Review

Submarine Tailings Disposal (STD)—A Review

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Abstract: The mining industry is a fundamental industry involved in the development of modern society, but is also the world's largest waste producer. This role will be enhanced in the future, because ore grades are generally decreasing, thus leading to increases in the waste/metal production ratio. Mine wastes deposited on-land in so-called tailings dams, impoundments or waste-dumps have several associated environmental issues that need to be addressed (e.g., acid mine drainage formation due to sulphide oxidation, geotechnical stability, among others), and social concerns due to land use during mining. The mining industry recognizes these concerns and is searching for waste management alternatives for the future. One option used in the past was the marine shore or shallow submarine deposition of this waste material in some parts of the world. After the occurrence of some severe environmental pollution, today the deposition in the deep sea (under constant reducing conditions) is seen as a new, more secure option, due to the general thought that sulphide minerals are geochemically stable under the reduced conditions prevailing in the deep marine environment. This review highlights the mineralogical and geochemical issues (e.g., solubility of sulphides in seawater; reductive dissolution of oxide minerals under reducing conditions), which have to be considered when evaluating whether submarine tailings disposal is a suitable alternative for mine waste.

Keywords: tailings; acid mine drainage; waste management; marine pollution; solubility; reductive dissolution; sulphide; iron oxide; oceanography; ore deposit

1. Introduction

Mining was, is, and will also in the future be a fundamental industry involved in the development of human society. There is no doubt that mining had and will always have a negative environmental impact, as it is a destructive activity. There is also no doubt that humanity cannot progress without metals. Environmental impacts will continue to increase because the ratio of waste/element produced by mining operations is, and will increase in the future, as high-grade ores become rarer and as low-grade ores are exploited. There is little to question about the value of mining to society, but questions remain about how to best proceed to exploit our resources. Due to the increasing volume of waste associated with low-grade ores and the associated environmental impacts of this waste, mining has increasingly competed with other land uses, making environmental and social issues more and more prominent. Nowadays, base metal mining mainly exploits sulphide mineral ores (*i.e.*, minerals which form in the earth's crust under reducing conditions, for example porphyry deposits; Cu, Mo, Au). This is mainly true for the exploitation of metals like Cu, Zn, Pb, Ni, Mo, Au, Ag, while Al, Fe, and Rare Earth Elements (REE) are extracted mainly from oxide ores (Table 1). Coal mining also exploits a resource that was formed under reducing environment, and therefore which can contain sulphide minerals like pyrite. Sulphide minerals are the primary component responsible for the principal environmental impact of mining, the formation of acid mine drainage (AMD). AMD occurs, when sulphidic mine waste is exposed to atmospheric oxygen and water, as occurs in waste rock dumps and mine tailings storage areas and in underground workings or on the walls of an open pit mine. Due to the problems of AMD formation and the geotechnical instability of mine tailings (fine milled material like sludge) impoundments (reviewed elsewhere in this Special Issue [1]), the mining industry is searching for alternative means of waste management, as this is one of the main issues confronting mining operations. Due to the aforementioned problems of on-land deposition of tailings, one option, which has recently regained atention is submarine tailings disposal (STD). In order to evaluate which waste management option is most suitable for a particular site, many parameters have to be considered. Submarine tailings disposal seems to be an attractive option for preventing AMD because sulphide minerals in the mine waste should be geochemically stable in the long-term due to reduced redox conditions in this environment. Although from a geochemical standpoint this idea is sound, the reality (*i.e.*, nature) is more complex. This review draws attention to several parameters that are often mentioned but poorly documented in the literature [2,3], but are important to consider. The review is not comprehensive and the examples selected mainly highlight important processes occurring in these systems. For this purpose, we discuss the history and the lessons learned from mine waste deposition and the formation of our potential resource (the ore deposit) to understand the biogeochemical interactions occurring between the seawater and the deposited mine waste.

Table 1. Simplified overview of the principal elements extracted by mining and their associated ore deposit type and with the associated environmentally problematic elements and their mineral assemblage. Only the principal minerals and elements are shown; this list can be much more extensive depending on the ore deposit. Hypogene: hydrothermal formation; Supergene: liberation and enrichment processes due to meteorization; AMD: acid mine drainage; REE: Rare Earth Elements.

Target Elements	Principal Ore Deposit Type	Principal Economic Mineral Assemblage	Associated Non-Economic Minerals and Polluting Elements	Environmental Problems Associated to Mineralogy	Environmental Problems Associated to the Process
Cu, Zn, Pb, Ni, Au, Ag, Sb	Hydrothermal (hypogene), e.g., porphyry types, epithermal veins, high-sulfidation	Chalcopyrite, bornite, chalcocite-digenite, covellite sphalerite, galena	Pyrite, Enargite, tetrahedrite-tennantite, e.g., As, Se, Th, Cr, Cu, Zn, Ni, Cd, Pb	AMD, geochemical and geotechnical stability of tailings impoundments	Flotation reagents, cyanide, geochemical and geotechnical stability of tailings impoundments
Fe	Hydrothermal and Laterites (Supergene)	Hematite—magnetite (goethite-ferrihydrite)	e.g., As, Se, Th, Cr, Cu, Zn, Ni, Cd, Pb	Release of associated elements under reducing conditions (reductive dissolution)	Flotation reagents, geochemical and geotechnical stability of tailings impoundments
Al	Bauxites (Supergene)	Gibbsite, boehmite, diaspore	Goethite, hematite, kaolinite, e.g., As, Se, Th, Cr, Cu, Zn, Ni, Cd, Pb		geochemical and geotechnical stability of tailings impoundments. Alkaline tailings sludge (NaOH digestion)
REE	Clay deposits (Supergene) and Pegmatites	e.g., bastnäsite, monazite, allanite, loparite	Clay minerals and Fe and Al hydroxides. Radioactive elements associated	Release of radioactivity	Desorption reagents like $(NH_4)_2SO_4$
Coal	Coal and Lignite	Coal, Lignite, anthrazite	Pyrite, sulfur, volatiles	AMD	Extensive pit lakes

2. A Little Historical Background

When the flotation process was developed at the beginning of the 20th century, the mining process was revolutionized due to the ability to exploit low-grade ores. This also increased considerably the volume of tailings, the waste material remaining after the ore is passed through crushing, milling, and flotation stages in order to extract the target minerals. Other waste materials associated with a mine include overburden (the soils and rocks overlying the ore without economic mineralization), and the country waste rock extracted in the mining process, which are without economic value at the time of mining (but can contain considerable amounts of sulphide minerals). Both types of materials are deposited in so-called waste-dumps, or in stock-piles if there is any remaining economic value, mostly as a coarse grained material called run-of-mine (ROM) [4]. Nowadays, the mining industry is one of the largest waste producers in the world. Consequently, sustainable waste management is in general the most relevant task for humanity to solve in the future. For the mining industry, it represents the most important environmental problem, due to the enormous volume and space it occupies [4–6].

Historically, tailings were deposited close to the mining operation in natural depressions, lakes, or were sent via gravity into rivers, where they sometimes end up at the shoreline of the sea. Some historic operations include Chañaral, Chile [7–9], Ite Bay, Perú [10], Cerro de Pasco, Perú [11], and Bahía Portman, Spain [12–14], while Freeport-Grasberg, Indonesia [2,3,15] still operates this way (Figure 1). Sulphide oxidation and AMD formation in riverine, lake, or marine shore tailings deposits have damaged water resources (superficial and groundwater, and the sea) and the image of mining in the society, and the deposition of these materials in waterbodies or the sea is forbidden in most countries. (e.g., the lawsuit of the village of Chañaral against the Chilean National Copper Corporation (CODELCO) [7].

Nowadays, most exploited metalliferous ore deposits are sulphide deposits, whereas shallow-depth and surface-exposed oxide deposits have been exploited since roman times in Europe, or since Pre-Colombian times in South and Central America. The newer ore deposits are usually located deeper below the Earth's surface and usually are discovered with geophysical methods, unlike the more easily located surface oxide deposits of the past (Figure 2). Therefore, nowadays, as well in the future, the main sources of metals are and will be sulphide ore deposits.

Sulfide minerals form and are stable under reducing conditions generally deep in the Earth's crust or below water, without dissolved oxygen, and in some cases occurring in the presence of reducing agents like organic matter such as peat, or in the deep-sea. Recognizing the stability of sulfide minerals under these conditions, there was increased interest in the 1970s to deposit sulfide mine tailings at depth in the sea, to lessen the potential for sulfide oxidation. With this idea in mind, several operations around the world realized marine tailings disposal.

Riverine, lake, and marine disposal of tailings has a long history, like for example the cases of Chañaral, Chile (Potrerillo-El Salvador, 1938–1975) and Bahía de Ite, Peru (Cuajone y Toquepala, 1960–1997), which are mainly riverine deposits with subsequent formation of marine shore tailings deposits [7,10]. About 40 years ago, the so-called "Deep Sea Tailings Disposal" started with the first operation in 1971 (Atlas mine, Filipinas; Island Copper Mine, Canada) and 1972 (Jordan River Mine, Canada; Black Angel Mine; Greenland). We will see in the following that the expression "Deep Sea" is relative (it can range between a few tens to several thousands of meters of depth). Most scientific

studies are published using the term Submarine Tailings Disposal (STD) 41, Submarine Tailings Deposition (STD) 10, Deep Sea Tailings Disposal (DSTD) 18, Deep Sea Tailings Placement (DSTP) 5, and Sub-Sea Tailings Deposition (SSTD). In this review, the most generic term Submarine Tailings Disposal (STD) is used. There are relatively few peer-reviewed papers published (the numbers behind the terms represent the hits in Scopus [16], a scientific publication database) on this topic. This is possibly due to the high costs for oceanographic investigations. Most of the information is produced in the frame of Environmental Impact Studies (EIS) for the permitting process and often there is no public access to the data.

Figure 1. Locations of coastal areas impacted by tailings deposition (including shore deposition, shallow, and deep-sea disposal). In brackets are the economically exploited metals. Adapted from Koski [3].

1. Nome Pacer, USA (Au)	20. SØrfjord, Norway (Cu, Pb, Zn)
2. Prince William Sound, USA (Cu)	21. St. Ives bay, Hayle estuary, England (Sn)
3. Bokan Mountain, USA (U)	22. Rio Tinto and Odiel estuaries, Spain (Cu)
4. Klag Bay, USA (Au, Ag)	23. Portman Bay, Spain (Pb, Zn)
5. Salt Chuck mine, USA (Cu, Ag, Au)	24. Grado and Marano lagoons, Italy (Hg)
6. Kisault mine, Canada (Mo)	25. Cayeli Bakir mine, Turkey (Cu, Zn)
7. Britannia mine, Canada (Cu, Zn)	26. Gulf of Benin, Togo (P)
8. Island Copper mine, Canada (Cu, Zn)	27. Macquarie Harbor (estuary), Australia (Cu)
9. Jordan River mine, Canada (Cu)	28. Southwest Lagoon, New Caledonia (Ni)
10. Little Bay, Tilt Cove mines, Canada (Cu)	29. Misima Island, Papua New Guinea (Au)
11. Callahan mine, USA (Zn, Cu)	30. Bougainville Island, Papua New Guinea (Au)
12. Boleo, Lucifer mines, Mexico (Cu, Mn)	31. Lihir Island, Papua New Guinea (Au)
13. Levisa Bay, Cuba (Ni)	32. Simberi Island, Papua New Guinea (Au)
14. Ite Bay, Peru (Cu, Mo)	33. Ok Tedi mine, Papua New Guinea (Cu, Au)
15. Michilla mine, Chile (Cu)	34. Grasberg mine, Indonesia (Au, Cu)
16. Ensenada Chapaco, Chile (Fe-oxides)	35. Buyat Bay, Indonesia (Cu, Au)
17. Chañaral Bay, Chile (Cu)	36. Benete Bay, Indonesia (Cu, Au)
18. Black Angel mine, Greenland (Zn, Pb)	37. Atlas mine, Philippines (Cu)
19. Synvaranger mine, Norway (Fe-oxides)	38. Marinduque Island, Philippines (Cu)

Figure 2. Schematic model of a sulphide ore deposit (porphyry), with the zones, where sulphides, oxides, and sulphates/chlorides may dominate the mineral assemblage. This zoning is a strong simplification and the different mineral groups may coexist. On the left, the different tailings disposal options in water bodies and their dominant geochemical regimes are highlighted.
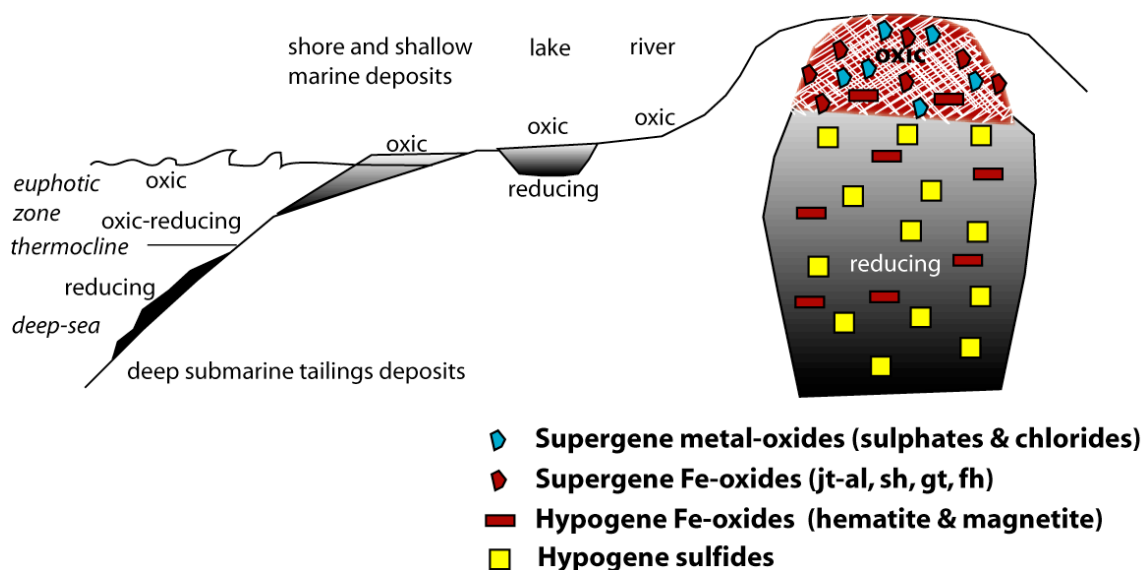
Recently, there has been a movement developing against STD around the world, most actively by Earthwork and MiningWatch Canada, who published two reviews about the locations and the mining companies using STD [17–19]. Government and non-government organizations have also been re-evaluating this issue recently [2].

The following is a summary of the evolution of the tailings disposal techniques and their associated environmental problems:

(1) At the beginning of the implementation of flotation, the tailings were deposited by gravity in the closest location available, like rivers, lakes, and in some cases, they reached the sea, depositing the tailings as marine shore tailings deposits. Examples in South America are the valley of El Salado and the Bay of Chañaral in Chile or the river Locumba and the tailings deposited in the Bay of Ite, Perú [7,10]. If the treatment plant was located at the coast, the tailings were directly deposited into the sea; for example, tailings from the mine Michilla and the deposition of tailings from an iron oxide pellet plant at Ensenada Chapaco [20,21]. Sulphide minerals in these types of tailings deposits are exposed to an oxidizing environment during transport and in final deposition, allowing them to oxidize and produce mine drainage and the associated pollution of water resources by the released elements. In the case of the direct deposition of the tailings into the sea, there have been visible effects of increase turbidity and high sedimentation rates in the deposition area, directly impacting the marine fauna [20]. In both cases, the effects were easily visible and the increased pressure of public opinion resulted in a change of the tailings management practice;

(2) In the case of Chañaral, a lawsuit against CODELCO (1989) forced the company to stop tailings deposition in the bay of Chañaral and to build an alternative tailings impoundment called Pampa Austral [7] on-land, which is currently the final disposal facility for the tailings of

the El Salvador mine. The tailings in the valley El Salado and in the Bay of Chañaral, as well as the tailings of the beaches in the north coast of Punta Palitos are in the same condition as directly after deposition and remain as a source for metals pollution to the environment due to sulphide oxidation. In the case of the bay of Ite, Southern Peru Copper Corporation completed a clean-up of the Locumba valley and remediation of tailings deposited at the Bay of Ite, and constructed the on-land tailings impoundment Quebrada Honda, where the tailings from the mines Cuajone and Toquepala are currently deposited. The option of STD for the tailings in the Bay of Ite was evaluated [22], but not implemented. In both cases, the pending tasks to complete are the prevention of AMD formation in the active on-land tailings impoundments, and in the case of Chañaral the remediation of the whole system. In the case of Michilla mine, the sea disposal of the tailings was halted and the tailings were removed and deposited in an on-land tailings impoundment. In the case of the Ensenada Chapaco, the deposition point was changed in 1994 due to problems with turbidity and sedimentation in the intertidal zone, and the tailings are now deposited at between 35 and 130 m depth [21]. As these tailings are mainly composed of iron oxides (magnetite and hematite), liberation of associated contaminant elements is observed due to reductive dissolution;

(3) Due to the visible problems of marine tailings deposition at the shore line and in the euphotic zone, deep submarine tailings disposal started in the early 1970s (ideally <150 m depth to ensure being below the euphotic zone) in Atlas Mine, Filipinas [23], Island Copper Mine (50 m), Canada, Jordan River Mine, Canada and Black Angel Mine, Greenland. The cases of Island Copper Mine and Black Angel Mine have shown the difficulties of predicting the behavior of the oceanographic system and the importance of mineralogical and geochemical characterization of the tailings before marine deposition. In the latter case, soluble and oxide minerals liberated significant amounts of contaminants into the sea [24], similar to the situation of Ensenada Chapaco [21], and clearly showed that oxide minerals should not be deposited in a reducing environment.

As this historic overview shows, inappropriate tailings management and a lack of mineralogical, geochemical, and oceanographic characterization of the systems can lead to environmental damage, and has resulted in a shift by the mining industry back to on-land deposition in tailings impoundments. With the increasing pressures of society on the on-land deposition, the submarine tailings disposal option is nowadays again being considered.

Commonly Mentioned Advantages of STD Are:

- Prevention of acid mine drainage: Reducing environment and lower concentrations of dissolved oxygen limit or prevent sulphide oxidation and any acidity produced through sulphide oxidation will be neutralized by the buffer capacity of marine water;
- Tailings are more geotechnically stable and the possibility of catastrophic failure of tailings dams (on land tailings dam heights may reach several hundred meters), especially in areas with high seismic activity and high rainfall is eliminated [25];
- Minimal land surface is used. This is a strong argument in Norway where, due to the Fjord topography, on-land space for the tailings deposition is very limited;
- Less long-term maintenance required after deposition compared to on-land disposals.

Commonly Mentioned Disadvantages and Risks of STD Are:

- Smothering benthic organisms and physical and geochemical alteration of bottom habitat;
- Reduced number of species and biodiversity of marine communities;
- Risk of liberation of toxic elements from the tailings to the seawater;
- Bioaccumulation of metals through the food chains and ultimately into fish consumed by humans, with associated human health risks;
- The water content of the tailings cannot be recovered; this is especially critical in dry climates;
- The deposited tailings cannot be recovered (possible loss of valuable resources);
- Larger footprint on the seabed than on land;
- Potential toxicity of the flotation reagents used on the marine ecosystem;
- Plume sharing and dispersal of the fine particles throughout the sea;
- Relocation of the tailings in different compartments of the marine ecosystem due to upwelling and currents.

3. Revision of the Legislation Framework and Practice of STD around the World

The London Convention (1972) and its updated version from 1996, the London Protocol (in place since 2006) on the prevention of marine pollution by waste disposal or other materials, are the principal international instruments for the protection of the oceans from anthropogenic pollution. Currently, 42 countries ratified the London Protocol including the significant mining countries such as Australia, Canada, China, and Sweden. This list also includes the main countries which practice STD, like Philippines (9 May 2012), Chile (26 September 2011) and Norway (16 December 1999), but Indonesia and Papua New Guinea (PNG) did not sign. PNG did sign the London Convention (signed by 87 countries) [26].

The United States also did not sign the London Protocol, instead regulating their water quality with the "Clean Water Act", which has been in place since 1991. This being said, most of the developed mining countries do not permit disposal of mine waste into the sea or allow it only in very exceptional cases. Additionally, the UN and World Bank have shown to be very critical of STD and have recommended not using this option.

The London Convention lists materials that are not allowed to be deposited into the sea. In contrast, in the London Protocol, all deposition is forbidden, except for a "reverse list" of some waste types. For example, it allows deposition of "inert inorganic geological material" into the sea. A requirement for following the London Protocol is therefore to show that a material is geological, inorganic, and inert. By definition, nearly all minerals and composites of minerals like rocks form part of the geological–geochemical element cycles. There are only some minerals which could be classified in a geological sense as nearly inert (e.g., quartz, rutile, zircon), but there exist great differences in the solubility and kinetics of dissolution of the different mineral groups in certain geochemical conditions, as explained above (see Table 2).

4. Mineralogical and Geochemical Processes Associated with Ore Deposits and Mine Waste Deposition

The following subsection analyzes the geochemical processes that occur in the different tailings systems to assist in the prediction and prevention of environmental contamination associated with each of the tailings management options.

4.1. Distribution of Minerals and Associated Elements in an Ore Deposit

Understanding the genesis of ore deposits is vital for the exploration of new exploitable mineral deposits. Although the general formation process of some ore deposit types, like porphyry copper deposits, is quiet well understood [27], there remains significant contention in explaining the co-existence of sulphide and iron oxide minerals in the same deposit type as they represent two different geochemical systems (reducing and oxidizing) [28–32]. Although the genesis of this phenomenon is not crucial for final waste management, the fact that the ore body contains both mineral groups (*i.e.*, hypogene sulphides and oxides groups) is a critical factor in determining appropriate waste management. In an ore forming environment, high concentrations of all elements may be involved in the mineralizing process, and there are many trace elements incorporated in the different minerals. Consequently, the final stability of these host minerals is key for the stability of the environmental hazardous elements associated with the final waste material of the mining process. For example, sulphides like pyrite (FeS_2), the most abundant iron sulphide mineral and main mineral responsible for AMD formation, can contain significant amounts of arsenic and other toxic elements. Oxide minerals like magnetite can also contain high concentrations of toxic elements [33].

Coming back to the original hypothesis that sulphide minerals are stable in a reducing environment, but if in a sulphide mineral assemblage there are also associated oxides like for example magnetite, hematite, or goethite, these oxide minerals will not be stable under a reducing environments and will suffer reductive dissolution, resulting in a liberation of the associated elements into the environment.
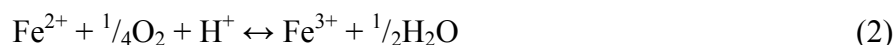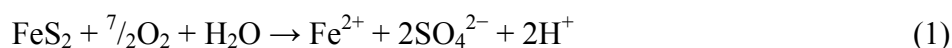
4.2. Sulphide Oxidation and the Formation of Acid Mine Drainage (AMD)

To better understand why the STD option is again being considered as an option for tailings disposal by the mining industry, we review some key aspects about the formation of acid mine drainage. This chapter is taken from Dold [5] for the convenience of the reader and more details on this issue can be found in this reference and in another review in this Special Issue [1]. The problem of sulphide oxidation and the associated acid mine drainage (AMD), or more generally acid rock drainage (ARD), as well as the dissolution and precipitation processes of metals and minerals, has been a major focus of investigation over the last 50 years [34–38]. There has been less interest in the mineralogical and geochemical interactions taking place within the tailings and waste dumps itself [38,39], despite these reactions being essential for understanding the parameters controlling acid mine drainage formation and for developing effective prevention methods. The primary mineralogical composition of a waste material has a strong influence on the oxidation processes. This has been well illustrated [40–42] and has shown that reaction rates are dependent on the sulphides being oxidized, by the type of oxidant (e.g., Fe(III) or O_2) and the presence of Fe(III) hydroxide coatings. Kinetic-type weathering experiments

indicate the importance of trace elements in the stability of individual sulphides. Where different sulphides are in contact with each other, electrochemical processes are likely to occur and influence the reactivity of the sulphides [43].

Most mining operations are surrounded by piles, dumps, or impoundments containing pulverized material or waste from the benefaction process, which are known as tailings, waste rock dumps, stockpiles, or leach dumps or pads. Waste rock dumps contain generally material with low ore grade, which is mined but not milled (run of mine, ROM). These materials typically contain large concentrations of sulphide minerals, which may undergo oxidation, producing a major source of metal and acid contamination [11].

The most common sulphide mineral is pyrite (FeS_2) which oxidizes in several steps including the formation of the meta-stable secondary products ferrihydrite ($5Fe_2O_3 \cdot 9H_2O$), schwertmannite (between $Fe_8O_8(OH)_6SO_4$ and $Fe_{16}O_{16}(OH)_{10}(SO_4)_3$), and goethite ($FeO(OH)$), and the more stable secondary minerals jarosite ($KFe_3(SO_4)_2(OH)_6$), and hematite (Fe_2O_3) depending on the geochemical conditions [35,38,41,44–47]. Pyrite oxidation may be considered to take place in three major steps: (1) oxidation of sulphur (Equation (1)); (2) oxidation of ferrous iron (Equation (2)); and (3) hydrolysis and precipitation of ferric complexes and minerals (Equation (4)). The kinetics of each reaction are different and depend on the conditions prevailing in the tailings.

$$FeS_2 + {}^{7}/_{2}O_2 + H_2O \rightarrow Fe^{2+} + 2SO_4{}^{2-} + 2H^+ \tag{1}$$

$$Fe^{2+} + {}^{1}/_{4}O_2 + H^+ \leftrightarrow Fe^{3+} + {}^{1}/_{2}H_2O \tag{2}$$

reaction rates strongly increased by microbial activity (e.g., *Acidithiobacillus* spp. or *Leptospirillum* spp.)

$$FeS_2 + 14Fe^{3+} + 8H_2O \rightarrow 15Fe^{2+} + 2SO_4{}^{2-} + 16H^+ \tag{3}$$

Equation (1) describes the initial step of pyrite oxidation in the presence of atmospheric oxygen. Once ferric iron is produced by oxidation of ferrous iron (Equation (2)), oxidation by ferric iron will be the primary oxidant (Equation (3)) of pyrite. Pyrite oxidation by ferric iron is strongly accelerated by microbial activity particularly at low pH [36,48,49]. Under abiotic conditions, the rate of oxidation of pyrite by ferric iron is controlled by the rate of oxidation of ferrous iron, which decreases rapidly with decreasing pH. Below about pH 3, the oxidation of pyrite by ferric iron is about 10–100 times faster than by oxygen [50].

It has been known since the 1960s that microorganisms like *Acidithiobacillus ferrooxidans* or *Leptospirillum ferrooxidans* obtain energy by catalyzing the oxidation of Fe^{2+} to Fe^{3+} [51] and in doing so may increase the rate of reaction (2) up to a factor of about 100 over abiotic oxidation [52]. More recent results show that a complex community of microorganism is responsible for sulphide oxidation [48,53–56]. Nordstrom and Southam [57] state that the initiating step of pyrite oxidation does not require an elaborated sequence of different geochemical reactions that dominate at different pH ranges. *Acidithiobacillus* spp. form nano-environments to grow on sulphide mineral surfaces. These nano-environments can develop thin layers of acidic water that do not affect the bulk pH of the surrounding water. With progressive oxidation, the nano-environments may change to microenvironments. Evidence of acidic micro-environments in the presence of near-neutral pH for the bulk water can be inferred from the presence of jarosite (this mineral forms at pH around 2) in certain soil horizons where the current water pH is neutral [58]. Barker *et al.* [59] observed microbial colonization of biotite and measured pH

in microenvironments of surrounding living microcolonies. The solution pH decreased from near-neutral at the mineral surface to 3–4 around microcolonies living within confined spaces at interior colonized cleavage planes.

When mine water, rich in ferrous and ferric iron, reaches the surface it will fully oxidize, hydrolyze and may precipitate to ferrihydrite (fh), schwertmannite (sh), goethite (gt), or jarosite (jt) depending on pH-Eh conditions, and the availability of key elements such as potassium and sulphur (Figure 2). Jarosite, schwertmannite and ferrihydrite are meta-stable with respect to goethite [46].

The hydrolysis and precipitation of iron hydroxides (and to a lesser degree, jarosite) will produce most of the acid in this process. If pH is less than about 2, ferric hydrolysis products like $Fe(OH)_3$ are not stable and Fe^{3+} remains in solution:

$$Fe^{3+} + 3H_2O \leftrightarrow Fe(OH)_3(s) + 3H^+ \tag{4}$$

Note that the net reaction of complete oxidation of pyrite, hydrolysis of Fe^{3+} and precipitation of iron hydroxide (sum of reactions 1, 2 and 4) produces four moles of H^+ per mole of pyrite (in case of $Fe(OH)_3$ formation (Equation (5)), *i.e.*, pyrite oxidation is the most efficient producer of acid among the common sulphide minerals (net reaction 5; Table 2). Nevertheless, it is important to be aware that the hydrolysis of $Fe(OH)_3$ is the main acid producer ($^3/_4$ of moles of H^+ per mol pyrite):

$$FeS_2 + {}^{15}/_4O_2 + {}^7/_2H_2O \rightarrow Fe(OH)_3 + 2SO_4^{2-} + 4H^+ \tag{5}$$
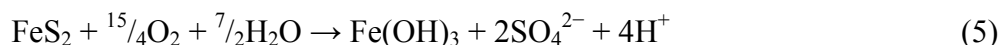
The process of sulphide oxidation concerns all sulphide minerals once exposed to oxidizing conditions (e.g., chalcopyrite, bornite, molybdenite, arsenopyrite, enargite, among others). In this process, different amounts of protons are liberated by the oxidation of the different sulphide minerals [5] and the metals or other harmful elements contained by these sulphides are liberated into the environment.

Table 2. Summary of the most reactive mineral groups and their stability in the environment, associated minerals, and trace elements.

	Sulphides	Oxides & Hydroxides	Carbonates	Sulphates & Chlorides
Stable conditions	reducing (below water cover or in the earth crust with presence of reducing agents like organic matter, or in the Earth crust)	oxidizing (under atmospheric conditions or in the presence of oxidizing agents like dissolved oxygen)	neutral to alkaline	Oxidizing and dry conditions
Unstable conditions	oxidizing (exposure to the atmosphere) or in presence of oxidizing agents like Fe^{3+}, => acid rock drainage (ARD, AMD). There are some indications that high concentrations of Cl could also enhance their dissolution	reducing (below water cover and in the presence of reducing agents like organic matter, sulphate or Cl, for example in lakes with high productivity, or in the sea)	Acid, CO_2	Contact with water (humidity, fog, rain)
Minerals	Pyrite (FeS_2), Chalcopyrite ($CuFeS_2$), Arsenopyrite (FeAsS), Bornite (Cu_5FeS_4), Chalcocite-digenite (Cu_2S), Covelite (CuS), Molibdenite (MoS_2)	Hematite, Magnetite, Goethite, Jarosite-Alunite, Schwertmannite, Ferrihydrite, MnO_2 Birnesite	Calcite, Dolomite, Siderite, Ankerite	Halite, Gypsum, Chalcantite, eriochalcite, *etc.*
Associated trace elements	As, Cr, Se, V, Cu, Zn, Ni, Pb, Cd, REE's	As, Cr, Se, V, Cu, Zn, Ni, Cd, Pb	Fe, Sr, Co, REE's	Metals cations like Cu, Zn, Ni, *etc.*, and anions like SO_4 and Cl

4.3. Stability of Sulphides in Reducing Environment

There is evidence that sulphide minerals are not as stable in marine reducing environments as originally thought. Both in nature [60–62] and in the laboratory, the liberation of heavy metals from the sulphides under reducing conditions [63,64] has been observed. It is not clear which are the associated processes and the controlling parameters, or if it is a problem of some pre-oxidation of the used samples suffering reductive dissolution of trace amounts of oxide minerals. However, as there is contradictory information of the influence of marine water in these processes, more systematic research is needed to understand the long-term stability of sulphide minerals in marine reducing conditions. There are also indications that high Cl concentration might increase the corrosion of sulphides.

4.4. Reductive Dissolution of Oxide Minerals

A metal oxide or hydroxide forms and is stable in oxidizing conditions; therefore, these minerals are unstable under reducing conditions and/or in sediments with high concentrations of silica and/or organic matter [65]. Under these conditions, oxides will suffer reductive dissolution [10,66–69], which will also liberate associated trace elements, which might be toxic to the environment [70–73]. Reductive dissolution, which is catalyzed by microorganisms that use the organic matter as electron source and $Fe(III)$ as an electron sink, is recognized as one of the most archaic forms of bacterial metabolism [66], and is a key process in the biogeochemical cycle of iron in the oceans [74,75]. Reductive dissolution of oxides has only recently been used in a new biohydrometallurgical process for the exploitation of Ni-laterites [73,76].

Two different types of iron oxides in a wider sense can be distinguished: (1) those from hypogene origin, *i.e.*, hydrothermal formation; and (2) those which form due to supergene processes, resulting from meteorization processes of the primary mineralogy, for example during sulphide oxidation (Figure 2 and Table 1). The most relevant hypogene oxides are principally iron oxides like magnetite and hematite, while the supergene $Fe(III)$ hydroxides or oxyhydroxide sulphates are goethite, ferrihydrite, jarosite-alunite, schwertmannite, and in hot climates also hematite can result as a dehydration product of the former minerals and form a gossan [5]. The reductive dissolution of these minerals is a key source for the limiting element iron for the phytoplankton production in the southern oceans [75]. The instability of magnetite in reducing marine sediments is well known due to the problem of paleomagnetic record in marine sediments [77,78]. Therefore, the liberation of iron as a limiting nutrient is not a problem for the ocean, however these iron oxides can contain other associated trace elements, which can be toxic to the environment, like for example Cu, Ni, Zn, Cd, Pb, V, As, Cr, Se, among others [33].

4.5. Dissolution of Sulphates and Chlorides

Sulphate and chloride minerals are very soluble (meaning they dissolve easily in contact with water) and they form from highly concentrated solutions like brines, most often due to evaporation, like in salt lakes in desert climates or in hydrothermal solutions. Exposed to water they dissolve rapidly into their respective ions and liberate the element into the aqueous phase (Table 1). They generally form in oxidizing environments, and in climates with high evaporation. They are also called

efflorescent salts [79], due to their tendency to effloresce above the surface due to capillary transport of the solution towards the surface were the water evaporates and the ions subsequent precipitate when the mineral reached supersaturation. With the next rain or fog, these minerals re-dissolve and the elements again enter the hydrogeological cycle [7,8,39].

Therefore, to stabilize the groups of reactive minerals, which can have environmental hazardous elements associated (sulphides, oxides, carbonates, sulphates-chlorides), it can be said as a simplification, that the sulphides have to be maintained under reducing conditions, the oxides under oxidizing conditions, the carbonates neutral, and the sulphates and chlorides dry. The problem for the waste management starts when these mineral groups are found together in one ore deposit and have environmental hazardous elements associated (see Table 2); unfortunately, this is normally the case in an ore deposit [39].

This overview on the mineral groups, which might liberate elements into the environment, makes clear that in many parts of an ore deposit, several of the mineral groups can co-exist in one rock type and therefore makes the waste management options very limited. However, in order to be able to predict the behavior of the material in different geochemical conditions, only a detailed mineralogical (quantitative and qualitative) and geochemical analysis gives the necessary information to prevent so called "un-predictable" environmental hazards, like that which has often occurred in the past—as for example at Black Angel mine [24].

5. The Receiving Environment

In most of the feasibilities studies of STD, the main part of the budget is used by the oceanographic study and the mineralogical study is often very weak or inexistent. As was hopefully clearly expressed above, the first step must be the detailed mineralogical and geochemical characterization of the future tailings to be deposited. This study will show whether the tailings are suitable to deposit into a marine environment, which is argued to be a reducing environment. Then, this receiving environment has to be studied in detail, in order to ensure the stability of the geochemical environment needed to ensure the deposited minerals are non-reactive and stable in place. As mentioned above, mine tailings can be a complex mixture of different mineral groups, which are stable in different geochemical conditions. Thus, these mineral assemblages can produce problems not only in the final waste deposit, but also in the mining process itself, as for example by way of solution contamination or decreasing the recovery amount [6]. Therefore, in addition to the mineralogical and geochemical characterization of the tailings material to be deposited in a certain mine waste deposit type or site, the geochemical characterization of the deposition site and long-term stability also has to be evaluated. In STD, this implies that detailed oceanographic studies, including baseline studies of the mineralogy and geochemistry of the sediments, their pore water geochemistry, microbiology and macro fauna, organic matter composition, studies of the complete water column, and long-term studies to predict El Niño-Southern Oscillation (ENSO) influences and to prevent upwelling, amongst other possible site-specific requests, have to be completed.

6. The Use of STD around the World

There are principally four countries, which use STD nowadays: Indonesia [15], Papua New Guinea, Philippines and Norway [2,3] (of which Philippines and Norway signed the London Protocol). There is

one active STD operation in Turkey [80] and one in Chile (Ensenada Chapaco) [20]. In most cases, the deposition is from Cu-Au sulphide mineralization (see Table 3). There exist only two operations, which deposit iron oxide ores (Sydvarangar, Norway and Ensenada Chapaco, Chile). Several ceased operations exist in Canada, United States, and Greenland [3,24,81].

Table 3. Summary of the project and sites where tailings disposal into water bodies occurs (lakes, rivers and the sea (STD)); Adapted from [18].

Body of Water	Mines and Location	Type of Ore	Type of Dumping
Basamuk (Astrolabe) Bay, Bismarck Sea	Ramu Nickel and Yandera mines, Papua New Guinea	nickel-cobalt; copper-gold	Marine (proposed)
Norwegian Fjords	Kirkenes, Kvannevann, Stjernøya, Hustadmarmor, Skaland, Engebøfjellet, & Repparfjorden	iron oxides, industrial minerals, titanium, copper	Marine (proposed & actual)
Canadian lakes	Across Canada	gold, nickel, copper, copper-gold, copper-zinc, iron, diamonds	Lakes (proposed & actual)
South American Pacific Coast	Ensenada Chapaco, Chile	iron oxides	Marine
Senunu Bay	Batu Hijau mine, Indonesia	copper-gold	Marine
Luise Harbor	Lihir mine, Papua New Guinea	gold	Marine
Pigiput Bay	Simberi mine, Papua New Guinea	gold	Marine
Black Sea	Cayeli Bakir,Turkey	copper-zinc	Marine
Otomina and Ajkwa Rivers, Arafura Sea	Grasberg mine, West Papua	copper-gold	River & Marine shore
Porgera River, Fly River system	Porgera mine, Papua New Guinea	gold	River
Ok Tedi River, Fly River system	Ok Tedi mine, Papua New Guinea	copper-gold	River
Auga River	Tolukuma mine, Papua New Guinea	copper-gold	River
Lower Slate Lake	Kensington mine, USA	gold	Lake

7. The Experience with STD around the World

7.1. The Chañaral Case, Chile (Ceased)

The Chañaral case represents one of the first riverine and subsequent marine shore tailings depositions (1938–1975) and was extensively studied to understand the effects on the associated ecological compartments (mainly the sea and the population of Chañaral). There are scientific studies available on the mineralogical-geochemical, hydrogeological processes occurring in the tailings deposit [7,8], microbiological [9], public health [82], and the impact on the marine environment [83–86].

It can be summarized that the deposition of tailings at the shoreline of the Bay of Chañaral and the beaches to the north towards the National Park Pan de Azúcar resulted in the oxidation of the sulphides and the formation of an acid oxidation zone on the surface of the tailings. This together with the climatic conditions in the Atacama desert resulted in Aeolian transport of mainly Cu, Zn, and Ni in water-soluble mineral form (eriochalcite; $CuCl_2 \cdot 2H_2O$) towards the village of Chañaral [7,8].

The levels of copper (20.2 ± 11.5 µg/L), mercury (2.2 ± 2.3 µg/L) and lead (2.1 ± 7 µg/L) in urine of the population of Chañaral were higher than the reported concentrations of the non-exposed population. Additionally, the concentrations were higher than in international studies of exposed populations. The levels of the people from Chañaral, which had higher levels than normal, were: 44.8% for copper, 29.4% for total arsenic, 21.1% for nickel, 16.9% for inorganic arsenic, 9.3% for mercury, and 8.3% for lead [82].

Towards the sea, a flux of dissolved elements present as oxyanions like As and Mo and heavy metals like Cu, Ni, Zn by colloidal transport was detected [7]. The liberation of arsenic from typical Fe(III) hydroxides from the oxidation zone (jarosite, schwertmannite, goethite, ferrihydrite) was confirmed by laboratory studies of the liberated arsenic that is adsorbed and co-precipitated in these minerals in seawater [87]. As a result, the incorporation of the heavy metals and metalloids such as arsenic in the flora and fauna in the associated marine environment was established [84–86].

7.2. The Ite Bay, Peru (Ceased Since 1997)

A similar case is the Ite Bay, Peru marine shore tailings deposit, where tailings from two porphyry copper deposits (Cuajone and Toquepala) were sent from 1960 to 1997 via gravity down the Locumba River towards the Ite Bay, where they finally formed the shore tailings deposit. The difference from Chañaral is that here enough water was available to start a successful remediation [10,88]. Also, the tailings in the Locumba River valley were removed by a clean-up initiated by Southern Peru Copper Corporation.

7.3. Island Copper Mine, Canada (Ceased Since 1994)

Island Copper, Canada and Atlas Mine, Philippines were the first operations in the world to implement STD in 1971. Island Copper was in operation until 1994. All studies in this case were carried out by Poling and Ellis [81,89,90]. Although, their book title "Underwater Tailing Placement at Island Copper Mine: A Success Story" [90] gives the impression that this is a good example of how STD should be done. However, the data on this case of the same authors presented in earlier papers indicate that there was displacement of the tailings at lower depths due to upwelling and unpredicted currents. Tailings with thickness >20 cm have shown minor biodiversity in benthic organisms and higher copper concentrations were registered in mollusks [81]. Also, the Canadian Department of the Environment released in 1996 a report that examined decades of environmental monitoring data at the Island Copper mine site and concluded that the sea floor showed widespread and permanent alteration by tailings. As a result of this, the Canadian site-specific regulations were repealed in 2002 and the marine disposal of tailings was banned [2].

7.4. Black Angel Mine, Greenland (Ceased since 1990)

The Black Angel Mine (Pb-Zn) in Greenland operated between 1973 and 1990 using seawater in the flotation process and STD into the fjord Affarlikassa "A". After one year of operation, high Pb and Zn concentrations were detected in the Fjord Qaumarujuk, outside of fjord "A" and later Cd contamination was also detected. Geochemical, mineralogical and oceanographic studies have shown that the tailings contained significant amounts of oxides and soluble Pb-Zn minerals, which were not

stable at the deposition site. There was also a temporal stratification detected in the fjords, which allowed dispersion of the fine particles in the water column between the fjords [24,91,92]. This case shows the problem of soluble oxide minerals in deep-sea deposition. Similar conditions occurred in the Chilean case Ensenada Chapaco (dissolution and reductive dissolution). One, two, and three decades since operation at Black Angel ceased, independent scientific studies showed that the pollution persists [93–98] and is having significant long-term effects on the benthic macro fauna through the presence of heavy metals [99,100]. The study of Josefson *et al.* [100] showed that 33 years after deposition ceased at the Black Angel Mine, degradation of the integrity of the benthic community was directly correlated with persisting, high Pb concentrations in the sediment (>200 mg/kg).

7.5. Kitsault Molybdenum Mine, Canada (Ceased since 1982)

The Kitsault Molybdenum Mine reopened temporarily in 1981–1982 after operation between 1967 and 1972. Consultants originally proposed STD similar to that at Island Copper Mine, but shortly after, new oceanographic instrumentations revealed that water currents, which were originally not predicted, were present. Between 1983 and 1989, the after-closure monitoring program detected that the tailings pore water was enriched in Mo, possibly liberating this element into the marine environment. Additionally, a biological impact on the benthic community of the fjord was observed in the deposition zone [101–103].

7.6. Marcopper Mine, Marinduque, Philippines (Ceased)

The Marcopper Mine in the Philippines experienced some accidents, in which tailings were dispersed into the sea. As a result, studies have shown increased concentrations of different metals in the sediments as well as in the pore water, suggesting toxicity in the marine environment [61,62].

7.7. Ensenada Chapaco, Huasco, Chile (Iron Oxide Ore, Active)

In the Bay of Enenada Chapaco, Huasco, Chile, an iron pellet plant had deposited since 1978 the tailings of several iron oxide deposits (mainly from Algarrobo and Los Colorados) from the Chilean Iron Belt directly into the sea, first directly at the shore and since 1994 at 35 m depth. There is only one scientific publication about the effect of the Ensenada Chapaco tailings deposition on the benthic community [20]. This study investigated the impact of 16 years of tailings disposal in the intertidal zone (1978–1994) on the macro benthic community. Data on the macro fauna between 20 and 50 m depth obtained four months before the intertidal deposition was ceased show the community suffered significantly in terms of abundance, species richness, diversity and high dominance, and caused deep changes in community structure due to the tailings deposition. The complete disappearance of opportunistic species like poliquetos from the families Capetellidae, Spionidae and/or Cirratulidae are attributed to the turbidity and the high sedimentation levels in the bay.

In 1994, the deposition point was changed to 35 m depth, resulting in deposition of the tailings down to a depth of 130 m. There is some information on the impact of the deposited tailings in the recently published Environmental Impact Study (EIS) of an expansion project to deep-sea tailings deposition between 200 and 800 m depth ("Actualización del Sistema de Depositación de Relaves de

Planta de Pellets"), information, which is public and available online [21]. The baseline study for the EIS suggests that hematite-magnetite in the submarine deposited tailings (35–130 m depth) undergo reductive dissolution and release associated trace elements to the seawater [21].

7.8. Sydvarangar, Norway (Iron Oxide Ore, Active)

Sydvarangar is one of two operations that dispose tailings from iron oxide ores into a marine environment (deposition point at 28 m depth). No scientific study on the environmental impact is available and no information is given if there is reductive dissolution occurring. On the Internet, there are some presentations with limited information on this case. The main concern is the potential contamination by the flotation reagents used (Magnafloc 1707).

8. Conclusions

There is a wide consensus among industry and stakeholders that riverine and shore marine disposal should be generally banned due to the high risk of environmental contamination, but there are still some mines operating using these methods, for example Grasberg, Indonesia. At the moment, there are several mines using STD as their tailings management option, but most are in Indonesia, Philippines, Papua New Guinea and Norway. Disposal depths vary from 20 to several hundred meters and the final deposition depth of the tailings in some cases reaches 3000–4000 m. For new projects, deep-sea submarine tailings disposal is typically considered. Forty-two countries have signed the London Protocol, among which nearly all are important mining countries, and therefore the marine deposition of waste is effectively forbidden, with the exception of inorganic, inert geological material. Most of the STD operations are sulphide mines exploiting Cu, Zn, Pb, Mo, Au, and Ag. Only two operations deposit iron oxide tailings into the sea (Ensenada Chapaco, Chile and Sydvarangar, Norway), with some indication of reductive dissolution and subsequent liberation of trace metals into the marine environment in the case of Ensenada Chapaco. There are some cases where in three decades of post-closure the marine ecosystem has not yet recovered. Therefore, it can be concluded that tailings from metal mines are usually not composed of inert geological minerals, and only detailed mineralogical and geochemical studies can give light to the question of whether this material will remain stable in submarine disposal.

In all operations, the following risks of STD have to be evaluated before a decision can be taken:

(1) Liberation of elements associated with oxide minerals due to reductive dissolution under reducing conditions and/or dissolution of soluble sulphate or chloride minerals (e.g., Ensenada Chapaco, Chile and Black Angel Mine, Greenland). Therefore, this type of mineral is not suitable for marine disposal;

(2) Liberation of metals from sulphides. In some studies, the liberation of heavy metals from sulphides in reducing marine conditions is reported. However, due to the lack of detailed mineralogy and geochemistry, it is not clear if this is due to liberation from sulphide minerals under reducing marine conditions, or if these samples contained some oxide minerals. There is a need for more detailed research to address these questions;

(3) Smothering of the benthic fauna due to the high sedimentation rates at the point of tailings deposition. Some studies report a fast repopulation of the tailings by the benthic community after deposition has ceased [104], while other studies present data which indicate that benthic community structures suffered strongly from contamination and open the way to opportunistic species, with a reduction in biodiversity [100,105]. Toxicity effects were detected in some species [62,94,106];

(4) Failure of the tailings tubing (technical problems, tides, earth quakes, tsunamis or storm events) and subsequent dispersion of the tailings in the sea without any control and associated pollutions [61,62];

(5) Dispersion of the tailings to greater distances than predicted by models and increase of turbidity and plume shearing (e.g., Misima Mine, Papua New Guinea);

(6) Re-deposition of the tailings in more shallow levels, due to upwelling and unforeseen currents (e.g., Island Copper Mine, Canada; Bahía Portman, Spain). This will increase the risk of sulphide oxidation in the euphotic zone;

(7) Toxicity of the flotation reagents. Little is known about the toxicity of the flotation reagents in the marine environment;

(8) A resource will be lost. Considering that the efficiency of the exploitation of an ore deposit ranges today between 80% and 90%, 10%–20% of the resource will end up as waste. With new metal recovery technology, old tailing impoundments can in some cases be exploited as mines. This has to be considered in the context that once the tailings are deposited into the deep-sea, this potential resource will be lost forever and future generations will not have the option to re-exploit the resource with improved techniques.

Summarizing these points, the conditions which enable a secure submarine disposal of sulphide tailings are: stable reducing condition; no upwelling or other currents which could remobilize the tailings; and the tailings must contain only sulphide minerals and insoluble silicate minerals, without associated contaminant trace elements.

In order to be able to predict the behavior of the tailings in the marine setting, the first step is to execute a thorough mineralogical and geochemical study of the future tailings that will be deposited in the marine environment. This must include qualitative characterization and quantification of all minerals present in the tailings (e.g., silicates, sulphide, oxides, sulphates-chlorides), and a study of the trace element concentrations associated with the different mineral groups, *i.e.*, sulphides, oxides, soluble minerals with the methodology described by Dold and Weibel [6]. Once this analysis provides the conclusion that the mineral assemblage is suitable for deposition in a reducing environment, then, but only then, is it worth starting an extensive oceanographic study to search for a suitable site in the marine environment. The reason to follow this order is that a mineralogical and geochemical study is more cost-effective and faster than an oceanographic study. Most of the environmental hazards experienced by STD would have been possible to predict and to prevent if good mineralogical and geochemical data were available at the time of decision-making.

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Conflicts of Interest

The author declares no conflict of interest.

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