) in the Aznalcóllar mining spill, and estimation of the costs produced using DAS and ASE&C applied to the water and sludge residues from the "Los Frailes" mine.

	Aznalcóllar Characterization [a]		DAS Removal		ASE&C Removal		DAS Profit		ASE&C Profit	
	W (mg L^{-1})	S (g kg^{-1})	W (t yr^{-1})	S (t yr^{-1})	W (t yr^{-1})	S (t yr^{-1})	W (k\$ yr^{-1})	S (k\$ yr^{-1})	W (k\$ yr^{-1})	S (k\$ yr^{-1})
As	0.27	2.784	0.0059	61.0	0.063	609	0.019	195	0.189	1951
Cd	0.854	0.107	0.02353	2.95	0.187	23.4	0.061	7.66	0.486	60.9
Zn	462.8	38.82	12.92	1083	101	8501	25.85	2168	202	17,003
Cu	0.021	9.509	0.0006	265	0.004	2082	0.004	1595	0.028	12,495
CrT	0.03	0.009	0.0008	0.237	0.006	1.97	0.006	1.89	0.053	15.7
Fe	138.5	234	3.875	6550	30.3	51,267	0.678	1146	5.308	8972
Mn	91.7	0.27	n.e.	n.e	20.0	59.1	n.a.	n.a.	n.a.	n.a.
Hg	<0.008	0.053	n.e.	n.e	0.002	11.6	n.a.	n.a.	n.a.	n.a.
Ni	1.115	0.003	0.0305	0.082	0.244	0.657	0.394	1.06	3.150	8.47
Pb	3.655	39.9	0.0969	1058	0.800	8738	0.165	1800	1.361	14,855

Notes: n.e.: not efficient; n.a.: not available. Assumptions: [a] Water and sludge characterization reported by [56]. Market price for elements reported in [37].

Different approaches were used to mitigate the impact on the aquatic ecosystems affected by the mining spill. Some of them included the retention of contaminated water in different structures prepared for this purpose, although they were not 100% efficient [50]. There are several studies that determined the presence of metals and metalloids coming from the spill up and down the retention ponds and reaching the mouth of the Guadalquivir River, the aquatic ecosystems of the Doñana National Park, and the Atlantic Ocean, provoking significant, biologically adverse effects in the different river basins, the estuary of the Guadalquivir River, and the coastal zone [55,57]. Refs. [58–61] reported different levels of adverse effects from acute toxicological impacts in benthic communities and chronic effects in communities of the Guadalquivir River to the identification of a sequel related to the bioaccumulation of Cd in some of the organisms in the rivers and the estuary impacted by the spill [59,60].

Efficiency of removal of elements from the DAS system is based on Table 1 and, therefore, the dimensions described by [24]. Unfortunately, in those days, both technologies were not available, but estimation was conducted from the data recorded by [56]; however,, the calculation was also considered for a total average flow of water of about 7 Hm^3 and of sludge of about 2 Hm^3 reported by different authors (e.g., [55]. For instance, correct exploitation of the metal recovery of Zn, Cu, Pb, etc., could cover most of these costs. In any case, the recovery of these metals will require additional effort for their exploitation on the basis of the mixture between them and most clays, minerals, etc.

These technologies might be applied to the 20 Hm^3 that remained immobilized according to [56] or future residues associated with the re-opening of mines from the IPB.

DAS technology

The application of DAS technology could require the construction of a potential energy system adequate to treat about 7 Hm^3. It would need a specific extension of land selected in the area in where the mining spill was retained and that at those times was near by the Doñana Natural Park [57].

Regarding the efficiency of DAS treatment, considering the flow treatment described in [27] that reported about 28,000 m^3 per year, it would need about 250 years for the total treatment of the mining spill. The time needed for the remediation could be decreased as a function of the DAS system set-up (adapted design for the caudal and chemical characterization of the residue). However, taking into account the large extension of land and the specific characteristics (potential energy) needed to ensure the efficiency of the system, it is not easy to set up a large number of DAS systems to remediate a spill such as the Aznalcóllar mining spill. There are also some limitations in the depuration of sludge by the DAS system, which would require a pretreatment or extraction of lixiviates.

In any case, if a significant number of DAS systems could be constructed and installed, it could take about 25 years using about 100 DAS systems with a CAPEX of about 200 k\$ each, or a total of 20 M\$ plus the OPEX costs that were not estimated here. On the basis of its efficiency, a complete remediation of the water will be conducted fulfilling the European Legislation like WFD. Due to the high volume of contaminated water and sludge to be treated, specific monitoring programs should be designed to address the efficiency, especially in elements reported as less effective (sulfates, Mn, and Fe) and in the production of calcium [27]. On the other hand, the efficiency demonstrated by DAS could produce a secondary source of metals that could cover part of these costs, as previously reported by [37].

ASE&C technology

The use of ASE&C technology does not need to be set up or limited to an extension of the landfill to the treatment of contaminated water and sludge. The ASE&C modules that are closed in a 40 feet container can treat up to 600 m^3 per day. The container is mobile and can be transported to any place and specifically to the area in which the 7 Hm^3 of spill were retained. Additionally, depending on the kinetics needed for the remediation of the impact of the spill, an additional container could be constructed and transported to the area to treat the total amount of metal-contaminated water and sludge. Depending on the number

of containers running, the final treatment time will be decided. For example, if only one container is working, it will need about 30 years to finish the treatment and purify all the water and sludge with the numbers used for the Aznalcóllar mining spill. If the number of containers increases, for instance to 10 running ASE&C modules, it will take about three years to clean all contaminated material, obtaining 7 Hm^3 of distilled water and a total amount of metal conglomerates depending on their concentration in the contaminated fluid (Table 3).

The CAPEX and OPEX cost of the ASE&C are still under estimation because it is a very recent and disruptive technology. In any case, for the OPEX consideration, in this case the use of thermo-solar energy is viable because of the location of the spill and the high solar radiation in the area. It will keep the OPEX cost very low and lower than DAS. Although CAPEX is still under estimation as commented previously, as the number of modules increases, the CAPEX decreases. In any case, the estimate of CAPEX should be of the same magnitude as the estimated cost for DAS.

The ASE&C will fulfill the International Legislation for the output water, including the WFD defined by the European Legislation for all the elements and compounds contaminating the water and sludge. Similarly to DAS technology, ASE&C will recover a second by-product compared to distilled water, providing a secondary source of metals that will fairly cover all the costs associated with the use of ASE&C. In this case, the metal conglomerates obtained from the contaminated water will have about 100% of metals without interferences from other minerals, soil, clays, silt, etc.

Using a parallel approach to that applied for DAS, the total amount of some selected metals from the Aznalcóllar mining spill can be estimated by using their concentration in contaminated water and sludge (Table 3) and taking into account that ASE&C has 100% of recovery as previously described. For most of the metals, the total amount (ton) recovered per year is one order of magnitude higher compared to the DAS technology. In the case of the metal conglomerates obtained from water purification, it would be easier to recover metals than in the case of DAS due to avoiding interferences from soil, clays, etc. In any case, the recovery of metals requires additional effort for the exploitation of them based on the mixture.

In general, ASE&C technology shows significant advantages when compared to DAS in the treatment of a spill such as the Aznalcóllar mining spill to improve the ecosystem services of the associated river basin: (a) it does not need additional space and a large extension; (b) although CAPEX is not estimated yet until the industrialization of the technology, the approached values are cheaper than DAS; (c) the OPEX could be approached for the use of renewable energy, based on the situation of the spill, where there is plenty of sunlight most days of the year, etc.; (d) the portable characteristics of the ASE&C system that could treat 600 m^3 per day in a container will make easier the remediation; (e) the cleaning kinetics of the 7 Hm^3 would be faster in the case of ASE&C than DAS by more than one order of magnitude, as well as the efficiency per year in the recovery of metal conglomerates. A similar list of advantages can be listed by comparing both technologies with the purification of different metallic fluids and water in running mining exploitation. The comparison of both technologies to the treatment of abandoned mines and natural AMD shows basically the same advantages except the definition of the kinetics and the extension of land needed for the final treatment in the purification of the metal-contaminated fluids (water and sludge).

3.4. Other Mining Spillages

Throughout history, different mining disasters have occurred due to different causes. However, the result of all of them has been the spillage of highly contaminated tailings into the environment (Table 4). In some of them, mining leakages reached fluvial networks to impact larger sectors and, occasionally, estuaries and coastal areas.

Table 4. Comparison of the elemental composition in sediments from fluvial networks affected by spillages from different mine accidents.

		Wheal Jane [a]	Aznalcóllar [b]	Aznalcóllar [c]	Aznalcóllar [d]	Ajka [e]	Colorado [f]	Mariana [g]	Mariana [h]
Spill volume	m^3	50,000	7 M	7 M	7 M	50 M	700,000	50 M	50 M
As	ppm	983–2803	6100				4.25 ± 0.25	89–249	
Cd	ppm		31	0.79–3.25	0.58–1.38		0.66 ± 0.01	0.11–0.20	
Co	ppm					60		15–41.6	10.7 ± 4.8
Cr	ppm					553		75–145	63.9 ± 15.1
Cu	ppm	1172–5073	2120	20.95–78.82	13.1–18.5	57	32.4 ± 0.5	17.8–47	21.3 ± 4.6
Fe	%			4.06–5.	14.6–23.7		51 ± 0.3		45.2 ± 2.8
Mn	ppm			1163–1562	412–535				433 ± 110
Ni	ppm					248		9.1–53.7	24.7 ± 10.4
Pb	ppm	217–570	8500	7.22–31.07	28.7–33.8	128	108.4 ± 1.8	4.7–12.5	20.2 ± 4.6
Zn	ppm	650–6600	21,200	162–290	166–395	105	729 ± 5.7	37.6–78.4	62.4 ± 28.4

Notes: [a] [62]. [b] Pyritic tailing slurry characterization by [63]. [c] Sediments from Guadiamar River by [7]; [d] sediments from Guadalquivir by [64]. [e] [65]. [f] [66]. [g] [67]. [h] [68].

Cornwall (UK) was highly impacted by the Wheal Jane incident that occurred in 1992, when a sudden discharge of 50 million liters of acid (pH 3.1) highly metal-contaminated mine water from a tin mine reached the Fal Estuary throughout Restronguet Creek. Maximum levels of As, Cu, Sn, Zn reached values of 2803, 5073, 3400 and 6600 ppm in surface sediments, respectively [62].

Another tailing spill occurred in the IPB in Spain in 1998, when 7 million m^3 of sulfide sludge from the Aznalcóllar mine reached a tributary of the Guadalquivir River, which drains the largest wetland in Europe, the Doñana National Park (Figure 1). [63] characterized this pyritic tailing slurry with a highly metallic load for Zn (21,200 ppm), Pb (8500 ppm), and Cu (2120 ppm). [7] reported high concentrations of elements after the mining spill in the Guadiamar River sediments; and [64] studied the sediments of the Guadalquivir River after the catastrophe, finding values ranging between 166–395 for Zn, 28.7–33.8 for Pb, and 13.1–18.5 ppm for Cu. Although the environmental risk has decreased, this area is still monitored [69], especially for Zn and Cd concentrations in sediment. Recently, [69] analyzed the impact after 20 years on the Guadiamar River, determining a significant decrease in associated risk, but with Pb and Zn as the most challenging elements.

In October 2010, in Ajka (Hungary), a dam caused a spread of 700 thousand m^3 of reddish mud as a by-product of the production of the alumina process [65]. Sediment characterization of red mud determined high concentrations of Ti, V, Cr, and Ni [60].

In August 2015, Gold King Mine wastewater (11,400 m^3 of AMD) (Colorado, USA) reached the Animas and San Juan rivers, affecting Colorado Parks; element concentrations found in sediments were 108 mg kg^{-1} Pb, 32.4 of Cu, 729.6 of Zn, and 51,314 of Fe [69].

In addition, in November of the same year in South East Brazil, 50 million m^3 of highly rich iron mine waste flowed to the Gualaxo do Norte, Carmo, and Doce rivers (approximately 700 km in total length), reaching the estuary in days [68]. The mine tailings from the Samarco dam failure were mainly made up of iron ([70], Table 4). The acid extraction of the sediments collected revealed a different distribution of contaminants due to the spillage of the tailings mud [67] in which As, Hg, and Mn exceeded the sediment quality guidelines [71].

These are just some samples of mining accidents that occurred in the last years, but with strong repercussions in the environment, which was not able to self-recover or be remediated. Therefore, it is important to reinforce the prevention of these events through active or passive remediation strategies.

As has been previously discussed, both technologies can be useful in the mitigation and remediation plans related to this kind of accidental spill. The main difference is related to the passive and active characteristics of DAS and ASE&C, respectively, as previously discussed.

4. Conclusions and Future Perspectives

The IPB, and more concretely the Odiel-Tinto River basin, is widely known for being a world reference of AMD watersheds polluted by metal(loid)s and other compounds; however, advances in science and technology are changing this paradigm by achieving the AMD treatment for the restoration of watersheds, improving their ecosystem services and at the same time obtaining new revalued products. Therefore, the chronic pollution of the Odiel-Tinto River might be attenuated or reverted by installing DAS and/or ASE&C systems that transform this area into a revalorized area with improved ecosystem services of useful water and materials of commercial interest (potential metal ores and metal conglomerates), while removing residues from the environment. These two technologies are technically sustainable and cost-effective.

Results of depuration of AMD and contaminated mining waters have demonstrated that DAS reduces more than 90% most of the elements except Fe and sulphates, and fulfills the international regulation guidelines to recover the impacted aquatic ecosystems. The disruptive technology has removed more than 95% of all the contaminants in the contaminated waters, obtaining distilled water with EC lower than 120 μS/cm.

The comparison of both technologies has identified their decrease in CO2 emissions, the recovery of biodiversity in impacted aquatic ecosystems, and in general the recovery of environmental quality in the impacted river basins.

As discussed, for the treatment of AMD or other contaminated fluids (water and/or sludge) in mining operations and in the remediation of the impact associated with accidental spills, active technology (ASE&C) is more efficient and convenient than passive technology (DAS) based on the lower requirements in time and land extension for the remediation of metal-contaminated fluids. Both technologies are suitable for the remediation of abandoned mines of natural leachates from AMD and then can be used efficiently to improve the ecosystem services of the river basin associated with them.

Future uses of these technologies in the recovery of metal conglomerates after AMD of contaminated mining waters will open a new research gap for the recovery of critical raw materials such as rare earth elements (REEs) and their commercialization. Furthermore, the reuse of the distilled water in the mining processes or their disposal in contaminated aquatic ecosystems will improve their environmental quality and the scarcity in areas of water shortage, such as the IPB, the mining areas of Australia, Chile, or Peru, and other areas around the world.

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