



Dispersed alkaline substrate passive treatment technology for highly contaminated acid mine drainage: 20 years of successful application

Rafael León^{a,*}, Ricardo Millán-Becerro^b, Francisco Macías^a, Carlos R. Cánovas^a, Carmen M. Neculita^c, Carlos Ayora^d, José Miguel Nieto^a

^a Department of Earth Sciences & Research Center on Natural Resources, Health and the Environment, University of Huelva, Campus 'El Carmen', 21071, Huelva, Spain

^b Department of Soil Science and Agricultural Chemistry, University of Granada, Avda. Fuente Nueva s/n, E-18071 Granada, Spain

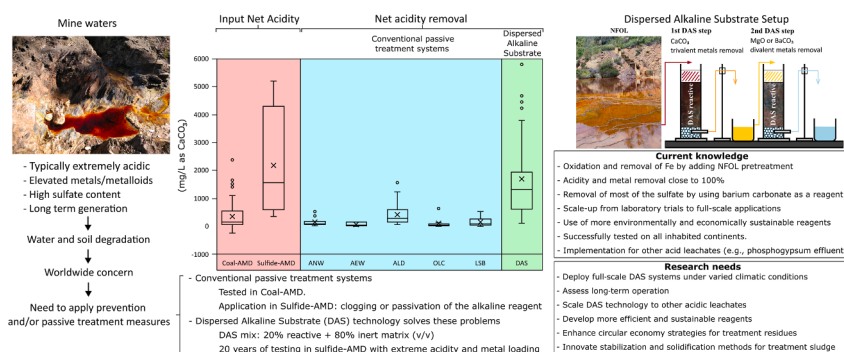
^c Research Institute on Mines and the Environment (RIME), University of Quebec in Abitibi-Témiscamingue, Rouyn-Noranda, QC J9 × 5E4, Canada

^d Institute of Environmental Assessment and Water Research (IDAEA-CSIC), Jordi Girona 18, 08034 Barcelona, Spain

HIGHLIGHTS

- Two decades of DAS tech deliver high acidity and metal removal (>95 %).
- Integration of NFOL pre-oxidation boosts Fe removal and system longevity.
- MgO-DAS and BaCO₃-DAS target divalent metals and sulfate, respectively.
- Alternative reagents (wood ash, by-products) reduce costs and carbon footprint.
- Valorization of sludges enables circular economy recovery of critical metals.

GRAPHICAL ABSTRACT



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ABSTRACT

Over the past two decades, Dispersed Alkaline Substrate technology (DAS) has emerged as a highly effective passive approach to treating acid mine drainage with extreme acidity and metal loading. By mixing alkaline materials - such as limestone, magnesia, barium carbonate or industrial by-products - into an inert wood-chip matrix, DAS systems maintain high porosity and neutralization capacity without rapidly clogging. This treatment technology has evolved from laboratory trials to pilot and full-scale field testing, using multi-step systems integrated with Natural Fe-Oxidizing Lagoons (NFOL) for pre-oxidation, which have demonstrated their long-term effectiveness for acidity and metal removal. The sustainability and applicability of the process has been improved by the search for new reagents (e.g. MgO for divalent metals removal, BaCO₃ for sulfate removal, wood ash or calcite-rich waste for cost reduction). Field trials in diverse regions - from the Iberian pyrite belt to South Africa, Canada, South America, Asia, Europe and Oceania - report net acid removal often exceeding 95 % and near complete retention of metal(loid)s such as Al, Cu, Zn, Pb and As. Mineralogical analyses indicate that contaminants precipitate primarily as hydroxides, oxyhydroxides, and sulfates (e.g., schwertmannite, basalmite, barite), allowing targeted valorization of metal-rich sludges. Remaining challenges include assessing long-term reagent life under variable hydrological conditions, extending full-scale use to phosphogypsum and

* Corresponding author.

E-mail address: Rafael.leon@dct.uhu.es (R. León).

other industrial leachates, and developing strategies for residue stabilization and resource recovery. The aim of this review is to synthesise these developments, assess current performance and identify future research needs for the advancement of passive DAS treatment technology.

1. Introduction

Mining is essential to sustain the demand for raw materials and energy necessary for the current development of humanity. However, mining is also one of the most contaminating human activities, given that it generates historically significant amounts of solid and liquid waste, dust and gases, and mine waters, among other derived contaminants (Lottermoser, 2010; Hudson-Edwards et al., 2011). In this sense, the highly acidic and metal-loaded waters resulting from the oxidation of sulfide minerals (mainly pyrite [FeS₂], but also pyrrhotite [Fe_{1-x}S], chalcopyrite [CuFeS₂], arsenopyrite [FeAsS], sphalerite [ZnS], among others) contained in the waste could be considered the main source of contamination in the mining districts (Olías et al., 2024). Furthermore, the exposure of sulfides can also occur during the excavation of mining pits or galleries. These sulfides can undergo weathering processes when water table recover following the cessation of mining activities. These leachates, known as acid mine drainage (AMD), are sometimes characterized by extremely high concentrations of sulfate and metal(loid)s (e. g., Fe, Al, Zn, Cu, As or Cd) and by low to extreme negative pH values. For instance, pH values of up to -1.5 or -3.6 have been measured in the vicinity of the Tharsis (Spain) and Iron Mountain (USA) mines, respectively (Nordstrom and Alpers, 1999; Nordstrom et al., 2000; Sarmiento et al., 2018). Acid leachates from mining districts often degrade the chemical quality of the surrounding water bodies, causing detrimental impacts on aquatic organisms and limiting their use for industry, agriculture, or human consumption (Akcil and Koldas, 2006; Tripole et al., 2006; Kaur et al., 2018; Anekwe and Isa, 2023). The AMD also severely damages soils, making them unsuitable for plant growth and for the proper development of the soil microbial community (Daraz et al., 2023). The generation of AMD is well known nowadays, but the prevention and mitigation of its detrimental effects on the environment have become a global problem. Different cases of this anthropogenic contamination have been reported in Africa (Arab et al., 2021; Khafouri et al., 2021), America (DeGraff, 2007; Oyarzún et al., 2012), Asia (Chan et al., 2021; Chen et al., 2021), Europe (Wisotzky and Obermann, 2001; Mayes et al., 2010; Abreu et al., 2011), and Oceania (Battaglia et al., 2005; Shakya et al., 2021). These AMD-related adverse effects can sometimes trigger a conflict between neighboring countries, an example takes place in South America, where Peru claims Ecuador for the contamination of the Puyango River, whose basin crosses both countries and is highly contaminated by acid waters from the Zaruma-Portovelo mining districts, located in SW of Ecuador (Betancourt et al., 2005; Delgado et al., 2019). Conversely, although less frequently, the environmental concern that other non-acid leachates associated with the inadequate management of mining wastes has been highlighted, given that they present high metal loads despite presenting a variable pH range, as is the case of saline, basic and neutral drainage (Nordstrom et al., 2015).

The increasing awareness of social and environmental issues, coupled with administrative pressures such as the European Union's Water Framework Directive (WFD, EU Commission, 2000), has led to the development of numerous remediation technologies over at least the past 60 years to address the global problem of acidic and contaminated mine waters (Deul and Mihok, 1967; Mihok and Deul, 1968; Hill, 1969; Wilmoth and Hill, 1970). Acid leachates from operating mining sites are often treated in active remediation systems, where chemical reagents are continuously added in controlled doses to neutralize the acidity (primarily, related to low pH and high amount of hydrogen protons in solution, and secondarily, related to the high concentrations of hydrolysable metals, such as Fe, Al, and Mn) and, subsequently, to precipitate

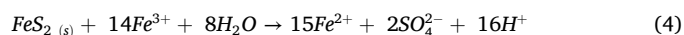
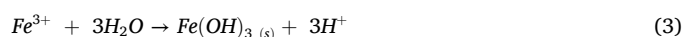
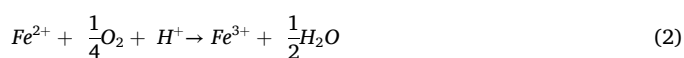
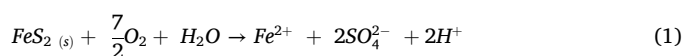
the dissolved metals. These treatment systems can treat large volumes of water; however, they require the continuous use of electrical energy and addition of chemical reagents, as well as constant monitoring and responsible management of contaminated residues that are produced. The use of active treatment may also not be feasible in many abandoned mining areas due to the long-lasting effects of AMD. This pollutant process is expected to persist for decades to centuries in coal districts and from hundreds to thousands of years in sulfide areas after mining activity has ceased, especially in the case when no AMD prevention measures were implemented (Younger, 1997). Thus, the utilization of active technologies for treatment would be impractical in these abandoned areas. Instead, passive technologies are typically employed to treat leachates from abandoned mining districts (Younger et al., 2002), since they do not require energy consumption, continuous addition of chemical reagents or frequent maintenance (Johnson and Hallberg, 2005; Akcil and Koldas, 2006). Different passive treatment techniques have been successfully used for the treatment of AMD with low to medium acidity and metal content, typically generated at coal mining sites (Younger et al., 2002; Ziemkiewicz et al., 2003). However, the use of these passive technologies for the remediation of AMD with high acidity and metal concentrations is not recommended, since the precipitation of high concentrations of contaminants causes a rapid logging of the treatment or a passivation of the material used to generate alkalinity (Rötting et al., 2005), reason why they are mainly designed for a polishing purpose. To address these issues, multi-unit systems (trains), consisting of chemical vs biological, aerobic vs anaerobic units are used for a progressive polishing of highly contaminated AMD (Johnson and Hallberg, 2005; Neculita et al. 2007; 2021), while a new passive biogeochemical technology known as dispersed alkaline substrate (DAS) was designed and implemented mainly to limit the hydrological issues related to porosity significant reduction in long-time operating reactors (Rötting et al., 2008a,b,c, Olías et al., 2024).

This technology is currently considered the most effective passive option to treat highly acidic and contaminated AMD according to environmental and economic criteria, as highlighted and thoroughly documented in several integratory review papers (Ayora et al., 2013; Kefeni et al., 2017; Martínez et al., 2019; Orden et al., 2021; Neculita et al., 2021). To date, however, there are no available studies that thoroughly review the development and degree of maturity for practical, full-scale applications of this technology, especially after the optimization performed in recent years. To bridge this gap, this manuscript provides a comprehensive review and integratory discussion of the development (design, implementation, optimization) and effectiveness of DAS-based passive treatment technology worldwide and its use for different types of leachates. The study also explores the potential for new, potentially more effective or economical, either natural or residual, alkalinity-generating materials, as well as the study of precipitated mineralogy and its avenues for valorization.

1.1. Acid mine drainage

The process of AMD generation is initiated by the oxidative dissolution of pyrite (FeS₂) or pyrrhotite (Fe_{1-x}S) in the presence of oxygen and water. This process firstly generates sulfuric acid (protons and sulfate), and releases ferrous (Fe²⁺) in solution, as well as other metal(loid)s (e.g., As, Cd, Co, Ni, Pb, Zn), resulting in a high acidity and dissolved metal concentrations (Eq. (1)). In the presence of oxygen, the Fe²⁺ is then oxidized to ferric iron (Fe³⁺), which consumes some of the previously released protons (Eq. (2)). However, its hydrolysis and precipitation as iron hydroxide result in the release of acidity (Eq. (3)). Other

sulfides, such as arsenopyrite (FeAsS), chalcopyrite (CuFeS₂), sphalerite (ZnS), or galena (PbS), undergo similar reactions, releasing acidity or metal(loid)s into the environment. Conversely, elements such as Mn, Al, Si, Ca, or Mg, which are not present in sulfides, manifest in elevated concentrations in AMD due to the dissolution of carbonates and aluminosilicates inherent within the host rock (Olías et al., 2024). The oxidative dissolution of pyrite is a slow process when it is driven directly by dissolved O₂ (Eq. (1)). The presence of Fe³⁺ in solution, which acts as an oxidant, has been shown to increase the oxidation rate of pyrite by a factor of between 20 and 200 (Eq. (4)). This effect is intensified at pH below 3.5 (Nordstrom and Alpers, 1999), when the solubility of ferric hydroxide increases, and Fe³⁺ replaces O₂ as a primary oxidant (Pierre Louis et al., 2015). The slow kinetics of Fe²⁺ oxidation to Fe³⁺ (Eq. (3)) would limit the indirect oxidation of pyrite, the catalytic role of extremophilic bacteria such as *Acidithiobacillus ferrooxidans*, *Leptospirillum ferrooxidans*, or *Acidithiobacillus thiooxidans* plays a key role in maintaining this high oxidation rate. These bacteria re-oxidize Fe²⁺ with increased kinetics (by a factor of 104 to 106 times) and maintain a high concentration of Fe³⁺ in solution (Singer and Stumm, 1970; Evangelou and Zang, 1995).



These leachates are primarily generated in the context of historical mining activities, including both sulfide and coal mines. This is due to the lack of environmental regulations, which have allowed water table recovery after mining operations cease, and inadequate management of the waste generated during mining processes. The process is referred to as AMD and it is causing a great concern worldwide due to its severe degradation of groundwater or surface water into which it is discharged (Akcil and Koldas, 2006), in addition to the longevity of this process. The attenuation of AMD through natural processes is not always effective. It is limited to areas where there is significant dissolution of carbonates or to dilution processes that depend on the flow ratios, metal load, and acidity/alkalinity of the waters (Olías et al., 2024). Therefore, it is imperative to take immediate action to limit this pollution by implementing prevention or treatment measures for all sources of contamination. Areas affected by AMD commonly suffer from scarcity of water resources to satisfy demands for population, agricultural and industrial activities, and this situation may worsen due to the change in rainfall patterns worldwide (Giorgi and Lionello, 2008). An example of this problem is the AMD-affected Odiel River basin (SW Spain), where there is strong social and legislative pressure regarding the future construction of the Alcolea reservoir for irrigation. This project has been halted since 2017, and the final construction of this infrastructure is being debated due to the expected poor quality of the water that would accumulate there (Olías et al., 2011). The use of treatment technologies, coupled with other contamination prevention measures, could help improving the water quality and resource availability, which are expected to decrease in the near future.

1.2. Treatment of acid mine drainage

Traditionally, AMD has been treated using passive or active systems (Johnson and Hallberg, 2005). Active treatment involves adding chemical reagents in controlled doses to neutralize acidity and precipitate metals and sulfate. This type of treatment typically requires a continuous supply of energy and chemical reagents. The reagents with the highest neutralization capacity are caustic soda (NaOH) ≥ calcium

hydroxide (Ca(OH)₂) ≥ lime (CaO) ≥ magnesite (MgCO₃) ≥ caustic magnesia (MgO) ≥ soda ash (Na₂CO₃) ≥ magnesium hydroxide (Mg(OH)₂) and, finally, limestone (CaCO₃), although the reagent cost may limit its use in some cases (Potgieter-Vermaak et al., 2006; Masindi et al., 2017). Active methods also involve the use of filtration technologies such as membranes, bio-barriers, adsorption, or ion exchange, among other processes (Masindi et al., 2022; Daraz et al., 2023). These methods can result in the management of contaminated metal-wastes incurring significant financial costs. Notwithstanding the high and adaptable efficiency of active treatment for the removal of metal, sulphate and acidity, the high cost and complexity of these technologies means that their use is restricted to operating mines with satisfactory economic potential for continuous maintenance. Passive treatment systems are more adapted for AMD long-term mitigation at orphan sites. They require less maintenance and utilize energy sources available in nature, such as gravity-driven flow, simple mineral dissolution reactions, microbial processes, or photosynthesis. These systems can be classified as biological (promote bacterial activity by organic matter consumption coupled to sulfate reduction) or chemical (utilize neutralizing reagents) to treat moderately contaminated AMD (Skousen et al., 2017). Among the biological systems, aerobic and anaerobic wetlands (AEW and ANW), vertical flow wetlands (VFW), passive biochemical reactors (PBRs), and permeable reactive barrier (PRB) are documented, while chemical systems include anoxic limestone drains (ALD), open limestone channels (OLC), and limestone leach beds (LSB), among others (Skousen et al., 2017). One of the most widely employed technologies is the reducing and alkalinity producing systems (RAPS), also referred to as successive alkalinity-producing systems (SAPS). These systems utilize a combination of biological and chemical processes, facilitated by a primary layer of organic matter that sustains reducing conditions. This is followed by a layer of alkaline reagent that elevates the pH, and thereby removing metals, culminating in an aerobic stage where residual metals precipitate through oxidation (Skousen et al., 2017; Neculita et al., 2021). utilize a combination of biological and chemical processes, and it is one of the most employed methods (Skousen et al., 2017; Neculita et al., 2021). Most of the passive treatment systems were developed in the Appalachian coalfield (Skousen et al., 2017) to address low-pH AMD with a low metallic load relative to sulfide mines. Applying traditional treatment systems to highly contaminated AMD can lead to technical problems, such as clogging or passivation of the alkaline reagent due to the precipitation of Fe and Al-rich phases, resulting in significantly reduced hydrogeochemical efficiency (Ayora et al., 2013). The DAS technology was developed to properly address these issues. The DAS-based systems use a combination of alkaline reactive and inert materials, mixture which has been shown to be highly effective in treating high-metal leachates (Caraballo et al., 2009a, 2011a,b; Macías et al., 2012a,b). Integrated or hybrid methods have emerged, allowing for the combination of several different units in a multi-step treatment process (Daraz et al., 2023).

1.3. Dispersed alkaline substrate technology

The DAS technology was initially designed for the treatment of high acidic and metals-rich waters from abandoned mines in the Iberian Pyrite Belt (IPB) (SW Iberian Peninsula), which is considered one of the main metallogenic provinces in the world (Sáez et al., 1999). The IPB has been intensively mined for over 4500 years, which makes it one of the oldest mining sites in the world (Nocete et al., 2005). This intense and prolonged mining activity has left as a legacy >80 abandoned mines (Grande, 2016), where significant amounts of pyrite-rich waste are exposed to water and oxygen, giving rise to the generation of acid mine leachates. These waters have caused severe contamination of the main fluvial basins that drain the IPB, the Tinto and Odiel Rivers (e.g., Olías et al., 2006; Cánovas et al., 2007; Nieto et al., 2013).

At the beginning of the current century, the European Water Framework Directive (EU Commission, 2000) set as a priority objective

to achieve good chemical and ecological quality for all surface water bodies located in its territory by 2015 (EU Commission, 2000). However, in the case of the Odiel River basin, it was not possible to comply with the WFD requirements before this proposed deadline due to the magnitude and ubiquity of the AMD contamination, and for this reason the regional government extended the deadline until 2027 (Macías et al., 2017b). The pressures exerted by the European Union on the recovery of the Odiel River basin has forced regional and national governments, as well as the scientific community to the implementation of passive remediation technologies to reduce the AMD contamination that reaches the Odiel River. Some traditional passive remediation processes (ALD, RAPS) were tested in the IPB; however, they presented clogging and passivation problems related to mineral precipitation, when used for highly contaminated AMD waters (López Fernández et al., 2003; Rötting et al., 2005). These problems are solved with the DAS technology, which is based on a mixture of a fine-grained alkaline reactive with high neutralization capacity (mainly limestone or magnesite) dispersed in a non-reactive matrix (i.e., wood chips) to raise reactivity and porosity while minimizing passivation and clogging problems (Rötting et al., 2008b; Macías et al., 2012c; Ayora et al., 2016).

DAS technology has been continuously optimized for nearly two decades to achieve a successful remediation of AMD from abandoned mines in the IPB and other similar mining regions worldwide. The AMD contains high concentrations of various metallic elements, which solubility is strongly pH-related. The development of this technology has entailed numerous steps aimed at addressing the unique characteristics of metal behavior in these leachates. A pivotal step in this process has been the transition from laboratory-scale tests to pilot and full-scale applications, with a focus on refining design parameters such as flow rate, reagent grain size, and reagent-inert matrix ratio. The dissolution of the optimal reagents increases the pH of the leachate and aids in its progressive removal, first of the trivalent metals, that precipitate at acidic pH, and afterwards divalent metals, which in some cases require alkaline pH values (pH 9–11) (Cortina et al., 2003). The oxidation and partial removal of Fe^{2+} , which constitutes the majority of Fe in AMD closed to the sources, and whose precipitation, along with the rest of the divalent metals at high pH, generates passivation problems in the system, was also integrated. The removal of sulfate, a major component of AMD, is accomplished by using Ca-rich alkaline materials, however the removal rate is limited by the solubility of gypsum, thus, once the equilibrium is reached it is not possible to remove significantly sulfate from waters. A comprehensive schematic illustrating the operational dynamics of the DAS treatment system can be consulted in the supplementary material (see Figure S1).

The subsequent sections will provide a comprehensive overview of the fundamental stages in the development of passive DAS treatment technology, encompassing the search for alternative low-cost reagents, the global dissemination of the technology, its application to other metal-rich industrial acid leachates, and its integration into diverse research contexts. These sections will delve into the analysis of treatment efficiency for the removal of metals and acidity, along with the primary mineralogical studies conducted up to now.

2. Methodological approach

2.1. Data source and bibliometric analysis

An exhaustive literature search was conducted to identify relevant studies on DAS passive treatment technology. Web of Science (WoS; <http://www.webofknowledge.com/>) and Scopus (<http://www.scopus.com/>) indexes databases were systematically queried using the keywords 'Dispersed-Alkaline-Substrate'. Articles were included if they provided substantial information on the application, improvements or modifications of DAS technology in treating acid leachates, both in mining and mineral processing industries. This process includes batch tests of reagents applied to the DAS, column experiments, pilot- and full-

scale treatment plants, as well as other fields of interest such as the mineralogical and geochemical characterization of the resulted solid waste after treatment and its potential valorization. A comprehensive search was also conducted using the same keywords in the Google Scholar search engine (<https://scholar.google.com/>) to identify any research studies or international conference contributions related to the application of DAS technology in other fields that were not included in the previously mentioned databases. The information extracted comprises the study location, treatment scale, leachate type, DAS reagent composition, and key findings related to the effectiveness of neutralizing acidity or removal metals during acid leachate remediation. The search yielded 32 papers that mentioned 'Dispersed Alkaline Substrate' in their title, abstract, or keywords, expanding to 138 papers that mention it throughout the manuscript. After an in-depth analysis of these articles, 46 papers were identified showing a relevant development in DAS technology for further analysis. The selection of these articles was based on the following criteria: the generation of new data through the application of DAS technology, the study of waste generated during treatment, or the conducting of studies or trials closely related to this technology. Fig. 1 was constructed using these articles, as well as those that describe DAS technology in some of its sections or compare results in their discussion section ($n = 71$), highlighting the interest of the scientific community in this field. It is evident that there has been a continuous increase of scientific publications on the DAS technology since its preliminary work in 2008.

Fig. 2.A presents the distribution of institutional contributions to research on the DAS technology. Although the development of DAS was initiated within the confines of the IPB, the figure illustrates the extensive geographic and institutional dissemination that has transpired. The University of Huelva (UHU) and the Spanish National Research Council (CSIC) continue to be the most prolific contributors, accounting for 52 % and 46 % of DAS-related publications, respectively (24 and 21 of the 46 publications). This reaffirms their foundational and leadership roles in the technology's inception. However, the involvement of institutions such Research Institute on Mines and Environment (RIME, Canada), and Newcastle University (NU), contributing 6 and 5 publications, respectively, or University of Cádiz (UCA), the University of Free State (UFS), the Polytechnic University of Catalonia - Barcelona Tech (UPC), Virginia Tech (VT) and the University of Seville (US), each contributing three publications, among other institutions, suggests that DAS has been adapted in a variety of mining environments. This international engagement not only attests to the technological transfer of DAS but also underscores its adaptive utility in varied regional contexts.

Moreover, the broad spectrum of journals in which these studies are published (Fig. 2.B) is indicative of the interdisciplinary nature of DAS research. The journals associated with the various DAS papers span environmental engineering, geochemistry, sustainability, and policy, indicating that DAS transcends a single disciplinary perspective and instead intersects multiple fields. Supplementary material details a list of referred studies (Table S1, S2). Furthermore, Table S3 provides a synopsis of the pH, net acidity, and concentration data for the primary elements in the influent and effluent water of the DAS treatment systems employed in the diverse works evaluated.

The information collected has been organised into different sections. Firstly, these cover the essential steps in the development of the DAS treatment system. These steps range from the first laboratory tests to its full-scale implementation, including improvements to address issues of effectiveness. This is followed by the transfer of DAS technology around the world in different mining contexts, the extrapolation of the technology to other acidic effluents and other studies related to this technology. Finally, there is a summary analysis of the effectiveness of this treatment for the elimination of acidity and metals throughout its development. The text also discusses the work focused on the study of the solids generated, their valorization and management.

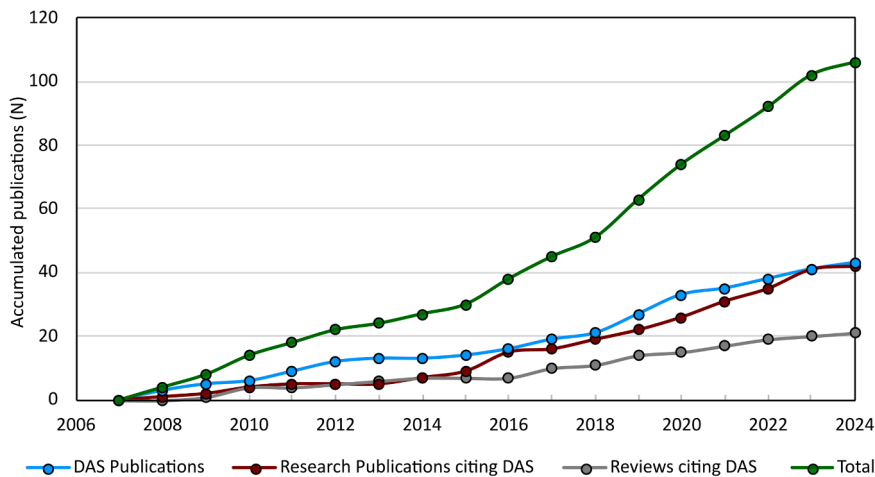


Fig. 1. Number of accumulated publications on Dispersed Alkaline Substrate, and research or review publications that cite DAS technology during 2006–2024.

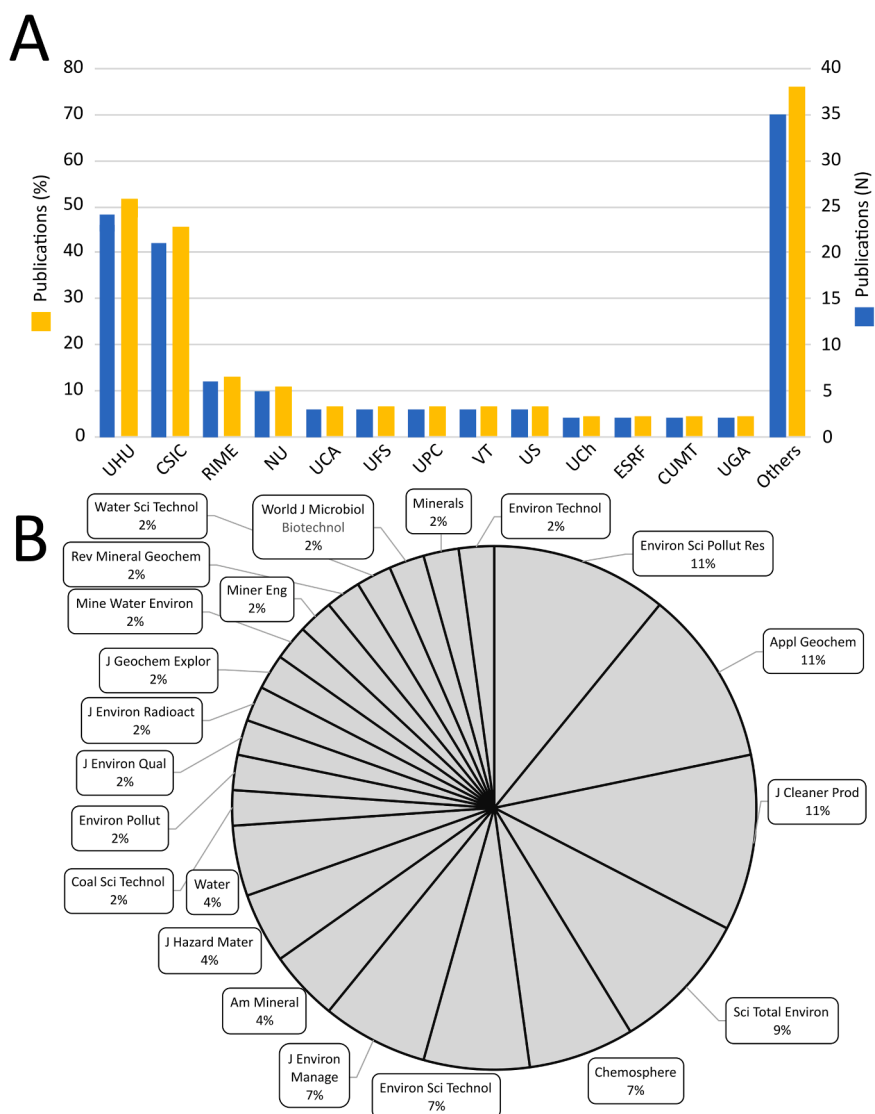


Fig. 2. Bar graph of the most productive institutions in terms of the number of publications on the DAS and percentage of the total publications in which they participate (A). Pie chart with the percentage of articles published in each journal (B).

2.2. Calculations

To assess treatment efficiency, the proportion of contaminant removal can be estimated as follows:

$$\text{Removal (\%)} = \frac{C_f - C_0}{C_0} * 100$$

where C_0 is the sum of the concentrations in mg/L of the contaminant in the input water (i.e., Al, Fe, Mn, Zn, Cu, As, Cd, Co, and Ni) and C_f is the sum of the concentrations of these metals in the treated water.

Net acidity (NA) has also been calculated, including proton acidity and the one from hydrolysable metals (e.g., Al, Fe, Mn, Zn). To estimate net acidity, the following equation was employed (modified by Rötting et al. 2008, according to Kirby and Cravotta, 2005a,b recommendations):

$$\text{NA (as mg/L of CaCO}_3) = 50045(3C_{\text{Al}} + 2C_{\text{Fe}} + 2C_{\text{Mn}} + 2C_{\text{Zn}} + 10^{-\text{pH}}) - \text{alk} \quad (5)$$

where C_x is the molar concentration of Al, Fe, Mn, and Zn (mmol/L), and alk is the gross alkalinity (mg/L as CaCO₃ equivalent). The 50,045 multiplier converts the molar concentration to mg of CaCO₃ equivalents.

Conversely, other acidic matrices exhibit specific chemical distinctions in relation to AMD. A leading example of this is phosphogypsum leachates, where the primary mechanism responsible for contaminant removal is the precipitation of phosphates. According to PHREEQC calculations, some of these phosphates have the capacity to generate acidity during their precipitation. A modification to the equation for calculating net acidity was proposed to include the influence of Ca and Mg on net acidity in the context of phosphogypsum leachate (Millán-Becerro et al., 2020). The resulting equation is as follows:

$$\text{NA (as mg/L of CaCO}_3) = 50045(3C_{\text{Al}} + 2C_{\text{Fe}} + 2C_{\text{Mn}} + 2C_{\text{Zn}} + 2C_{\text{Mg}} + 2C_{\text{Ca}}10^{-\text{pH}}) - \text{alk} \quad (6)$$

where C_x is the molar concentration of Al, Fe, Mn, Zn, Mg y Ca (mmol/L), alk is the gross alkalinity (mg/L as CaCO₃ equivalent) and the 50,045 multiplier converts the molar concentration in mg of CaCO₃ equivalents.

Finally, the acidity removed (%) has been calculated as follows:

$$\text{Net Acidity removal (\%)} = \frac{\text{NA}_f - \text{NA}_0}{\text{NA}_0} * 100$$

where NA_0 is the net acidity of the input water and NA_f is the net acidity of the treated water.

3. Research and development of DAS technology

3.1. From laboratory experiments to pilot and full-scale applications

The development of DAS technology started in the mid-2000s, with the initiation of column experiments that were then scaled-up to more realistic field settings. To be noted, preliminary work for the DAS treatment involved the remediation of a synthetic effluent loaded with metals (simulating AMD) from a column composed of caustic magnesia (Rötting et al., 2006). This is because synthetic AMD contained only divalent metals (Zn, Mn) and at the pH reached by limestone, a more common and less expensive neutralizing material (pH 7) it would not

have precipitated. This first approach was successful in raising the pH above 8.5 and removing a significant proportion of the metallic concentration from the effluent (Rötting et al., 2006). The effectiveness of the system was prematurely lost due to the coating of the reactive material by mineral precipitation. It was concluded that it was necessary to use a DAS mixture consisting of a fine-grained alkaline reagent dispersed in a thick inert matrix that would provide porosity to the system.

Then, Rötting et al. (2008a) conducted laboratory experiments with two columns, with different proportions of wood chips (87.5 % and 75 %, respectively) and magnesia of varying grain sizes (0.15 mm and 3 mm, respectively). Consistently, the objective was to evaluate their efficiency in the treatment of synthetic AMD containing divalent metals (Zn and Mn). After a year of monitoring the hydraulic performance of both columns, it was determined that the one with the coarse grain size exhibited a loss of reactivity and permeability due to mineral precipi-

tation, even though most of the reagent had not yet been consumed. In contrast, the column with the fine grain size showed good effectiveness and consumed 95 % of the alkaline reagent in the Zn and Mn precipitation fronts. As previously referenced, the chemical data for the influent and effluent water in this study and the other relevant studies can be found in Table S3.

To further develop and improve DAS technology, Rötting et al. (2008c) conducted a study to identify the optimal flow rate for treatment. To this end, they utilized two independent reactive DAS-type columns, employing limestone as a reagent. This alkaline reactive had already been tested and widely used for the treatment of AMD, although with low metal/acidity loads due to passivation or clogging problems at higher concentrations (Oliás et al., 2024). Both columns were composed

of a 25 % (v/v) limestone sand and 75 % (v/v) wood chips mixture, operating at average flow rates of 0.47 L/d (120 g acidity/m².day) and 0.14 L/d (35 g acidity/m².day), respectively, to treat AMD generated at Monte Romero Mine, characterized by a low pH (2.8) and high concentrations of Zn, Fe and Al (365, 250 and 106 mg/L, respectively), among others, presenting a net acidity of 1.7 g/L as CaCO₃ equivalent (IPB, SW Spain). The columns operated without clogging for 15 months, raising the pH to 6.5, and completely removing Al, Fe (III), Pb, and Cu. The low-flow column exhibited a significant decrease in the initial concentrations of Zn, Ni, and Cd. However, the necessity for extensive areas to treat AMD at these low-flow rates, when extrapolated to the field scale, suggests that the high-flow rate could be more efficient.

To assess the efficiency of this technology on a larger scale, pilot field trials were conducted to treat the same AMD from the Monte Romero Mine (T.S. Rötting et al., 2008b). A 3 m³ tank filled with a DAS mixture (25 % (v/v) limestone sand and 75 % (v/v) pine wood chips) was employed, followed by several ponds with a volume of approximately 6 m³ each and intermediate aeration waterfalls. The arrangement of the DAS resulted in removal of approximately 50 % of the input net acidity. This was achieved through an increase in pH to 6, and the subsequent precipitation of 93 % of Al, 95 % of Cu, 99 % of As, or 98 % of Pb. However, only 25 % of Fe or 14 % of Cd or 5 % of Zn was removed, and no Mn, Ni, or Co were removed. The initial removal of iron increased to almost 50 % in the ponds due to its oxidation and the alkalinity of the

DAS output. In addition to the limitations for the removal of certain metals previously mentioned, the Al precipitates formed a hardpan that generated clogging in the system.

To address the problem of effectiveness in the removal of divalent metals, Caraballo et al. (2009a) modified the DAS system of Monte Romero. The modified system was configured as a multistep process comprising two limestone-DAS tanks, separated each other by oxidation cascades and decantation ponds. This was followed by an MgO-DAS tank, which promoted the removal of divalent metals reaching higher pH values. During the 9-month operational period, the efficiency of the system was found to be significantly enhanced compared to previous tests. Up to 80 % of initial acidity was neutralized, together with the removal of 100 % of Al, Cu, As and Pb, 95 % of Cr, 75 % of Fe and 25 % of Zn. However, due to differences in the design of the MgO-DAS tank relative to the limestone tanks, preferential flows occurred, which resulted in a reduction in the performance of the system.

Because of these incremental developments, both in the laboratory and at field-pilot scale, the first full-scale passive DAS treatment plant for the remediation of AMD from Mina Esperanza (SW Spain) was built (Caraballo et al., 2011a; M.A. b). In this system, the AMD from the gallery was directed to the reagent tank via an open channel with a series of waterfalls, which facilitated oxygenation. The tank was filled with a 2.5 m layer of limestone-DAS (20 % v/v limestone sand and 80 % v/v pine wood shavings) with a 50 cm drain layer of coarse quartz gravel at the bottom. Finally, the water at the output of the tank was directed to a 90 m³ decantation pond. The hydraulic retention time (HRT) in the tank ranged between 2.5 and 5 days, with the inflow rates (86 to 43 m³/day) influencing this time. In the decantation pond, the HRT was approximately 2.25 days. Over the next 20 months, the system was able to completely remove all Al, As, Cd, Cr, Cu, Ti and V, in addition to significant concentrations of Fe (between 170 and 620 mg/L removed from a total of between 755 and 1 100 mg/L measured in the initial leachate). This resulted in a notable reduction in acidity (1 500 mg/L as CaCO₃). Despite the favourable outcomes, certain limitations remained, such as the continued presence of Fe in solution, the decreased efficiency of Al, Cu, or Cd removal after one year of operation, and the low pH and alkalinity at the end of the treatment.

3.2. Solving the problem of Fe in solution through the natural Fe-oxidizing Lagoon (NFOL)

The Fe that remains in solution in previous steps is in the form of Fe²⁺, and, because its solubility does not decrease until higher pH values, it usually does not precipitate in treatment systems that raise the pH to neutral. This phenomenon can lead to complications such as clogging or passivation of the subsequent reactive substrate, which results in an increase in pH to from 9 to 11. The pretreatment which promotes Fe²⁺ oxidation and precipitation is a key objective in improving the performance of DAS. A pivotal step was taken with the development of a pretreatment called the Natural Fe-oxidizing Lagoon (NFOL) (Macías et al., 2012b). This pretreatment, which was originally tested for the AMD of Monte Romero, exploited the topography's irregularities to promote Fe oxidation and its subsequent precipitation. However, the final version comprised a series of Fe-stromatolite waterfalls and terraces connected to a lagoon of 100 m³ in volume. This was established as a preliminary step to the DAS system, which consisted of two limestone tanks (3 m³ each) with their respective decantation ponds. The Fe oxidation rate in the NFOL reached efficiency of up to 65 %, with 38 % of Fe precipitated in the NFOL during the study period. In this pretreatment stage, As initial concentration was also reduced by 80 %. These improvements collectively contributed to better system performance, with the net acidity substantially reduced (71 % of inflow) because of the complete removal of Fe, Al, Cu, Pb, and As, while a residual fraction of Zn (6 %) was retained.

This pretreatment system was also integrated into a multi-step treatment system with a limestone-DAS tank and another MgO-DAS

(Macías et al., 2012c), which facilitates the removal of divalent metals that are incompletely removed by limestone. The pretreatment system was followed by 3 reactive tanks, the first two of which were 3 m³ in volume and filled with limestone-DAS, while the third was 1 m³ in volume and filled with MgO-DAS. These three tanks were separated each other by several waterfalls and 6 m³ decantation ponds. During the NFOL step, the removal of 60–70 % of Fe and 75 % of As occurred. This treatment system achieved a total removal of acidity from the AMD inflow (1.4–1.6 g/L as CaCO₃ equivalent), resulting in the complete retention of trivalent metals, including Fe, Al, As, and Cr, as well as divalent metals such as Cu, Pb, Zn, Mn, Cd, Co, and Ni, within the system.

Finally, the efficiency of the multi-step treatment system with an NFOL-type pretreatment for the mitigation of an AMD with high acidity (2 g/L as CaCO₃ equivalent) and metal content (683 and 117 mg/L of Fe and Al, respectively) was demonstrated at full scale in the Esperanza mine (SW Spain) (Orden et al., 2021). The treatment plant commenced operations at the end of 2014 and consisted of a NFOL pretreatment comprising a series of aeration cascades and a 100 m² sedimentation lagoon, followed by two limestone-DAS. The reactive tanks, with dimensions of 960 m³ and 720 m³, respectively, were followed by a 100 m² decantation pond. The system was operational for a period of 28 months, treating an average flow of 0.8 L/s without experiencing significant clogging or exhaustion of the alkaline substrate. This allowed the treatment of approximately 56 000 m³ of AMD. The NFOL step facilitated the oxidation and removal of 17 % of Fe, which precipitated as schwertmannite (Fe₈O₈(OH)₅(SO₄)_{1.5}•nH₂O), and the sorption of 100 % of Sb, 83 % of Mo, 60 % of As, 53 % of V, and 11 % of Cr in this mineral. The high efficiency of the system led to the complete removal of Al, Cu, REE, As, Cr, Mo, V, and Pb, as well as high proportion (above 70 %) of Zn, Cd, Co, and Ni. This resulted in the removal of >2 g/L as CaCO₃ equivalent of net acidity. Despite the promising outcomes of this initial full-scale DAS treatment plant, the objective was to enhance the retention efficiency of Fe (10 % remains in solution with respect to the inflow) or sulfate (of which only 30 % precipitate as schwertmannite, basaluminite (Al₄(OH)₁₀SO₄•5H₂O), and gypsum (CaSO₄•2H₂O)).

3.3. Barium carbonate DAS reagent as a driver of advanced sulfate removal

As the DAS treatment system has been specifically designed to remove high acidity and metal concentration from AMD, the early configurations proved ineffective for sulfate removal by gypsum precipitation (e.g., 30 % sulfate removed in the full-scale DAS treatment at the Esperanza mine; Orden et al., 2021). To address this issue, several experiments were conducted using barium carbonate (BaCO₃) in DAS system (BDAS). This treatment not only increased the pH but also facilitated the precipitation of sulfate as barite (BaSO₄). The initial tests of this modification were conducted to treat alkaline drainage generated by a coal mine in South Africa. The tests were firstly conducted on a laboratory scale (Gomez-Arias et al., 2015; Cason et al., 2017) and then at a field scale (Castillo et al., 2023). In the initial laboratory column experiment, various proportions of BaCO₃: wood chips were tested, with 764 L treated over a 6.5 months period. This resulted in the removal of 93 % of sulfate, as well as of significant concentrations of Mn, Na, Fe, Al, and Zn (93 %, 91 %, 90 %, 82 %, and 68 %, respectively) (Gomez-Arias et al., 2015). In contrast, Cason et al. (2017) combined a BDAS column with a bioreactor-based pretreatment and achieved high sulfate removal (90 %). Then, the field test was designed and implemented by combining DAS units in a multistep system, starting with limestone-DAS, followed by the BDAS and, finally, a decantation pond (Castillo et al., 2023). The system achieved the removal of 99 % of sulfate, along with metals (e.g., 98 % of Fe, Al, or Mn). Conversely, the use of BDAS was tested for AMD treatment at lab-scale using Poderosa mine (SW Spain) waters (Torres et al., 2018). A multi-step column system was used, with an initial limestone-DAS, followed by another BDAS, with approximately 30 h of

HRT. The initial limestone-DAS column increased the pH from approximately 2.5 to 6, resulting in the retention of 100 % of Fe, Al, Pb, and Cu, in addition to 70 % of the sulfate (from 7 500 to 1 800 mg/L). The pH of output waters from the BDAS column increased up to 7.6, and resulted in the complete removal of residual sulfate and metals (i.e., Zn, Mn, Ni, CO, Cd, and Tl) to below the detection limit.

Finally, this modification of the technology was applied at full scale for the treatment of acidic and metal-rich waters from Concepción mine (SW Spain) (Guerrero et al., 2024). The treatment plant consisted of a 100 m² NFOL, followed by 3 reactive tanks (divided into two vessels each) with their respective decantation ponds (except the last reactive tank) of 100 m². The first two tanks had dimensions of 960 m³ and 720 m³, respectively, and were filled with limestone-DAS. Finally, the third tank had dimensions of 400 m³, also divided into two vessels. Each vessel was filled with a different material. One of the vessels was filled with MgO-DAS, while the other was filled with barium carbonate-DAS. The treatment plant was able to completely remove elements such as Al, Cu, Zn, Be, Co, Ni, Pb, V, o As, in addition to significant concentrations of Fe (98 %), Cd (97 %), and Cr (93 %). Regarding the performance of the BDAS reactive material, there was a notable improvement in sulfate removal. The initial concentration of sulfate in AMD decreased from approximately 2 g/L to 0.5 g/L at the output of the BaCO₃-DAS vessel, with a sulfate retention efficiency of 76 %. This represents a significant improvement over the MgO-DAS vessel, which retained 49 % of the sulfate. The removal of Mn in the system also improved, with 82 % and 62 % of retention at the output of the BaCO₃-DAS and MgO-DAS vessels, respectively. Finally, the alkalinity generated increased in the BaCO₃-DAS tank, doubling the alkalinity of the MgO-DAS tank (approximately 300 mg/L compared to 150 mg/L as CaCO₃, respectively). In summary, the utilization of BDAS for the remediation of AMD showed a higher performance compared to the use of MgO-DAS, particularly in terms of the generation of alkalinity and reduction in net acidity, as well as the improved removal of S and Mn.

4. Alternative by-products or wastes AS substitutes for alkaline reagents

The progressive development of DAS technology has led to high effectiveness in AMD treatment. However, the cost of neutralizing materials may act as a limiting factor in its broader utilization. Limestone is a commonly used reagent, with a cost of between 10–50 €/t (Guerrero et al., 2024). According to Orden et al. (2021), the treatment of AMD with DAS-limestone at the full-scale treatment plant at the Esperanza mine would incur a cost of 0.27 €/m³ during the study period, one of the least expensive passive systems vs conventional passive treatment systems and up to 8–12 less expensive than active treatment systems. However, the cost of the full-scale treatment plant at the Esperanza mine (Orden et al., 2021), added-up to 13 treatment plants of this type required in the Odiel River basin (Macías et al., 2017b), would entail an annual cost of replacing the reactive limestone material up to €100 000. If other alkaline materials to achieve higher pH values are considered, such as barium carbonate and caustic magnesia, these costs could increase significantly, as their market price ranges between €700–800/t and €250–600/t, respectively (Guerrero et al., 2024). According to estimates by Torres et al. (2018), the use of barium carbonate instead of limestone in DAS systems would increase the cost by up to 10 times. The environmental cost is also high, as mining of alkaline materials has high environmental footprint (Martínez et al., 2019). Numerous studies have been conducted throughout the development stage of the DAS, with the objective of identifying low-cost alternative alkaline reagents that could replace commercial reagents, thus promoting a more sustainable and cost-efficient treatment.

One of the most extensively tested possibilities has been the use of wood ash in DAS systems, as reported by Rakotonimato et al. to treat AMD in Canada (Rakotonimaro et al., 2016, 2017, 2018). Wood ash is typically regarded as a waste material, but its high pH paste value (up to

12), metal removal potential, and neutralization capacity indicate that it has the potential to be used as an alkaline reactive in wood ash DAS (WA-DAS). To assess the effectiveness of this alkaline waste, column tests were conducted at varying reagent-inert matrix ratios (Rakotonimaro et al., 2016) and different HRT (Rakotonimaro et al., 2017), with results compared to commercial reagents columns (e.g., limestone and dolomite). In both studies, WA-DAS was tested and compared for the treatment of a Fe-rich AMD (2 500 mg/L of Fe, at pH 4), demonstrating satisfactory results in terms of Fe removal (up to 99 %), and exceeding the performance of DAS with commercial reagents (Fe retention between 22–66 %). The WA-DAS, limestone-DAS, and dolomite-DAS were also found highly efficient to remove Al, Zn, and Pb in AMD. The WA-DAS also showed higher effectiveness for sulfate removal (18–40 %) vs conventional reagents, which exhibited a sulfate removal efficiency of <10 %. In other column tests (Rakotonimaro et al., 2017), the contaminant removal efficiency and hydraulic performance of a mixture consisting of organic matter mixed at 70 % (w/w) with an inert substrate was also analyzed, working as passive biochemical reactors (PBRs) for sulfate removal (Neculita et al., 2007, 2021). The combination of PBRs and WA-DAS was also successfully tested in different multi-step treatment scenarios in the laboratory (Rakotonimaro et al., 2018), when the WA-DAS was used as a pre-treatment of the PBR, leading to the removal of 76–99.6 % of Fe and 46–82 % of sulfate.

More recently, Larraguibel et al. (2020) conducted tests to assess the viability of utilizing agri-food industry waste (i.e., mussel shells, clam shells, and eggshells) as a limestone replacement in DAS treatment systems. Various reagents were used for the treatment of a synthetic AMD, mimicking AMD waters reported in the Chilean and Argentinean Andes. The results demonstrated comparable efficiency of the waste material in removing Fe, Al, and Cu during AMD treatment, with even greater efficiency than commercial limestone. The study also achieved sulfate residual concentrations to below 500 mg/L from 1 234–2 468 mg/L in AMD, by using BaCO₃ for sulfate removal. Consistently, Millán-Becerro et al. (2024) conducted DAS-type laboratory column experiments using a calcite-rich waste resulting from the treatment of industrial leachates as a reagent, with the objective of treating AMD-contaminated waters from the IPB. The X-ray diffraction analysis revealed that the waste contained gypsum (54 wt %), calcite (44 wt %), and minor amounts of halite (2 wt %). The results of the treatment trials demonstrated the complete removal of Fe and Al, with 90 % of Cu also being removed. Moreover, during the initial two weeks of treatment, between 76 % and 92 % retention of Zn and Cd was achieved, with the treatment being ineffective for the removal of other divalent metals, such as Co or Ni. These results are comparable with those previously obtained using commercial limestone, indicating that this calcite-rich waste with no previously reported use could be a suitable low-cost material in DAS treatment systems.

5. Extrapolation of DAS technology to other locations

In addition to the extensive tests conducted to improve the DAS concept and to avoid the effectiveness issues that have emerged throughout the evolution of this technology, a multitude of studies have also been carried out with the explicit objective of extrapolating said technology to other mining regions worldwide with comparable AMD contamination issues (Table 1). Although some of these studies have been published in international journals, many of them correspond to studies published in international conferences or academic research studies. These studies have facilitated the expansion of the in situ applications of DAS beyond the initial IPB (SW Spain), South Africa, and Canadian settings, to include Ecuador, Chile, Colombia, and Peru in South America; China in Asia; England, Wales, and France in Europe; and New Zealand in Oceania. The transfer of technology has resulted in the implementation of DAS applications across all inhabited continents, involving the testing in a wide variety of different climatic regions,

Table 1
Studies that extrapolate DAS technology to other regions.

References	Country	Climate	Type of work	Scale	Type of leachate	Type of treatment
Caraballo et al., 2010	England	Oceanic - Marine west coast	Research paper	Column	Synthetic	MgO-DAS
Guayasamín, 2016	Ecuador	Subtropical highland with uniform rainfall	Bachelor's Thesis	Column	AMD	Limestone-DAS + MgO-DAS
Moreno and Palacios, 2017	Chile	Warm-summer Mediterranean	Research work	Column	AMD	Limestone-DAS + MgO-DAS
León Castro, 2018	Perú	Dry-winter subtropical highland	Master's thesis	Column	AMD	Limestone-DAS + MgO-DAS
Hillman, 2018	New Zealand	Oceanic - Marine west coast	Master's thesis	Column / Pilot	AMD	Limestone-DAS + MgO-DAS
Delgado et al., 2019	Ecuador	Subtropical highland with uniform rainfall	Research paper	Column	AMD	Limestone-DAS + MgO-DAS
Dube et al., 2019	South Africa	Dry-winter humid subtropical	Conference paper	Column	AMD	Limestone-DAS
Schwarz et al., 2020	Chile	Warm-summer Mediterranean	Research paper	Column	Synthetic	Limestone-DAS
Li et al., 2020	China	Humid subtropical	Research paper	Column	Synthetic	Limestone-DAS
Wenbo et al., 2021	China	Humid subtropical	Research paper	Column	Synthetic	Limestone-DAS
Rötting et al., 20021	Wales	Oceanic - Marine west coast	Conference paper	Pilot	AMD	Limestone-DAS + MgO-DAS / BaCO ₃ -DAS
Vasquez et al., 2022	Colombia	Subtropical highland with uniform rainfall	Research paper	Pilot	AMD	WDAS as pretreatment
Millán-Becerro et al., 2023	Wales	Oceanic - Marine west coast	Research paper	Column	AMD	Limestone-DAS + MgO-DAS / BaCO ₃ -DAS
Jacob et al., 2023	France	Oceanic - Marine west coast	Conference paper	Column	AMD	Limestone-DAS
Bonnail et al., 2023	Spain (Aznalcollar)	Hot-summer Mediterranean	Research paper	Pilot	AMD	Limestone-DAS
Collahuazo et al., 2025	Ecuador	Subtropical highland with uniform rainfall	Research work	Column	AMD	Limestone-DAS + MgO-DAS
Xu et al., 2025	China	Dry-winter humid subtropical	Research paper	Column	Synthetic	Thermal activation magnesite

under different precipitation, humidity, and temperature conditions (Table 1; Table S1). According to the Köppen–Geiger climate classification system (Kottek et al., 2006), although most of the DAS studies have been conducted in hot-summer ($n = 24$) and warm-summer ($n = 3$) Mediterranean climates, there have also been studies in a range of other climates, including humid continental–subarctic ($n = 5$), oceanic–marine west coast ($n = 5$), subtropical highland with uniform rainfall ($n = 5$), dry-winter humid subtropical ($n = 4$), humid subtropical ($n = 2$), and dry-winter subtropical highland ($n = 1$).

6. Application of DAS technology in the treatment of acid effluents from phosphogypsum leachates

The effectiveness of DAS technology for the treatment of sulfuric acid and metal-rich leachates has been widely demonstrated. Consequently, Millán-Becerro et al. (2020, 2022) performed several column experiments focused on evaluating the potential application of DAS technology for the passive treatment of phosphoric-sulfuric-hydrofluoric acids and metal-rich waters such as phosphogypsum leachates and process waters. These highly acidic and contaminated solutions derived from the manufacture of phosphoric acid in the phosphate fertilizer industry.

To assess the effectiveness of DAS technology in treating acid phosphogypsum leachates and select the most suitable alkaline reactive material for their effective remediation, Millán-Becerro et al. (2020) conducted a laboratory experiment with 7 columns each filled with 20 cm of DAS reactive mixtures. These DAS materials consisted of an alkaline reagent (i.e., limestone, BaCO₃, biomass ash, fly ash, MgO, Mg(OH)₂, or Ca(OH)₂) and wood shavings in a volume ratio of 1:4. Each DAS column was followed by a 445 cm³ decantation vessel. The HRT of the leachate in the reactive columns was set to be 25–28 h. In these experiments, the most suitable alkaline reagent was calcium hydroxide (Ca(OH)₂), based on its effectiveness and economic criteria for the treatment of phosphogypsum leachates. This reagent achieved the highest net acidity removal (i.e., 3 825 mg/L as CaCO₃) and a total removal of dissolved contaminants (PO₄³⁻, F⁻, Fe, Zn, Cu, Al, Cr, U, and As). The MgO-DAS was also demonstrated to be a promising treatment option, achieving near complete removal of F⁻, Fe, Zn, Cu, Al, Cr, and U.

However, it showed lower performance in phosphate and As removal (83 % and 52 %, respectively). On the other hand, the barium carbonate-DAS and Mg(OH)₂-DAS treatments also achieved a notable improvement in the quality of the polluted waters, achieving removal between 87 and 100 % for F⁻, Fe, Zn, Cu, Al, Cr and U. However, these treatment systems were not as effective for other contaminants such as phosphate, As or sulfate. Conversely, it was demonstrated that limestone, biomass ash, and fly ash were not effective alkaline reagents in DAS systems for the treatment of phosphogypsum leachate. In all cases, the leachate flowed through the treatment without clogging problems, indicating that the DAS system is hydraulically effective for this type of acidic solution.

Subsequent experiments on MgO-DAS and Ca(OH)₂-DAS columns (Millán-Becerro et al., 2022) validated the efficiency of both materials as alkaline reactants, with Ca(OH)₂ emerging as a particularly promising option. Moreover, the precipitation of a waste rich in calcite and gypsum, without impurities, observed in the decantation ponds of the treatment with this reagent, indicated its potential as a reagent in the DAS treatment of AMD. This was subsequently demonstrated in the work of Millán-Becerro et al. (2024).

7. Application of DAS technology in other research contexts

The advancement of DAS technology has enabled its adaptation to diverse geographical regions and other acid leachates. There are also studies that have benefited indirectly from the insights gained from decades of DAS experiments or have analyzed the impact of water treatment on living organisms in its vicinity. Some studies followed guidelines already used in DAS treatment, such as mixing wood chips and a reference material in a volume ratio of 1:4 to increase the porosity of different treatments. As a leading example, De Pourcq et al. (2015) devised a permeable reactive barrier for the removal of Cs-137 from groundwater. To meet the required reactivity and permeability, a mixture of clays (with a high sorption capacity, especially for Cs-137) and wood chips was employed to provide an adequate porosity to the system, as is done in DAS technology. In this same sense, Diaz-Vanegas et al. (2022) tested the removal of Fe and As from an AMD by oxidation

and phase precipitation through the action of a microbial community. Previous attempts to increase the biofilm surface area (a limiting factor for treatment) resulted in clogging problems. Therefore, they decided to use a mixture of wood chips and pozzolanic ash as bacterial growth support media, mimicking DAS technology.

Some studies conducted multicomponent reactive transport modeling to investigate the acid water-rock-Portland cement interaction in various settings, including the full-scale treatment plant of the Esperanza mine (Cama et al., 2019). Other studies have focused on the evaluation of the quality of water treated by DAS passive treatment systems, with a comparison to untreated leachate, through toxicity tests in freshwater clams (such as mortality or bioaccumulation of metals) (Bonnaill et al., 2019). Finally, Macías et al. (2017) employed geochemical modeling using PHREEQC software to assess the economic and environmental sustainability of remediation in the Odiel River basin, which is severely contaminated by AMD. The modeling contributed to the development of a restoration strategy based on the implementation of 13 DAS treatment plants in selected acid disposal sites.

8. Evolution of DAS efficiency for metal removal and acidity reduction

The passive DAS treatment system has undergone significant development in recent decades, resulting in enhanced efficacy for the treatment of acidic metal-rich leachates, such as AMD and phosphogypsum-related leachates. This section presents a summary of the evolution of the effectiveness of passive DAS treatment systems for net acidity mitigation and metal removal (Table S3). Fig. 3 shows the input AMD samples (red circles) and the water samples treated by the DAS systems (blue circles), classified according to their pH and metal content (i.e., Al, Cu, Fe, Mn, Zn, As, Cd, Co, and Ni) (diagram modified from Ficklin et al., 1992). Results show that most of the AMD samples are classified as highly acidic and extremely metallic samples (HA-EM), with some samples exhibiting characteristics of acidic water (A-EM). Regarding the treated samples, two principal groups can be discerned. The first group showed a notable pH improvement, although the metal removal was moderate, resulting in a shift towards the field of near-neutral and extremely metallic samples (NN-EM), which would correspond to the early stages of DAS development. In contrast, most of the treated samples showed more effectiveness in pH increases and metal removal, exhibited near-neutral pH and high metal concentrations (NN-HM), although a few samples exhibited moderately alkaline (Malk) and even highly alkaline (Halk) pH, accompanied by low metal concentrations (LM).

An analysis of the evolution of the effectiveness of these treatments to remove the most important metals (i.e., Al, Fe, Mn, Zn, Cu, As, Cd, Co,

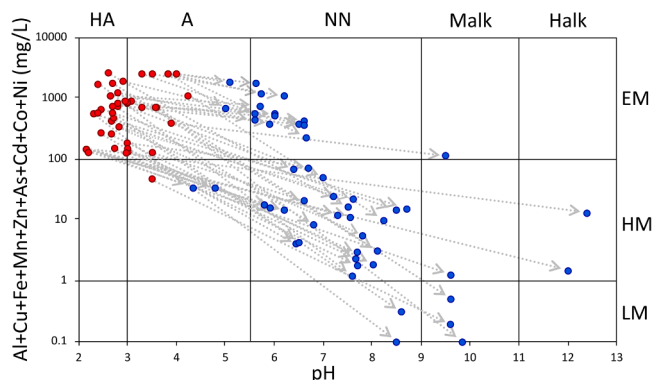


Fig. 3. Classification of AMD samples (red circles) and samples treated by DAS technology (blue circles) according to their pH and metal concentration (modified from Ficklin et al., 1992). HA: high acid, A: acid, NN: near neutral, Malk: moderately alkaline, Halk: highly alkaline, EM: extreme metal, HM: high metal, LM: low metal.

and Ni) and to decrease acidity reveals an improvement in the DAS treatment system over the last decades (Fig. 4). Firstly, it can be observed that the effectiveness of the first treatment stage of the DAS development (in 2008) for net acidity was relatively low, with net acidity removal of approximately 1 000 mg/L as CaCO₃ (between 45 and 75 % of the total net acidity). Then, metal removal was inadequate, with <500 mg/L removed (between 20 and 50 % of the total metal load). Despite the low efficiency, the acidity removed was significantly higher than that of other conventional passive treatment systems, which achieved average removal of approximately 250 mg/L as CaCO₃ (Ziemkiewicz et al., 2003). The effectiveness of the process was enhanced using MgO-DAS for the removal of divalent metals (between 2009 and 2011) and the application of NFOL-type pretreatment, resulting in a significant increase in the net acidity retention percentages (up to 70–100 % in recent years) and in the retention of metals (between 50 and 100 %). From 2016 on, higher effectiveness in the removal of both net acidity and metals was reported, with removal of up to 4 000–6 000 mg/L of acidity as CaCO₃ or up to 1 000–2 500 mg/L of metals, with removal rates up to 100 %. Lower values were in turn observed in trials using new reagents or leachates that eventually lowered the effectiveness of the DAS system. The efficiency of metal removal using DAS applications for the treatment of a distinct acid matrix (i.e., phosphogypsum leachate treatment by Millán-Becerro et al., 2020) was lower due to the higher acidity of these leachates.

A comparison of the effectiveness of DAS treatment systems in removing net acidity with traditional passive methods (see Figure S2) reveals that these traditional methods adapt to the net input acidity of coal-AMD, which can be an order of magnitude lower than the net acidity of sulfide-AMD. This is the reason why traditional passive treatment methods have historically demonstrated signs of clogging or passivation of the alkaline reagent. In contrast, DAS treatment, which is specifically designed for these leachates with high metal content and acidity, is capable of achieving complete removal.

9. Mineralogical studies of the precipitates from the DAS treatment

The treatment of these highly acidic and metal rich effluents lead to the formation of huge volume of metal-rich sludges which should be properly managed. To achieve an environmentally friendly and cost-effective management of these sludges, an in-depth study of their chemical and mineralogical properties must be accomplished. Numerous studies that have contributed to the development of DAS have also identified the principal mineralogy of newly formed precipitates in the DAS treatment systems. Table 2 presents a summary of the mineralogy identified in these studies for a range of DAS systems in terms of leachate treated and reagent. A variety of analytical techniques have been employed in these studies, including X-ray diffraction (XRD, DXRD, and μ -XRD), scanning electron microscopy (SEM-EDS), electron probe micro-analyzer (EPMA), micro-X-ray fluorescence (μ -XRF), and X-ray photoelectron spectroscopy (XPS). A significant mineralogical variety has been identified, as evidenced by the extensive array of tests conducted with various reagents and the treatment of diverse acid leachates in terms of their hydrochemical characteristics. The main result of these mineralogical characterization has been to establish that the main retention mechanism of most metals is the precipitation of oxides, hydroxides, oxyhydroxides and hydroxysulfates of Fe or Al. The precipitation of Fe typically occurs in the form of metastable phases, such as schwertmannite (Fe₈O₈(OH)₅(SO₄)_{1.5}•nH₂O), jarosite (KFe₃(SO₄)₂(OH)₆) or ferrihydrite (Fe₅OH₈ · 4H₂O). However, its transformation to more stable phases can result in the formation of goethite (α -FeOOH) and hematite (Fe₂O₃) (Bigham et al., 1996). These Fe phases also tend to retain other contaminants through coprecipitation mechanisms, mainly As, and to a lesser extent Cr, Se, Pb, Ti, V, Sb (Olías et al., 2019). Al typically precipitates as basaluminite, microcrystalline gibbsite or amorphous Al hydroxides (Al(OH)₃), and alunite

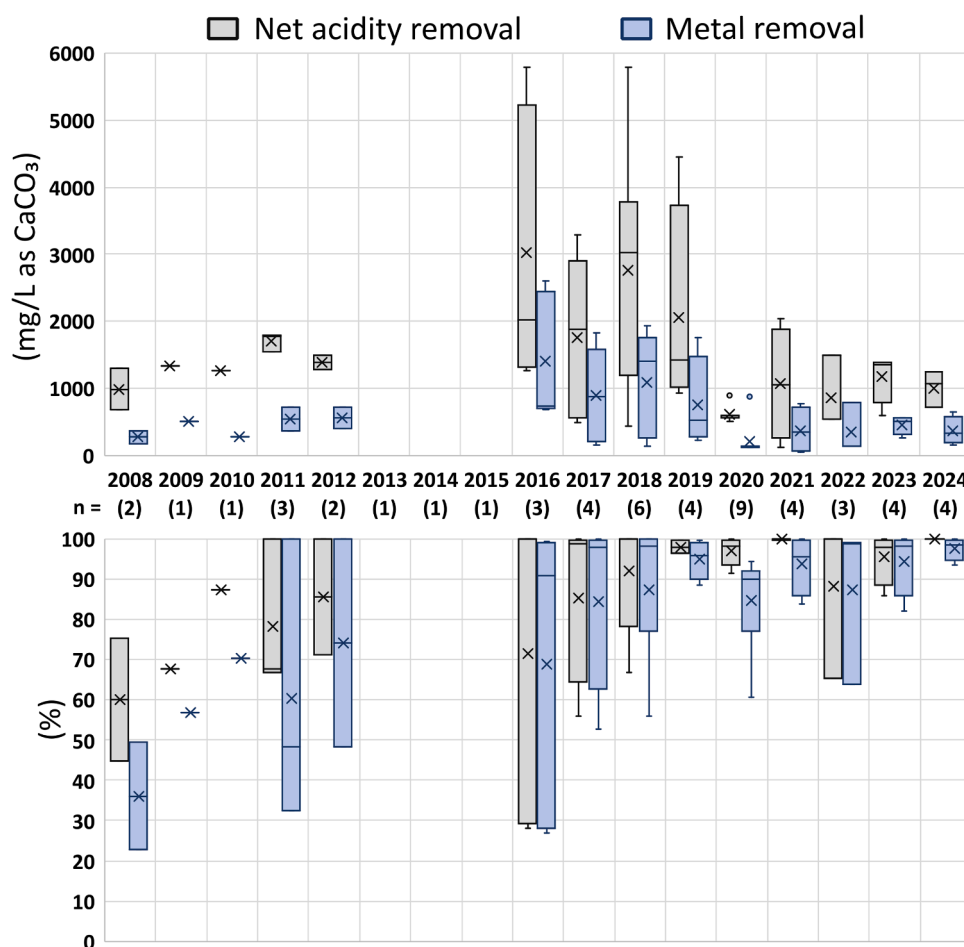


Fig. 4. Evolution of metal and net acidity removal (in percentage and concentration) in cases reported in literature during 2008–2024.

($KAl_3(SO_4)_2(OH)_6$), which can also retain other elements such as Cu, Zn, REE, or Co through coprecipitation. The presence of minerals such as gypsum or barite, which are essential for the removal of sulfate from AMD, has also been confirmed. Conversely, in addition to the mineralogical studies, some studies have also investigated the reactivity of the newly formed solids in the DAS treatment systems. Significant discrepancies were identified in the primary regulated leaching tests, including the European standard leaching test EN 12,457–2 and the US EPA TCLP test. Their applicability in metal-rich wastes generated during the neutralization of AMD may be limited due to the absence of essential metals in such regulations (e.g., Al or Fe) (Macías et al., 2012a). However, the application of other leaching tests (European Community Bureau of Reference [BCR] sequential extraction to assess metal mobility; Ure et al., 1993) or kinetic tests indicated that to ensure the full stability of the wastes generated during AMD treatment with DAS systems, contact of the wastes with water or other leaching solutions should be avoided by maintaining a dry environment (Macías et al., 2012a; Jouini et al., 2019a,b; Millán-Becerro et al., 2024). Similar tests on wastes generated during the treatment of acid phosphogypsum leachates by DAS systems also indicated that deposition should occur under dry conditions, thus avoiding weathering under reducing conditions (deposition without vegetation or organic cover) (Millán-Becerro et al., 2024). In view of the reactivity of the waste generated after the treatment of mine water using DAS technology, there have been several studies in recent years that have focused primarily on studying their stability, with the goal of achieving their stabilization/solidification to avoid the leaching of contaminants (Jouini et al., 2019a,b, 2020a,b). The developed method entailed the amalgamation of DAS treatment waste with wood ash (35 %) and sand (25 %), to which varying

proportions of a hydraulic binder (GU) or pozzolanic materials (GGBFS and FAC) were added for stabilization. The results obtained demonstrated that the mixture presented an improvement in the mechanical resistance of the material and in the stability of the metals in static and semi-dynamic leaching tests. The study concluded that the waste from the treatment of AMD mixed with the different binders is environmentally safe and can be disposed of in a landfill.

Finally, to promote the circular economy or the maximum reuse of mining resources, a recent study focused on the geochemical-mineralogical analysis of the precipitation profile at the full-scale treatment plant at the Esperanza mine and the assessment of the potential for valorization of these wastes (León et al., 2025). The plant was operational for 28 months until the depletion of the alkaline reagent. After the cessation of operations, the waste contained within the first reactive tank was removed and examined. This analysis revealed the retention of significant quantities of metals of economic interest, with a total value estimated to be up to €24 000. This included 4.3 tons of Al, 670 kg of Zn, 370 kg of Cu, 35 kg of REE, 16 kg of Co, 1 kg of Y, or 0.6 kg of Sc. Furthermore, it was determined that undesirable elements such as Fe, As, V, and Sb precipitated in a surface layer, while interesting elements such as Cu and Co were associated with the basaluminite precipitation fronts, which also contained a significant portion of other elements such as Zn, Co, REE, and Y, which were dispersed along the precipitation profile. Consequently, it was determined that 80 % of the waste's economic potential was selectively found in these basaluminite fronts. Finally, in this study and in some previous ones, an attempt is made to preliminarily estimate the cost-effectiveness of recovering metals from the waste (Macías et al., 2017a; Orden et al., 2021; León et al., 2021, 2025). Although more in-depth work is necessary, it was

Table 2
Mineralogical studies on the precipitates generated in DAS systems.

References	Reactive	Type of leachate	Analytical techniques	Main mineralogy and findings (In addition to unreacted reagent)
Rötting et al., 2008a	Limestone	AMD	XRD, SEM-EDS	schwertmannite, gypsum, Al–S–O-rich precipitates with Zn, Cu and Pb retention
Rötting et al., 2008b	Limestone	AMD	XRD, SEM-EDS	schwertmannite, goethite, gypsum, calcite, Al-hydroxysulphates and Al-hydroxides precipitate (basaluminite type) with Zn, Cu, Pb, and Cd
Rötting et al., 2008c	MgO	Synthetic	XRD, SEM-EDS	hydrated zinc hydroxycarbonate with minor Mg and Mn, hydrozincite, brianyoungite, $Zn_4CO_3(OH)_6 \cdot H_2O$, gypsum
Caraballo et al., 2009a	Limestone / MgO	AMD	XRD, DXRD	schwertmannite and goethite with As, gypsum, calcite, basaluminite and amorphous $Al(OH)_3$ with Cu, Pb and Cr, schulenbergitte, minor sauconite
Caraballo et al., 2009b	Limestone	AMD	XRD, DXRD, SEM-EDS	schwertmannite, goethite, gypsum, hydrobasaluminite, amorphous $Al(OH)_3$
Caraballo et al., 2010	MgO	Synthetic	XRD	hydrobasaluminite, gibbsite, amorphous $Al(OH)_3$, manganite, pyrolusite, amorphous $Zn(OH)_2$, zincite
Caraballo et al., 2011a	Limestone	AMD	XRD, EPMA-WDS	schwertmannite with Zn, goethite, gypsum, calcite, basaluminite with Ca, Si, Cu, Co, and Ni.
Pérez-López et al., 2011	MgO	AMD	XRD, EPMA-WDS, μ -XRD, μ -XRF	hydrozincite and minor loseyite with Co and Ni.
Macías et al., 2012c	Limestone / MgO	AMD	XRD, SEM-EDS, EPMA-WDS	gypsum, Zn-rich precipitates with minor contents of Si, S, Mn, Ni and Co, close to the chemical composition of hydrozincite or Zn-hydroxides.
Ayora et al., 2016	Limestone / MgO	AMD	XRD, SEM-EDS, μ XRF	schwertmannite, basaluminite with sorption and coprecipitation of REE, Y, and Cu, gypsum, bechererite, cuprite, REE–Ca-bearing phase (probably fluorite)
Gomez-Arias et al., 2015	$BaCO_3$	AMD	XRD, SEM-EDS	barite, calcite, aragonite
Rakotonimaro et al., 2016	Wood ash / Limestone / Dolomite	Synthetic	XRD, SEM-EDS	gypsum, chukanovite, srebrodolskite, magnesioferrite, and hydroniumjarosite
Rakotonimaro et al., 2017	Wood ash / Limestone	Synthetic	SEM-EDS	Fe-Si-Al oxides/oxyhydroxides, siderite, gypsum, wustite, srebrodolskite, calcined ankerite, anhydrite
Torres et al., 2018	Limestone / $BaCO_3$	AMD	XRD, SEM-EDS, EPMA-WDS	barite, calcite with minor amounts of Mg, Zn and Mn, Zn-rich precipitates with minor amounts of Ca
Jouini et al., 2019a	Wood ash / Limestone	AMD	XPS	hematite, goethite, magnetite, calcium carbonates, gypsum
Jouini et al., 2019b	Wood ash / Limestone	AMD	XRD, SEM-EDS	hematite, magnetite, magnesium calcite, siderite, gypsum, jarosite, troilite, native sulfur
Larraguibel et al., 2020	Calcite-rich waste / $BaCO_3$	Synthetic	XRD, SEM-EDS	malachite, $Cu_2CO_3(OH)_2$, hydrobasaluminite and gypsum in mussel shells-DAS; calcite, aragonite and barite in BDAS
Millán-Becerro et al., 2020	Limestone / $BaCO_3$ / Biomass ash / Fly ash / MgO / $Mg(OH)_2$ / Ca(OH) ₂	Phosphogypsum	XRD	barite and zhangpeishanite in BDAS, gypsum and fluorite in the rest of DAS-columns
Millán-Becerro et al., 2022	MgO / Ca(OH) ₂	Phosphogypsum	XRD, EPMA-WDS	brushite, despujolsite, brucite, fluorapatite, cattite, struvite, struvite-(K), and $Mn_3Zn(PO_4)_2 \cdot 2H_2O$ in the MgO-DAS; brushite, gypsum, brucite, and calcite in the Ca(OH) ₂ -DAS
Millán-Becerro et al., 2024	Calcite-rich waste	AMD	XRD, SEM-EDS	basaluminite with Cu and Fe, schwertmannite, hydrozincite, malachite
Delgado et al., 2025	Limestone / MgO	AMD	XRD, SEM-EDS	schwertmannite, jarosite, coquimbite, gypsum, azurite, malachite, rhodochrosite, calcite
León et al., 2025	Limestone	AMD	XRD, SEM-EDS	ankerite, calcite, gypsum, quartz, schwertmannite, basaluminite, native Cu, Cu-S mineral, Zn-S mineral, REE phosphate.

*XRD: X-ray diffraction, SEM-EDS: Scanning Electron Microscope coupled with Energy Dispersive Spectrometry, DXRD: Differential X-ray Diffraction, EPMA-WDS: Electron Probe Micro-Analyzer, using Wavelength-Dispersive Spectroscopy, μ -XRD: Micro-X-ray Diffraction, μ -XRF: Micro-X-ray Fluorescence, XPS: X-ray Photoelectron Spectroscopy.

concluded that, although the economic potential of the waste is not comparable to that of an active mine, valorizing the waste can promote the circular economy and offset part of the costs of environmental remediation.

10. Current knowledge and research needs

10.1 Current knowledge on DAS treatment

Highly contaminated AMD presents a significant environmental concern, particularly for natural water, while conventional passive methods are unable to fully address the associated treatment issue when dealing with highly acidic, sulfate and metal loaded AMD. To address the problems of clogging or passivation, the DAS passive treatment system has been developed and successfully tested for over two decades.

The DAS, which consists of a mixture of a reactive neutralizing agent and an inert support (wood chips), has proven its effectiveness and is considered one of the most adapted options for AMD treatment at remote locations, on closed and abandoned mine sites. Despite numerous review articles on AMD passive treatment, there is a lack of evaluation of DAS systems and their evolution over time. This paper reviews the development and improvements of this technology, as well as its efficiency. Significant developments in the DAS history include the following: i) successful scale-up from laboratory trials to full-scale applications; ii) removal of high metal loading using reagents such as caustic magnesia and barium carbonate; iii) oxidation and removal of Fe by adding NFOL pretreatment; iv) removal of most of the sulfate by using barium carbonate as a reagent, inducing precipitation of $BaSO_4$; v) use of more environmentally and economically sustainable reagents (wood ash or calcite-rich waste), yielding results comparable to those of

conventional reagents. The high efficiency and interest generated by this technology have led to its extrapolation to other regions, having been successfully tested on all inhabited continents. Moreover, given its considerable performance in AMD treatment, the implementation for other acid leachates, such as phosphogypsum-based ones, has been thoroughly investigated. The development of this technology has resulted in acidity and metal removal close to 100 %, making DAS a promising technology for the passive treatment of AMD and other acid leachates, in important abandoned mining regions or industrial wastes such as phosphogypsum. This review can be useful in analyzing the potential for applying DAS to such areas.

10.2 Research needs on DAS technology

Knowledge gaps related to the DAS technology are still identifiable and need to be addressed in future research. Firstly, although there is full-scale experience of treating AMD generated at the Concepción and Esperanza mines (IPB, SW Spain), more full-scale applications are needed under different climatic conditions, and AMD salinity and metal loading, as treatment efficiency may vary upon these conditions. The long-term performance of full-scale systems need still to be assessed, to determine the optimal time for replacement of alkaline reagents, and the effects of changes in flow rate and water chemistry due to concentration effects from evaporation and dilution by rainfalls. Under other climatic conditions, the concentration/dilution effects due to freeze/thaw cycles must be assessed. It is also imperative to extend the scaling of this technology to full scale in other acid leachates, such as those from industrial wastes like phosphogypsum, whose treatment has only been tested on a laboratory scale. Regarding the reagents used, there remains an important line of research that should focus on the search for more efficient or sustainable reagents. Modification of existing reagents, such as thermal activation of magnesite or calcination of dolomite, is a very promising way to increase the efficiency of these reagents. In addition, the search for alkaline waste or by-products that can be used as part of DAS treatment can be an important way to increase the sustainability of these systems without compromising their effectiveness. As for the reagents used, research should focus on the search of more efficient or sustainable reagents. Modification of existing reagents, such as thermal activation of dolomite, is a very promising way to increase the efficiency. The search for alkaline waste or by-products that can be used as part of DAS treatment can be an important way to increase the sustainability of these systems without compromising their effectiveness. With respect to the contaminated residues generated during treatment, a fundamental step in promoting the circular economy of treatment and its sustainability is to maximise the recovery of precipitated metals of economic interest. Currently, there are limited studies on this topic, as mineralogical studies have focused on contaminant retention and not on elements of economic interest. The identification of the minerals that host these elements, the mineral grade of these precipitates and the assessment of their long-term economic potential is a priority research. It would also be very useful to integrate mineral separation/metallurgical techniques for the commercialisation of these elements. This line of research would have direct application and could help to offset some of the costs of constructing and maintaining DAS treatment plants, thus encouraging the construction of these systems on a large scale. Finally, as the stability of these treatment residues is little known, while various leaching tests do not give consistent results, more research is needed for the development of new ways of stabilising these contaminated residues to minimise their geochemical reactivity for safe disposal.

11. Conclusions

This review demonstrates that Dispersed Alkaline Substrate (DAS) technology constitutes a robust and adaptable passive chemical treatment, combining a high-porosity wood chip matrix with a grain fine alkaline reagent to neutralise acidity and retain metals in highly

contaminated mine waters. Its scalability, from laboratory to large-scale facilities, and its flexibility to use alternative reagents, make DAS particularly suitable for remote and resource-poor sites where historical mining has generated waste that poses a long-term acid leachate contamination problem. However, the performance of the system is subject to a number of variables, including the influent chemistry, hydraulic loading/acidity, reagent type and grain size, and climatic conditions. Furthermore, significant knowledge gaps persist, as evidenced by the limited long-term field data and the scarcity of studies on reagent longevity, waste stabilization, and valorization. It is therefore evident that the advancement of DAS, and its subsequent application, is contingent upon the execution of new full-scale trials in diverse mining areas worldwide. Such trials must be complemented by systematic testing with a range of more efficient or sustainable reagents. Furthermore, explicit strategies for waste management and resource recovery are imperative.

CRedit authorship contribution statement

Rafael León: Writing – original draft, Visualization, Formal analysis, Data curation, Conceptualization. **Ricardo Millán-Becerro:** Writing – original draft, Data curation, Conceptualization. **Francisco Macías:** Writing – review & editing, Supervision, Conceptualization. **Carlos R. Cánovas:** Writing – review & editing, Supervision, Funding acquisition. **Carmen M. Neculita:** Writing – review & editing, Supervision. **Carlos Ayora:** Writing – review & editing, Supervision. **José Miguel Nieto:** Writing – review & editing, Supervision, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Supplementary materials

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Data availability

Data will be made available on request.

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