ECOLE POLYTECHNIQUE FEDERALE DE LAUSANNE
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EPFL

Master project in Bioengineering

Microbe-mediated recovery of critical metals from electronic waste, using bio-mining processes

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1. Current Review

Panem et circenses

This old roman saying (literally *bread and games*) is interesting to understand how people coped with the quarantine. Without the usage of entertainment, teleworking and household appliance, civil dissatisfaction would certainly have risen. Indeed, during the lockdown many activities are possible only thanks to smartphones, computers, and televisions. The same comment goes for food, where without ovens and fridges, people would not last very long alone at home.

For the manufacturing of these useful products, there are not numerous possibilities: "*If you can't grow it, you have to mine it*" (Earle 2015b). Therefore, indirectly, mining is one of the most strategic industry worldwide and many countries are acknowledging its critical role (Liger 2016). Even though it is less profitable[1] than the food industry[2], without the exploitation of the variety of ores worldwide, there would be no more production of machines, manufactured goods, or technological advances. Among other examples and uses, steel (a product of iron) is used for transport and constructions, silicon for electronics and platinum for energy production and chemical processes, as a catalyst[3]. Therefore, even the economy of developed countries, based mostly on services, deeply relies on mining.

Once metals are extracted from the ores, three problems arise. The first is pollution (Chen et al. 2016): to extract the metals from the surrounding rock and to purify it, large amounts of chemicals and much energy are often used, producing wastes called Acid Mine Drainage (AMD) and tailings. For instance, the production of 1 ton of Alumina, precursor of Aluminium, generates 1 to 2 tons of bauxite tailings (Hind, Bhargava, and Grocott 1999). Annually it is more than 150 million tons of bauxite tailings that are produced, and 2.7 billion tons that are stored as they cannot be recycled nor disposed yet (K. Evans 2016; Qu and Lian 2013). The bauxite tailings, also known as red mud, are highly alkaline and contain many minerals dissolved, such as iron oxides and precious minerals, such as Rare Earth Elements (Boudreault et al. 2012; Qu and Lian 2013). They can leach out of the mine, the storage facility or the factory and pollute soils and rivers, causing deaths, health issues or degrading the environment and fertile lands. This happened at the Ajka Alumina plant in Hungary, where 10 people died and 150 were injured because of the sudden spill of 700 000 m^3 of red mud (Gelencsér et al. 2011). These consequences apply for all the minerals and not only for

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[1] The 40 biggest mining companies' revenue alone is worth 683 billion US$,
https://www.statista.com/statistics/208715/total-revenue-of-the-top-mining-companies/
[2] The whole food industry is worth almost 4 trillion US$,
https://www.statista.com/outlook/40000000/100/food/worldwide
[3] Usage of Platinum
http://www.mineralinfo.fr/sites/default/files/upload/documents/Fiches_criticite/fichecriticiteplatine180103.pdf

Aluminium: the breach of the tailings pond of the Mount Polley, a gold, silver and copper mine in Canada, led to the release of 25 million cubic meter of mud, containing heavy metals such as lead, in the surrounding areas (Byrne et al. 2018).

The second problem is that mining is non-renewable. Earth is a finite system: once a mine is depleted from its richest ores, only low grade and complex ores are available (Jia et al. 2019). In these poor ores, the metal can be exploited only after even more extensive chemical processing and larger energy expenditure to concentrate the ore until it reaches appropriate levels of metal (the example of Copper was studied by (Bleiwas 2012)). This increases the cost of the raw material and the pollution due to the extraction. Furthermore, by studying again the example of Copper, *in theory* there should be enough metal in Earth's crust: with an annual production of almost $20 * 10^9$ kg and a total reserve[4] of at least 10^{16} kg (Emsley 2001; Peterson and Depaolo 2007), this should satisfy the needs for several millions of year. *In practice* however, as for oil production[5], even if the mining of low grade ore is possible, it will be done only if an extraction technology exists and if the metal's price is high enough to pay back the costs of mining and processing, which is the limiting parameter instead of the absolute reserves contained on Earth.

The third problem is the heterogenous distribution of commercially viable mines around the world, causing a geostrategic issue. The concentration of production in the hands of a few countries has raised concerns in the western world, as they lack some minerals and therefore need to import them. France has created the national Comité pour les métaux stratégiques (COMES, (Liger 2016)) and the French Senate[6] has already talked about the supply of Rare Earth Elements (REE), a group of metals used in very small quantities in the industry yet essential, as it will be explained in next sections. The CIA[7], and the European Commission (through the Critical Raw Materials Initiative)[8] listed respectively 35 and 27 minerals as critical, REE being part of them. Furthermore, even without open conflict with the mining countries, a simple problem with the supply chain is enough to interrupt all the exchanges. This is visible this year with the pandemic: the transport routes can be cut, the miners may not be able to work, or brokers cannot agree on the prices of the good, because they cannot meet. Hence, freezing the whole system.

One way to circumvent this geostrategic problem is through the 3R's (Reduce, Reuse and Recycle) as stated by the Waste Framework Directive (WFD) (*Directive 2008/98/EC of the*

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[4] 50 parts per million in Earth's crust https://environmentalchemistry.com/yogi/periodic/Cu.html
[5] https://www.forbes.com/sites/dominicdudley/2018/04/04/why-bahrains-huge-oil-discovery-might-not-provide-the-windfall-it-is-hoping-for/
[6] Minutes of Meeting of the French Senate https://www.senat.fr/rap/r10-782/r10-782.html
[7] List by the CIA of critical elements https://www.cia.gov/library/publications/the-world-factbook/appendix/appendix-h.html
[8] List by the European Commission of Critical Raw Material https://ec.europa.eu/growth/sectors/raw-materials/specific-interest/critical_fr

European Parliament and of the Council of 19 November 2008 on Waste and Repealing Certain Directives (Text with EEA Relevance) 2008) of the European Union:

1) Reduce the amount of metals needed for a product (such as a machine or an electronic device)
2) Reuse or repair a product as much as possible
3) Recycle what cannot be reused anymore (instead of throwing it in landfills).

This directive also establishes a framework on the environmental issue, which is its primary purpose: the management of the wastes and the minimization of their effect on health and the environment (Article 6 of the 2008/98/EC Directive). Indeed, by reducing the initial quantities needed to manufacture a product and by repairing it, the resulting amount of waste produced and possibly filling the landfills will be lower.

Because of the increasing amounts produced, the management of wastes becomes more and more problematic. The electronic wastes (e-wastes) in particular are critical. Their amount was already of 41.8 million metric tons worldwide in 2015 and expected to be 65.4 million metric tons in 2017 (Collins 2013; Priya and Hait 2017). The European Union, the USA and China, the three biggest e-waste generators, have produced respectively 9.5, 7 and 6 million metric tons in 2015. Totalizing 22.5 million tons, which is more than half of the world's 41.8 million metric tons e-waste production that year. Grossman, as cited by (Sjödin 2006), showed that only 10% of the e-wastes in USA were recycled, the rest being incinerated or sent to landfills. Many of these wastes are exported to developing countries (Li and Achal 2020). There, recyclers try to scrap valuable or easy to extract metals such as gold and copper out of these e-wastes. However, the lack of knowledge and safety prevents a clean rehabilitation (Hicks, Dietmar, and Eugster 2005). The result is pollution, as the e-wastes contain a variety of toxic materials, such as heavy metals or PolyBrominated Diphenyl Ether (PBDE) (Sjödin 2006) that can poison recycling workers, or leach out of the pile of wastes and contaminate lands, making them improper for drinkable water and food production (Li and Achal 2020). Leading to the same health and environmental issues as ore tailings.

However, it has been shown that these e-wastes contain useful material, such as gold, silver, copper or REE (Huang, Guo, and Xu 2009; Işıldar et al. 2016; Zhang and Xu 2016). This is no surprise, as these are all the elements needed for an electronic device. Furthermore, as metals are not degradable with respect to time, they could potentially be recycled with a very high yield (Norgate, Jahanshahi, and Rankin 2007). In addition, every country produces e-wastes, making this material readily available locally.

Therefore, taking all these parameters together, finding a way to reuse the metals from wastes could help decrease primary and secondary pollutions (coming from the mines and the landfills respectively) while also securing a steady supply of metals and preventing a shortage in western countries. Knowing that the landfills have more valuable metal concentration in comparison with "natural" mines makes this procedure even more appealing and inspired the concept of "urban mining" (Kuroda and Ueda 2011). A concept in which

secondary metal resources could be extracted directly within cities (Krook and Baas 2013). For instance, natural copper ore must have a concentration of 1% to be economically viable (Earle 2019).

Several approaches to recycling have already been tested, like pyrometallurgy and hydrometallurgy, which are already used in mining. The pyrometallurgical technique uses heat to extract metals, whereas in the hydrometallurgical technique, metals are leached out of their matrices using lixiviants (Priya and Hait 2017). Even though these techniques are fast and have a good efficiency, they are not very satisfying. Because of the heterogeneity of the raw material, much energy is consumed and/or toxic lixiviants are used to separate the components. This emits toxic products that must be captured, creating additional cost, and making these expensive processes even more costly. If these products were not captured, they would contaminate surrounding areas (Priya and Hait 2017).

In this context, another method is being more and more investigated and carry much promises: biohydrometallurgy. It was for instance studied by the BioMinE initiative of the European Commission (Morin et al. 2006). This technique uses microorganisms growing in mine wastes to leach metals out of their gangues (their matrix) (Priya and Hait 2017), the same way as hydrometallurgy do with lixiviants. It is already used in some mines either with very poor ores or with mine wastes, to extract as much metals as possible. Most notable examples are copper mines, such as the Escondida mine, in Chile, and the Jinchuan mine, in China (H. R. Watling 2006). Despite its slowness, biohydrometallurgy is energy efficient, low cost, low maintenance, and the resulting pollution very small (Jia et al. 2019; Helen R. Watling 2015).

The goal of the present review is to present a detailed analysis of the present status of biohydrometallurgy, and especially in relationship with the recycling of electronic wastes and on the recovery of Rare Earth Elements (REE). REE are a class of metals used in very few quantities, but nevertheless essential for high tech products (Qu and Lian 2013). Their recycling is becoming a topic of research more and more investigated: more than 14 000 articles were written the last 20 years and almost 5 500 the last 5 years[9].

This review will illustrate an overview of the technologies currently used for mining and recycling, which are pyrometallurgy, hydrometallurgy, electrometallurgy and biohydrometallurgy. Their costs and their impact will be assessed. Finally, a detailed presentation of the critical parameters involved in biohydrometallurgy will be made, to know how to set up a bioreactor and have an optimal rate of recovery of REE. The parameters assessed will be: the type of bioreactor, the organisms and the mechanisms being involved, the temperature, the pressure, the stirring mechanisms, the duration, the depth, the pH, the concentration of metals, the type of material, the size of the powder, the number of cells and the single strain vs consortium aspect.

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[9] https://www.sciencedirect.com/search?qs=recycling%20of%20rare%20earth%20element

Finally, recycling could help achieve the goals of sustainable development, as defined by Dallas et al: work to preserve our environment, lift people from poverty, and reduce economic and social inequalities, all while looking to ensure inter-generational equality (Dallas et al. 2020; Rosa 2017).

Objectives of the current review

1) Overview of current processes used in mining and recycling (that are pyrometallurgy, hydrometallurgy and electrometallurgy) as well as their impacts (from an energy consumption and pollution production point of view)
2) Review of the critical parameters for the setup of a bioreactor for REE retrieval

Objectives of further research

1) Isolation of efficient metal-oxidizing bacterial consortia
2) Building of a low-cost and scalable biotrickling fermenter for e-waste leaching
3) Running of this fermenter in continuous mode

Sources

Most of the relevant data used for this project come from the scientific literature, which should have been peer reviewed or from governmental or supranational sources, like the USGS (United State Geological Survey), BRGM (Bureau de Recherches Géologiques et Minières), CIA, the United nations (and its subsidiaries, like UNEP or IPCC). Their data should be reliable as they are official and verified.

1.1. Economic and strategic value

Mining is the science of extracting valuable mineral substances from the Earth's crust (Hartman and Mutmansky 2002b). On a purely economic point of view, mining is a flourishing business as its 40 biggest mining companies' revenue were worth 683 billion US$[10] in 2019. Its five biggest companies' valorisation combined was worth 343.7 billion US$ (more precisely, in billion US$, BHP Billiton is valorised to $138.3 Bn[11], Rio Tinto to $100 Bn[12], Vale to $68.3 Bn[13], Glencore-Xstrata to $60.5 Bn[14] and China Shenhua to $57.3 Bn[15]).

Certainly, it is pale compared to other sectors, such as oil companies or technology companies. Aramco, the Saudi Arabian state owned oil company, had alone a revenue of $355 Bn[16] and hit a valorisation of 2 trillion US$[17], while Apple had revenues of $261.7 Bn[18] and hit

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[10] https://www.statista.com/statistics/208715/total-revenue-of-the-top-mining-companies/
[11] Market Cap https://www.forbes.com/companies/bhp-billiton/
[12] Market Cap https://www.forbes.com/companies/rio-tinto/
[13] Market Cap https://www.forbes.com/companies/vale/
[14] Market Cap https://www.forbes.com/companies/glencore-international/
[15] Market Cap https://www.forbes.com/companies/china-shenhua-energy/
[16] Revenue https://fortune.com/global500/saudi-aramco/
[17] https://www.cnbc.com/2019/12/12/saudi-aramco-hits-2-trillion-market-cap-on-second-day-of-trading.html
[18] Revenue https://www.forbes.com/companies/apple/

a valorisation of 1 trillion US$[19]. The same comment can be made at the level of Canada, a country that is rich in geological resources: the mining sector was worth $37 billion in 2013 and $44 billion in 2017, whereas the petroleum sector was worth more than $100 billion per year (Earle 2015a; 2019).

However, mining of metals is key to provide the raw materials for the oil and tech sectors and for all industrial sectors in general. Whether it be the electronic, construction, transport, weapon, energy production or jewellery industry (Hartman and Mutmansky 2002b; Earle 2015b). This is summarized by the saying "*If you can't grow it, you have to mine it*" (Earle 2015b). This versatility of the usage of metals comes from the variety of their physical properties: conductivity in the case of copper, lightness for aluminium, strongness for steel (made from iron)[20], or rarity for gold.

This variety come from the diversity of metals and they are not evenly distributed throughout the world as it is visible in Fig. 1. Some countries have some specific metals while lacking others, contributing to a competition over resources among countries. Indeed, on the contrary of agricultural lands, mining relies solely on the geological resources of a country, which are not spread evenly[21]. To better grasp the consequences of an unequitable distribution of the mines, one can think of water distribution (Earle 2015b). Some countries have plenty of access to pure water, whether others have access to improper water and finally some have difficulties to find it, causing tension in the population. One way to measure the distribution of a resource is through the normalized Herfindahl-Hirschman Index (HHI). The HHI can measure the concentration of the market for a specific resource. As used by the Bureau de Recherches Géologiques et Minières (BRGM), a resource with an HHI close to 0 means that it is spread evenly among many countries and there are no geopolitical issues with its supply. One can think of Oxygen: no matter in which country one stands, the supply of oxygen to breath is guaranteed. On the contrary, an HHI close to 1 show that it is produced by very few countries in situation of monopoly. One good example is the production of niobium, which is produced to more than 90% by Brazil[22].

A threshold of 0.4 has been chosen by the BRGM to show a threat on the supply chain of the metal (Christmann and Labbé 2015).

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[19] https://www.theguardian.com/technology/2018/aug/02/apple-becomes-worlds-first-trillion-dollar-company
[20] https://www.glencore.com/what-we-do/metals-and-minerals
[21] http://www.world-aluminium.org/statistics/massflow/
[22] https://www.visualcapitalist.com/measuring-competition-valuable-minerals/ (LePan 2018)
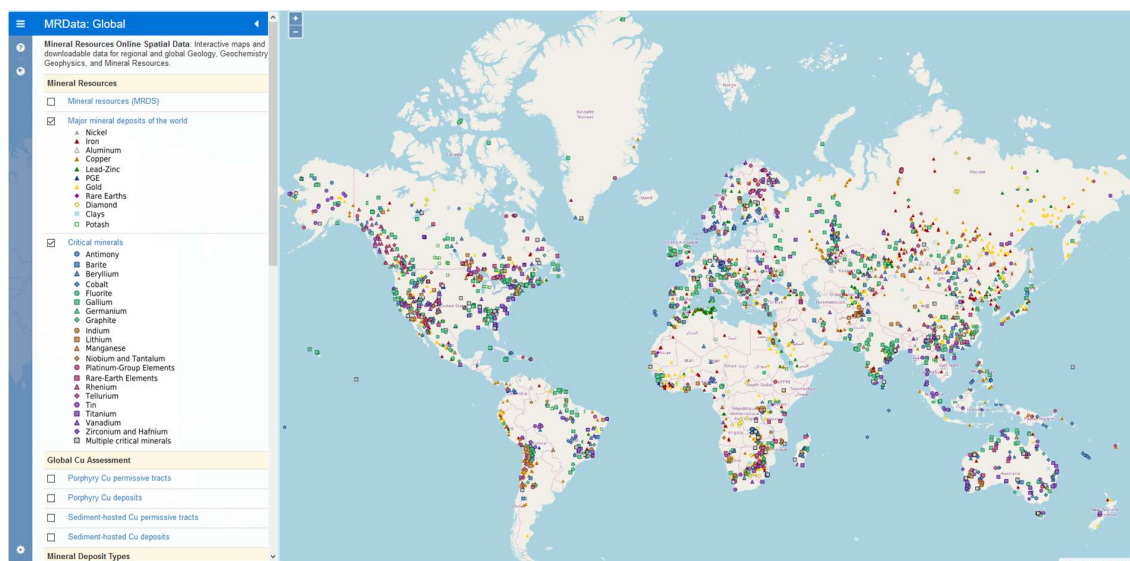
Figure 1: Distribution of different mineral resources around the world (USGS[23]). It should be noted that some mineral resources (like Rare Earth Elements and Antimony among others) are available in some countries, while not in others, creating possible inequalities.

1.1.1 Mines and metal deposits

Metals cannot be grown and must be mined. Metal deposits are areas in which one or more metals are concentrated (Earle 2015a). Areas with high enough concentration of metals to make profit are named ores and its worthless surrounding areas are named gangue (Hustrulid, Kuchta, and Martin 2013; Hartman and Mutmansky 2002b). All rocks at the surface of Earth have a basal concentration of metals, but only a few rocks have a concentration high enough to make them profitable to retrieve metals, as visible on Table 1. Iron is one of the few metals evenly distributed around the world. Furthermore, as it can be easily worked on[24], its use was early and constant throughout human history.

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[23] https://mrdata.usgs.gov/general/map-global.html

[24]

https://chem.libretexts.org/Bookshelves/General_Chemistry/Map%3A_General_Chemistry_(Petrucci_et_al.)/23%3A_The_Transition_Elements/23.3%3A_Metallurgy_of_Iron_and_Steel

Metal	Typical background level [ppm]	Typical economic grade [ppm]	Concentration factor (Ratio between economic grade and background level)
Copper	40	10 000 (1 %)	250
Gold	0.003	6 (0.006 %)	2 000
Lead	10	50 000 (5 %)	5 000
Molybdenum	1	1 000 (0.1 %)	1 000
Nickel	25	20 000 (2 %)	800
Silver	0.1	1 000 (0.1 %)	10 000
Uranium	2	10 000 (1 %)	5 000
Zinc	50	50 000 (5 %)	1 000

Table 1: Average concentration of some metals in typical rocks (background level), rocks of mines (economic grade) and the concentration factor differentiating these two categories. ppm stands for parts per million, meaning 1 milligram of metal per kilogram soil [mg/kg]. Data retrieved thanks to (Earle 2019)

An example to illustrate concentration of metals is the image of the body of an animal. All the parts of the body are supplied with blood, but in some places like arteries and *veins*, blood is much more concentrated. This is the reason why areas where gold is concentrated are called "gold veins". By extension, the same goes for any native metals which are named veins of the metal. One can almost follow the thread of a vein and extract the metal, by separating it from its surroundings (Figure 2 and 3).
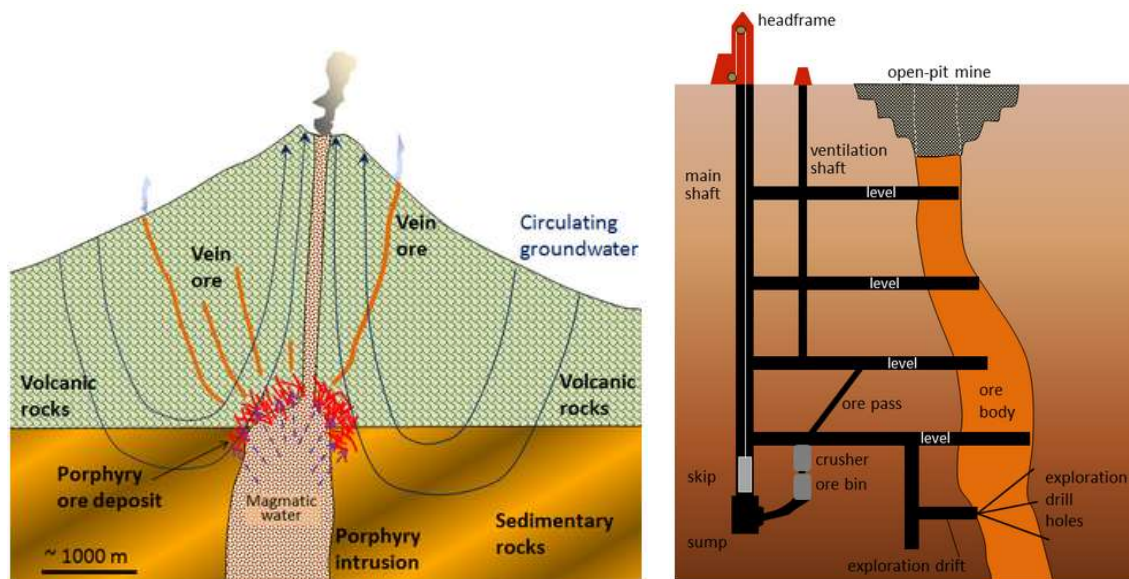
Figure 2 and 3: Left picture shows an example of veins in the case of gold, due to volcanic activities. Right picture shows the exploitation of a vein (ore body) by a mining site. Surface level metal can be exploited easily, but to recover the entirety of the seam, underground mining is needed. Illustration from (Earle 2019)

Table 1 shows background levels of some metals. For instance, the mean basal level of gold in any rock in Earth's crust is about 0.003 ppm (part per million). Meaning that in average, out of 1 kg of soil there will be 0.003 mg of Gold. In an economically viable gold deposit, the

concentration must exceed 6 ppm, so 2 000 times more than in typical rocks, to make a gold mine economically viable. However, this represents roughly 6 [mg/kg] or only 6 grams of Gold per ton of rock. So even by following a vein, the yield is very low. As a complement, with 2002's economics, only 1% of the Earth's surface has a commercial value (Hartman and Mutmansky 2002b). The rest of soils containing too few valuable materials (quartz and clays for instance, made of different types of oxides).

The economic viability of a mine depends of many factors, not only of its ore concentration. Most important factors are the size of the metal deposit, the model of the mine (open pit or underground mining), its environmental impacts (and therefore the corresponding costs of rehabilitations) and its workers' salaries (Earle 2015a). Open-pit mines are generally cheaper than underground mining, as the infrastructures are easier to maintain (Calcutt 2001). As an illustration, if these costs are high in a copper mine, the concentration of the copper ores will need to be greater than 10'000 ppm (as stated in Table 1), to allow the mine to make profits. On the contrary, with a silver mine with large open pit and few regards for safety and environmental issues, these costs will be low. Therefore, its ore concentration could be less than 1'000 ppm and still be viable.

Often, ores contain more than one metal to process. For instance, Rare Earth Elements (REE) are always co-products of other metals and never mined alone, due to their scarcity. More metals to extract could theoretically multiply the profit, as the amount of retrievable metal per quantity of ore is higher. However, they may also be discarded in the wastes if the extraction is too costly. This happen with red mud, the byproduct of alumina production (the precursor for aluminum). It is considered to contain a wide and complex variety of valuable metal, but the costs to extract them is too high (Qu and Lian 2013).

An external parameter that can affect the viability of a mine is the demand and price for the metal (Brierley 2010). For instance, in a period of economic development, iron's demand and price will go up, as it is needed for construction (in the form of steel). Thanks to the rise of the demand and the corresponding rise of the price, some expensive iron mines could become profitable. As the costs of mining would be lower than the profits made by mining. On the contrary, in time of crisis, less investment would be made on constructions. This translates in less demand for iron and its price would decrease. In this context, the prior mines would not have been used in first place[25]. This leads to high uncertainty and risk for mining companies, as external factors cannot be predicted. To prevent bankruptcy of mines and keep a geostrategic advantage, some Chinese mines are protected by the government, even though they may not be profitable[26].

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[25] http://www.mineralinfo.fr/ecomine/matieres-premieres-minerales-contexte-actuel-prospective-moyen-terme
[26] http://www.mineralinfo.fr/ecomine/matieres-premieres-minerales-contexte-actuel-prospective-moyen-terme

In this context, the main drawbacks for the construction of a mine and a steady supply of raw material are the profitability and the assessment of the resulting pollution. In 2004, a project for a mine of nickel could be started only if the mine was able to produce 40 kiloton of Nickel per year for 20 years (Dalvi, Bacon, and Osborne 2004). Furthermore, in the case of Nickel, the concentration in the ore had to exceed 1.3% in 2004. With the price of Nickel at that time, these were the constraints for making profit. Even if the mine was approved and the funds unlocked, ten to fifteen years are needed to build the mine. So, in case there is a shortage of Nickel, there would be a lag between the demand and the supply. The demand would not be handled immediately, and the price would increase. To add to the complexity of this situation, once investments are made and a Nickel mine is working after 10 years of construction, it can happen that the price of Nickel drops. In consequence, this would make this mine not profitable anymore. The causes may be another mine opened (increase of supply) or the buyers now use less Nickel or substituted it with another metal for their products (decrease of demand). In both cases, increasing the supply or decreasing the demand will lead to a decrease of the price of Nickel and hence the loss of profitability. The second drawback is the pollution: extracting and purifying a metal is extremely polluting, as it will be detailed in the corresponding section.

1.1.2 Examples of mines and their economic and social importance

Note: despite thorough attention, mistakes with metric tons (the standard definition of the ton, as opposed to the short ton) and mega tons (one million metric tons) may occur in the text, as the various abbreviation (mt or mT or Mt or MT) are not always explained precisely in the literature.

One of the largest mines still in use today is the Bingham Canyon Mine, Utah, USA. It is an open pit mine founded in 1903 and employs more than 2 000 people[27]. Through extensive extraction of copper, it became a 1.2 km deep and 4 km wide open pit visible from space[28]. This mine alone was responsible for in 2007 of 63% of the total value of metals in the state of Utah and produced 211 000 tons of copper that year (Bon and Krahulec 2008). Other examples of industrial metal mines are the Escondida copper open pit mine in Chile[29], the underground El Teniente mine and the Kiirunavaara underground mine in Sweden[30]. As per REE, the most important producer is the Bayan Obo mine in Inner Mongolia, China, with a production of 55 kiloton in 2005. It is the largest deposit of REE with an estimated reserve of 48 million of tons of REE oxides (Bru et al. 2015; Drew, Qingrun, and Weijun 1990). Some metals can also be produced as a by-product, as aluminium which can be recovered as a coal mining waste (L. Cui et al. 2015). In addition, apart from these large-scale mines, there are also numerous small mines throughout the world. According to (Hentschel, Hruschka, and

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[27] https://www.riotinto.com/operations/us/kennecott
[28] http://www.mining.com/rio-tintos-kennecott-wins-clean-air-lawsuit-in-the-us/
[29] https://www.mining-technology.com/projects/escondida/
[30] https://www.mindat.org/loc-10589.html

Priester 2002), artisanal and small-scale mining employs worldwide 13 million directly and more than 80 to 100 million are depending of these revenues, mostly in low income countries.

In the USA alone, mining is a business worth $35 billion per year thanks to its export and a sector that employs more than 355 000 people in 2002. To grasp the consumption of metals and the need for modern societies, it was also calculated that more metals were extracted during the twentieth century alone than since the birth of humanity. In addition, to keep modern comfort, 21 tons of minerals are needed per person (Hartman and Mutmansky 2002b).

To understand the criticality of mineral industry, Hartman and Mutmanskly (Hartman and Mutmansky 2002b) summarized its evolution and its impact on society:

1. Period of mine development
2. Period of smelter development
3. Period of industrial development: Increased standard of living
4. Period of rapid depletion of inexpensive raw materials at home: increasing costs of mining and more and more energy required to extract the same amount of raw materials
5. Period of decreasing internal and external markets: decreasing standard of living, political and social problems

In other terms, the mineral industry of a country goes through these five steps. Mines are discovered and smelters are developed to work first on rich ores (ores that have a large fraction of metals). As mine exploration and smelters improve, the costs of metals decrease and a period of industrial development begins, increasing the standard of life. However, rapidly, mines are becoming exhausted and ores are poorer and poorer. Importation of metals are needed, and its costs are increasing. Increasing by the same time manufactured goods and lowering the quality of life, leading to social and political issues (Hartman and Mutmansky 2002b). These are reasons for the strategic value of some metals. Once depleted, the society of a country could be fragilized and even begin to collapse.

1.1.3 Strategical and critical metals

Metals demanded for the development and the technologies of our societies will be exhausted (Helen R. Watling 2015), or more precisely their mining cost will be so high that they will not be affordable for consumer market, such as smartphones and TVs (or at a far higher price). Not only are they critical for all countries, but these metals are also an important parameter for geostrategic reasons as visible in Fig. 4. China, South Africa, USA, and Brazil having a monopolistic role on the production and supply of critical metals for the EU (Gislev and Grohol 2018), posing a threat to the EU's independence.
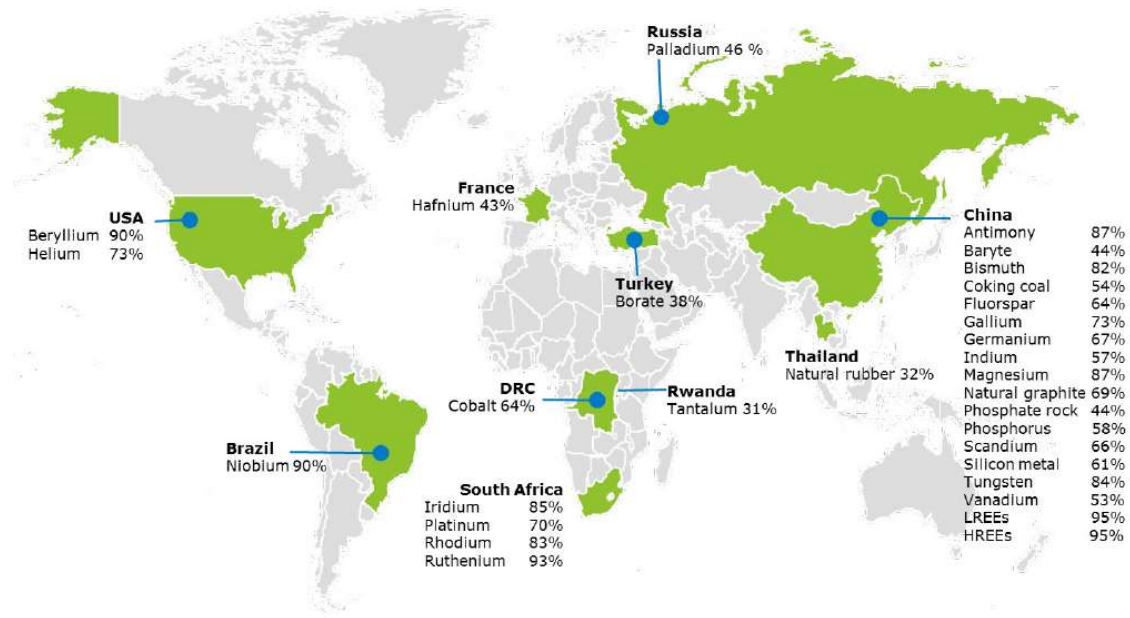
Figure 4: Countries' share for the supply of critical metals. Illustration from (Gislev and Grohol 2018)

Due to this essential role in our societies and the threat of a collapse of the society, the BRGM has made a list of the metals it considered critical to the French economy[31]. These elements' name, usage and annual production are summarized in orange in Table 2, along with metals among the most mined in the world. Some of the most critical metals now are platinoids and the Rare Earth Elements (REE) group.

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[31] http://www.mineralinfo.fr/page/fiches-criticite

Metal	Annual Consumption or production [kt]	Main Usage	Metal	Annual Consumption or production [kt]	Main Usage
Major deposits					
Nickel (Ni)	1 890	Stainless steel	Lead		
Iron*	2 500 000	Stainless steel	Zinc		
Aluminium*	100 770		Silicon	2 900	Steel, Silicone
Copper	23 430	Electronics + Buildings	Gold*	4.1	Jewelry, Investments
Critical Minerals					
Antimony (Sb)	206.6	Flame Retardant	Manganese		
Barite			Mercury		
Beryllium (Be)	0.31	Alloys	Molybdenum (Mo)	330	Steel
Cadmium (Cd)		Ni-Cd Batteries	Niobium (Nb)	55	Steel
Chromium (Cr)	8 400	Stainless steel	Rhenium (Re)	0.057	Super-alloy
Cobalt	92	Batteries	Selenium		
Fluorite			Silver	31.968	Electronical objects, jewels and ingots
Gallium (Ga)	0.25 - 0.3	semiconductor	Tantalum	2	Condensators
Germanium (Ge)	0.11 - 0.12	Optics	Tellurium (Te)	0.45 - 0.55	Solar panels
Graphite	1 000	Steel	Tin	394	Soldering
Hafnium (Hf)	0.07	Aeronavals	Titanium (Ti)	200	Industry (Energy, chemistry,…)
Indium (In)	1.44	Screens	Tungsten (W)	100	
Lithium (Li)	33	Batteries, ceramics	Vanadium (V)	89	Steel
Magnesium			Zirconium (Zr)	"1 300" (Zircon)	Ceramics
Platinum Group					
Ruthenium			Osmium		
Rhodium (Rh)	0.033	Catalyzor, LCD	Iridium		
Palladium (Pd)	0.292	Catalyzor	Platinum (Pt)	0.255	Catalyzor, Jewels
Rare Earth Elements					
Scandium (Sc)	0.015	Batteries	Gadolinium	1.02	Permanent Magnets, Alloys
Yttrium	7.65	Luminophore, ceramics	Terbium	0.29	Perm. Magnets, Luminophore
Lanthanum	31.5	Catalyzor, batt	Dysprosium (Dy)	0.854	Perm. Magnets
Cerium	45.5	"Polissage"	Erbium	0.54	Glass colorants, Luminophore
Praseodymium	4.9	Perm. magnets	Holmium		
Neodymium (Nd)	19.9	Permanent magnet	Thulium	0.075	
Promethium	-	-	Ytterbium		
Samarium	0.515	Perm. magnets	Lutetium		Tomography
Europium	0.425	Luminophore			

Table 2: major deposits worldwide and critical metals, as considered by the European Commission (EC). Among critical metals, are the Platinum Group and the Rare Earth Elements. In orange, as considered by both the EC and the BRGM (Gislev and Grohol 2018; Bru et al. 2015). Some cells are left blank: because for some metals considered critical, values of production or consumption were not found from reliable sources.

Even though they are critical, with the amount of REE at stake (170 kiloton (USGS 2019) or between 110 and 143 kiloton in 2014 (Bru et al. 2015)), one should not forget that other metals are also currently regarded as strategic. It can be because of their current use but also because of future utilization. For instance, renewable energy will need large supplies of copper, cobalt, lithium, and nickel[32]. So, without these metals, there could be no transition for cleaner energy production. It can also be because of the amount that are mined. Annual production of Aluminium is 41 million tons and Copper 23 million ton[33]. These amounts should be compared with the production of 33 tons of Rhodium, as it is summarized in Table 2. Among the REE, only the Dysprosium, the Neodymium and Scandium are currently considered critic, considering their current use[34].

In addition for the future and the green transition, the UNEP has shown that compared to the current energy mix (largely relying on fossil fuels), the renewable energies need more mineral resources than with fossil fuels (Hertwich, de Lardel, and Suh 2016). Meaning future "green" energy mix will consume more metals than fossil fuels. This is the trade off, as fossil fuels are the most "concentrated" source of energy, whereas solar panels and windmills need an initial energy and raw material investment.

Regarding current production, copper and zinc are already in supply deficit (UNEP as cited in (Helen R. Watling 2015)), meaning their use already consume reserves, instead of being renewed by *de novo* mining.

Price of platinoids are ever increasing because of numerous industrial applications. For instance, electric cars use 10x more Pd than gasoline powered cars (C.-J. Yang 2009). A visible commercial consequence was the stock piling purchase of Ford in 2001. The company feared its supply would be lowered (hence handicapping its growing electrical car market) and lost 1 billion $ once the "bubble" was burst[35]. On the other hand, these prices can force innovation and the finding of substitutes, but sometimes at the expense of a loss of effectiveness. As with the examples of permanent magnets: the replacement of the neodymium-iron-boron by another alloy would be made at the expense of the miniaturization (Bru et al. 2015).

Stockpile were once made by nations, but not anymore, as it is thought that metals can be readily bought through the open market. But this theory has its limitations. As it was visible with the global pandemic, some routes can be cut and common items (masks, manufactured products, food, raw materials, etc.) may not be available easily anymore. This could shift the mentality from an open and globalized market to a, still globalized market, but with some

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[32] Annual Report of Glencore 2019 https://www.glencore.com/dam:jcr/79fd3300-ee50-4ee1-870d-6372274c71b5/glen-2019-annual-report-interactive.pdf
[33] http://www.mineralinfo.fr/sites/default/files/upload/documents/Fiches_criticite/fichecriticitecu180205.pdf
[34] http://www.mineralinfo.fr/page/fiches-criticite
[35] http://news.bbc.co.uk/2/hi/business/1763406.stm

aspects being more local, where each country could have some basic production of needs, at some extent[36].

1.2.   Rare Earth Elements

Among the metals, the Rare Earth Elements (REE) are a group of fifteen to seventeen elements, that is composed of the Scandium, the Yttrium and the fifteen Lanthanides (Connelly et al. 2005), as visible in Figure 5. Although there is no convention, most authors classify them as:

- Light Rare Earth Elements (LRRE): Lanthanum (La), Cerium (Ce), Praseodymium (Pr), Neodymium (Nd)
- Intermediate Rare Earth Elements (IREE): Samarium (Sm), Europium (Eu) and Gadolinium (Gd)
- Heavy Rare Earth Elements (HREE): Terbium (Tb), Dysprosium (Dy), Holmium (Hm), Erbium (Er), Thulium (Tm), Ytterbium (Yb), Lutetium (Lu) and Yttrium (Y).

Note: Yttrium, even though it is quite light, is often found within the same ores as HRRE (hence its attachment to this group). Scandium (Sc) and Promethium (Pm) are being separate from this classification. Sc is not mined in the same areas as the rest of REE and Pm's production is neglectable. It is a radioactive element and there are only 0.54 kg of this element on the whole Earth at a given time (Bru et al. 2015).

Figure 5: Rare Earth Elements (REE) are highlighted in black. Wikimedia commons

The etymology of "Earth" comes from the French word "Terre" that was defined for materials that could not be reduced to metals (at the time). "Rare" is because the fraction of these "Earth Elements" was scarce among studied ores, compared to other "Earth Elements", such

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[36] https://www.rts.ch/play/tv/19h30/video/19h30?id=11304373 interview of Edgar Morin and Noam Chomsky during the Swiss News Broadcasting

as lime or magnesium oxide, hence the name of "Rare Earth Elements" was adopted (Bru et al. 2015).

REE were first used as igniters (flints) for lighters but had no true industrial usage until the 1970s, with the usage of Europium for cathodic TVs (Bru et al. 2015). In present days, they are mostly used as permanent magnets, polishing powders, catalysts and batteries (Bru et al. 2015) and in high tech equipment, such as solar panels, lasers, wind turbines' and hard disks' permanent magnet or smartphones (Jorjani et al. 2008). The specificity of their use makes REE not substitutable, or at the cost of a decrease in performance[37]. There are no REE-specific mines, as they are too dispersed around the globe (Haxel, Hedrick, and Orris 2002). They are always mined as byproducts of another metal[38] such as Lead, Iron or Zinc (Jowkar et al. 2018).

REE's production before 1965 was of 10 kilotons/year and peaked between 142 and 159 kilotons in 2010 (Bru et al. 2015). Therefore, compared to other metals, REE are considered as vitamins. The amount of REE needed by the industry are very low, yet they are essential to ensure the proper functioning of high-tech devices (Balaram 2019).

The dispersion of the resources in REE has led China to be the top producer by far of REE since the 1990s. This forced the USA to import 90% of their REE consumption from China in 1999 and 2000, after being one of the top producer (Haxel, Hedrick, and Orris 2002). In 2019, China produced 120 kiloton of the 170 kiloton produced REE worldwide (USGS 2019). Without considering the quantity of REE just discarded as waste in other mines (from aluminium, copper, iron, nickel, etc.) because they lack the factories or the technology to retrieve REE. The quantity of REE in these wastes could be significant (Qu and Lian 2013). Another issue preventing exploitation of some REE containing ores is the release of Thorium and Radon, radioactive elements that can harm workers' health (Bru et al. 2015).

This concentration of the market in the hand of a few countries is illustrated by the normalized Herfindahl-Hirschman Index (HHI), the higher it is, the more concentrated the market is. To be more precise, there are two HHI, one for the mining production and one for the refining production, describing the two aspects of the concentration of the means. The first is the ownership of mines (and therefore the actual raw material coming from the extraction from the Earth's crust). The second is the ownership of the means of production, which is the purification of the raw material (from the ores) into usable and useful metal[39].

These two aspects, the key role in modern societies and the scarcity of their production made the REE to be considered as strategical resources[40] [41]. Especially since China decided between

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[37] List of the Rare Earth Elements, see each element to know the consequences of a substitution
http://www.mineralinfo.fr/page/fiches-criticite
[38] List of the Rare Earth Elements http://www.mineralinfo.fr/page/fiches-criticite
[39] http://www.mineralinfo.fr/actualites/terres-rares-criticite-leconomie-francaise
[40] Minutes of Meeting of the French Senate https://www.senat.fr/rap/r10-782/r10-782.html
[41] List by the CIA of critical elements https://www.cia.gov/library/publications/the-world-factbook/appendix/appendix-h.html

2007 and 2011 to limit its export of REE, increasing the price of Terbium by nine suddenly[42]. Bowing *de facto* other countries and companies under China's will and letting China control the price and making some mine projects viable or not at will. This decision was since lift off, but many countries decided to search for alternative supply routes in order to reduce their dependence to China. This is done thanks to construction of new mines or recycling. It also explains why the data surrounding the consumption, the production, and the reserves of REE are scarce and not shared freely by the states. This method prevents the consuming countries to be at the mercy of producing countries, and vice versa. For instance, the USGS' numbers (USGS 2020) are denied by China, which says that its reserves are lower than what was stated by the USGS. In this example, the opacity allows the producer countries to keep a leverage on the consumer countries and to make a pressure on the prices of the goods. To add to the complexity of calculating the amounts of production and reserves at stake, most of REE are not traded via the public London Metal Exchange stock market (on the contrary of most of non-ferrous market) but comes as a result of arrangement between a producer and a buyer[43]. This leads also to a final issue: the importance of black market. By definition, the contribution of the black market to the amounts of REE traded is difficult to assess but has been estimated between 15 and 40% of the whole Chinese production (Bru et al. 2015).

China's monopoly could allow it to control willingly the price of REE and to make new mines successful or not. The method would be through price leveraging: when the prices are high, new mines can be financed. By lowering the price of REE once the project of a mine has begun, the mining company cannot afford to mine anymore and has to go bankrupt, preventing further exploitation. Such events happened at the Mountain Pass min, California. Its viability was threatened by the decrease of the price of REE before its shutdown (Haxel, Hedrick, and Orris 2002). In another case, the fragility of a mine allowed China to take shares at a minimum price (Bru et al. 2015). In both case, China could also ensure that valuable skills and workers cannot develop elsewhere and threaten its monopoly.

1.2.1 Mines and minerals containing REE

The current producers of REE are: China by far (through the mines of Bayan Obo, Ganzhou, Weishan, Maoniuping, Dalucao, Longnan, Xunwu), followed by Australia (Mount Weld), USA (Mountain Pass), Russia, India, Brazil, and South Africa (Fig. 6).

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[42] https://www.lesechos.fr/2012/12/la-bulle-des-terres-rares-nen-finit-plus-de-se-degonfler-384671
[43] 5.1 Etablissement des prix http://www.mineralinfo.fr/page/fiches-criticite
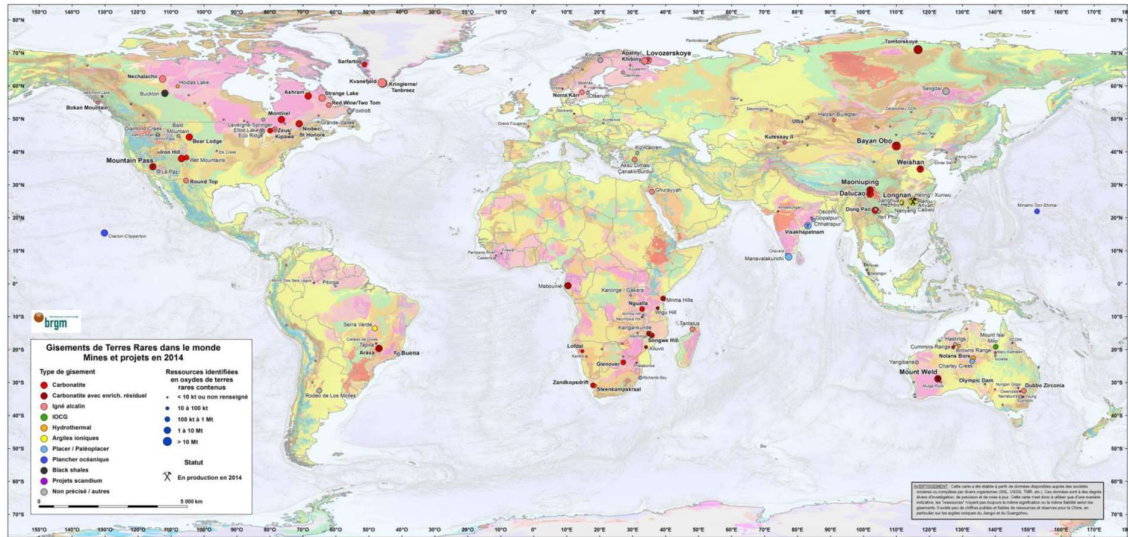
Figure 6: Main REE mines. Most are located in China, North America and South Africa. Illustration from (Bru et al. 2015)

Close to 250 minerals contain REE, but only twenty minerals contain them in valuable fractions, such as Monazite, bastnaesite and xenotime that are considered to have a sufficient amount of extractable REE (Corbett et al. 2017; Bru et al. 2015).

1.2.2 Main usage of REE and consumption

The main usage of REE are (Bru et al. 2015):

- Permanent Magnets: accounting from 20 to 23% of the tonnage of all the REE and almost 53% of the total value of REE. The most used REE are Samarium, for the Samarium-Cobalt (Sm-Co) magnets, and Neodymium, for Neodymium magnets (NIB, made from Neodymium, Iron and Boron). The first is known to resist demagnetisation at high temperature, while the latter is the strongest magnet at a reasonable price. NIB magnets' small size and efficacy allow them to be used in Hard disks or in Wind turbine. One 4 MW wind turbine can carry a 2.4 tonnes NdFeB magnet. This magnet is composed of 620 kg Neodymium, 108 kg of Praseodymium and between 11.2 and 96 kg of Dysprosium.
- Glass polishing powders: consume almost 15% of the tonnage of all the REE but is worth only 5% of the total value of the REE. This is due to two reasons. The first is because mainly Cerium (the second cheapest REE) is used for the polishing of glass. The second reason is only a small mass is needed, as it is pulverised in the form of Cerium Dioxide (CeO_2). These powders are used to smoothen the screens of smartphones and TVs or to etch processors and wafers.
- Catalysts: for the separation of petroleum into heavy and light parts through a process known as Fluid Cracking Catalyst. The light parts of this process can be used as fuel. Another usage as catalyst is in the exhaust systems of cars. They transform toxic gases

coming out of the motor as a result of the combustion of the gasoline, such as NO_2 or CO, into less harmful gases, such as CO_2 and H_2O.

- Batteries: Nickel Metal Hybrid (NiMH) batteries are less and less used to the profit of Lithium-ion (Li ion) batteries, which has a better charge. The transition was also accelerated after the 2011 REE-crisis, as the Li ion batteries were cheaper than the NiMH batteries.
- Alloys: in small quantities, REE mixed with steel can give better strength. This method is used by the military or space agencies rather than for consumer market.
- Luminophores and lasers: consume 7% of all the REE. It was the first usage of REE, as they were involved with Cathode-Ray Tube (CRT) television. Lasers are also used by the military (to guide missiles) or by consumers (to read Discs). This is due to the capacity of luminophores to emit at specific wavelength upon excitation.
- Health: Samarium, Gadolinium, and Erbium are used for cancer treatment and PET scan detectors.

1.2.3 Criticality of REE
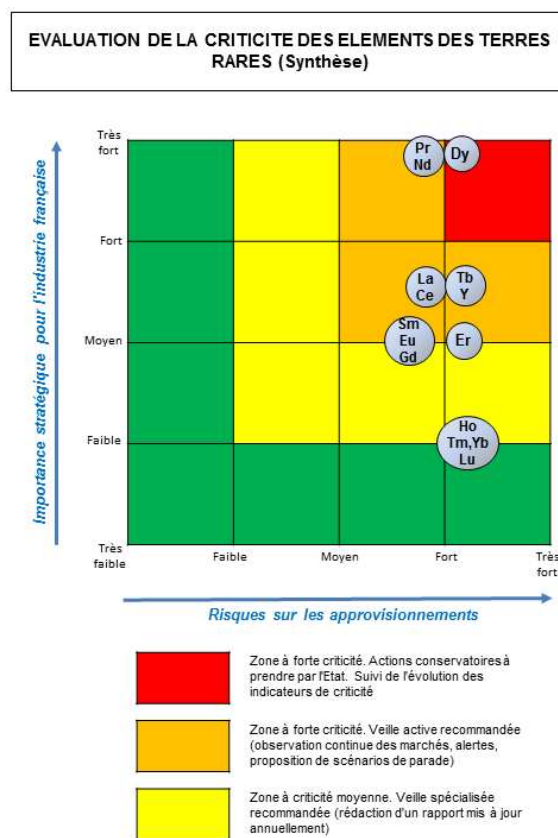
Figure 7: Graphical representation of the criticality of REE for the French industry, that also represents most of Western countries relationships with REE. The representation shows the risks on supply (x-axis) and the importance for the French industry (y-axis). Most of REE (in orange) are at least highly critical and need continual observations of the market to prevent a possible shortage of metals before it happens. Dysprosium (in the red range) already needs State based actions due to its necessity for permanent magnets. Illustration from (Bru et al. 2015)

1.3.   Electronic wastes (E-wastes)

1.3.1 Why target e-wastes?

The world produced 41 800 kilotons of different electronic wastes (e-wastes) in 2014 only. E-wastes is the category of waste with the highest growth (Priya and Hait 2017). Switzerland alone produced 110 kilotons in 2001 (Brandl, Bosshard, and Wegmann 2001) and the amount doubled to reach 213 kilotons in 2014 (Priya and Hait 2017). In 2001, of the 110 kilotons only 2400 tons of e-wastes were recycled and 4% of these are dust not recyclable using usual treatment facilities (Brandl, Bosshard, and Wegmann 2001).

So, each year this amount is only growing giving plenty of material to scavenge. Another advantage of these wastes is that they are already concentrated with the metals useful for the electronic industry. As a comparison, this is like finding organic matter in a compost. On the contrary of natural ores, in which metals must first be found, and in which yield is often uncertain. By finding a vein of gold, it is impossible to predict its concentration nor its size. As opposed to e-wastes landfills where they can be measured or assessed. Furthermore, landfills have often a higher concentration of metals compared to natural ores, earning the name of "urban mine" (Kuroda and Ueda 2011; Zhang and Xu 2016). Plus, mining's prices have ups and downs. By having a steady supply of metals, the prices would be more stable and investments less risky (Brierley 2010). Finally, these landfills are already dead zones. By recycling the wastes in it, the pollution can only decrease: the surface of the landfills will be diminished and be rehabilitated (Priya and Hait 2017). Helping the populations and the biodiversity around it. On the contrary of natural ores in which lands must be displaced and deforested, increasing nuisance and pollution. The last reason for recycling of e-wastes is its potential: less than 1% of REE were recycled in 2011 and this number did not change much since (Graedel, Allwood, Birat, Buchert, et al. 2011).

A linear economy is an economy where resources are extracted, used, and thrown away, whereas a circular economy will try to reinject the wastes at the beginning of the process, to extract less resources at the start. Going from a linear to a circular economy (Voulvoulis 2018) would allow to put less stress on our resources and economising them, making a more sustainable system. Finally, the main drive for recycling is "it turns e-waste into a secondary resource allowing the recovery and reuse of metals as well as mitigating the environmental impacts at the same time." (Priya and Hait 2017). Improvement in technologies (to extract poorer ores), use less metals for the same device (by sparing it), and recycling what cannot be used anymore are the keys to prevent exhaustion of resources (Calcutt 2001).

The limitations are the necessity of a recycling industry which is not fully developed yet and the cost of recycled material which is for most metals higher than for raw materials (Graedel, Allwood, Birat, Buchert, et al. 2011).

1.3.2 Best practices (Repairing and salvaging before recycling)

A smartphone is changed roughly every 3 years[44]. By reselling, the energetical and mineral investment is diminished. It is as if "-1" phone was made. It is also because of the manufacturing of an electronic device that most of the expenditure are made, not during its usage. By increasing its lifetime, we dilute its impact (Bakker and Mugge 2017).

If the device does not work properly, the issue must be found. If the screen, the processor, or the camera is broken, only this part should be replaced. By doing so, only a fraction of energy and metals are needed. By changing the processor, only 20g of waste (CPU) are made, as compared to 500g of waste if the entire phone was discarded. Without mentioning the cost of rehabilitation of an entire phone.

It is only with device beyond reparation or with previously mentioned broken pieces that recycling should be considered.

1.3.3 Composition of the wastes

Though it is difficult to quantify the composition of the electronic waste, depending of which types of electronics is embedded, the manufacturer or the year of production, it is still possible to have an approximate number of the concentrations involved (J. Cui and Zhang 2008).

Most e-wastes are constituted of metals, glass, plastics, and other variable compounds, such as polybrominated flame retardants, that complexify the recycling. Therefore, valuable content is concentrated, but also more difficult to retrieve.

Printed Circuit Boards (PCBs)

Printed Circuit Boards (PCBs) are the support on which connects all the components of an electronic device. As such, they are mandatory and with the increase of the production of electronic devices and the resulting production of e-waste, the production of PCBs also increases. PCBs' worldwide average growth rate production is 8.7% (Ma 2019).

PCBs are highly valuable due to their weight percentage of common metals (16% copper, 4% tin, 3% iron, 2% nickel and 1% zinc) but also rare metals (0.039% gold, 0.156% silver and 0.009% palladium), accounting to almost 30% of their weight (Ma 2019). According to (J. Cui and Zhang 2008), PCBs have 5.3 and 26.8 %weight of Fe and Cu respectively.

These concentrations may seem small, but once again, they are higher than in natural ores, as visible in Table 1. For instance, the 0.039% of gold is more than six times higher than the 0.006% occurring in natural ores. According to (Ma 2019), the concentration of rare metals in PCBs is 10 times higher than in natural ores.

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[44] https://www.statista.com/statistics/619788/average-smartphone-life/

Smartphones are a concentrate of valuable materials, as they should be light weight and small to be carried easily by the consumer. So here, the decision of the manufacturer on what component or material to use, has more impact than with other type of electronic objects.

1.3.4 Economics of wastes

From (Ma 2019), China recycled precious metals out of PCBs for an amount of "US$2.6 billion trillion", which look like a mistake, but in both case (US$2.6 billion or US$2.6 trillion), the revenues at stake are appealing.

1.4.   Ores and e-wastes processing

Before being able to use metals, they must be isolated from their worthless surroundings, called "gangue". This is done through the "Liberation and the Separation" steps (Habashi 2019). During the first step, the rock is broken and grinded so the metal can be liberated from its capsule. During the second step, the metal of interest is separated from the remainder of the rock. Some species, like diamonds or native metals, can sometimes be already retrieved at the first step without extensive physical or chemical treatment. For this step, the main caveat can be the time consumption, a fastidious process, and the water usage. A good example is placer mining of gold.

1.4.1 Native metal processing: gold

Starting with alluvium or mud or usual mined rocks containing particles of gold, the goal is to separate native gold from its surroundings. It is done thanks to sluices where the mud will be taken and washed. The sands and other light components of the mud will be washed away, while gold particles and nuggets will deposit at the bottom of the channel and can be collected (Fig. 8).

Figure 8: Sluice for gold washing. Mud is transported to the sluice to be washed. Gold nuggets and particles will deposit at the bottom because of its density and can be retrieved without further processes. Illustration from Wikimedia Commons[45]

As already stated, the drawbacks of this method are the amounts of water needed to wash the gold particles of the dirt, the amount of muds displaced to extract only a small quantity of gold, the resulting deforestation and the tailings. As an illustration, in 1989, the Carlin Trend Mine in Nevada worked on 129.8 million tons of mud to collect 105'000 kg of gold (Mineral Policy Center 2000).

In this context, this method is useful as gold appears here mostly in its native form and is easy to separate from its surroundings. For other forms of gold or for other metals that are combined with their surroundings, as it happens with e-wastes, additional steps are needed, such as cyanidation or roasting that can liberate and separate the valuable fraction of the mineral. For these refractory ores, further metallurgical processes are needed.

1.4.2 Metal processing: metallurgy

Metallurgy is the process of retrieving metals out of ores. It often consists of two consecutive steps: mineral processing (physical step, already explained in the previous section) and extractive metallurgy (chemical step) (Habashi 2019; Hartman and Mutmansky 2002a).

The goal of the mineral processing is to separate the material of interest of the gangue and make the chemical and extraction treatment more efficient. This step only uses physical means, like breaking of stones and separation of the different species, the gangue and the valuable material, from one another (by magnetic or density differences for instance). It is crucial for the next steps, as an optimal reduction of the size of the particles leads to better and faster physicochemical reactions and therefore to better recovery (Haldar 2018). This will also lead to lower costs, as less quantity of reactants is needed. But most often, before being

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[45] https://commons.wikimedia.org/wiki/File:Goldwaschrinne.jpg

able to recover the valuable metal, additional physical or chemical treatments are needed, such as pyrometallurgy, hydrometallurgy or electrometallurgy. For some metals, several routes can yield the same metal (for copper, both pyrometallurgy and hydrometallurgy can be used (Norgate, Jahanshahi, and Rankin 2007)). Here, the caveats are a big energy consumption, the usage and the production of very pollutant liquids and gases (Habashi 2019). Some of these processes are made at high temperature and/or high pressure. Others are made at standard temperature, but using very reactive lixiviants, as detailed in the following sections.

Pyrometallurgy

Pyrometallurgy consists in in the recovery of nonferrous metals from a material at elevated temperatures. Apart of the wanted metal, unwanted products (such as slag, flue gas or soot) are also produced (Ma 2019). To smelt, high temperatures (between 1300 and 1600 K) must be reached, using combustion of coal, coke, natural gas, and petroleum products. To reduce the amount of flue gas produced, pure oxygen can be injected in the combustion chamber. Nitrogen having no part in the combustion, eliminating it will decrease the volume of flume gas produced as compared with standard air. From the remainder volume of flume gas produced, heat can be retrieved to minimize the overall balance of flume gas (Ma 2019). Once a first smelt has been done, another may be needed to separate metals. Oxidative smelting is used to separate more precisely copper and nickel out of sulphide concentrates (Ma 2019). The goal is often to use the different fusion temperatures of the ores to extract them once they have reached a liquid phase one after the other.

Typically, iron, copper, cobalt, titanium, zinc and lead are extracted thanks to pyrometallurgy (Habashi 2019; Ma 2019). However, the processes at stake are not very well understood yet (Ma 2019), making it therefore difficult to optimize. Even though, pyrometallurgy is used intensively throughout the world, despite its high energy consumption and the production of heavy metals-polluted slags (Ashiq, Kulkarni, and Vithanage 2019).

E-wastes handling using pyrometallurgy

Only a few of pyrometallurgical smelters are commercially used for e-waste processing. Furthermore, it is more difficult to separate a complex network of metals and alloys than pure metals, meaning more energy is needed to process e-wastes (Priya and Hait 2017). In addition, smelting of e-waste produces toxic gases issued from organic compounds, such as (but not only) polybrominated dibenzodioxins, polybrominated dibenzofurans, phenols, and dioxins. Additional costs are therefore needed to take out and process these gases. Unprotected and artisanal local processing of e-waste, by burning them, can also lead to the liberation of heavy metals, causing important ecological and health issues to the workers (J. Cui and Zhang 2008). Classically, smelting allows for recovery rates of ca. 95.2 to 97.5 % Cu, 97.1 to 98.5 % Fe, (Xu, 2008) and 99.9 % Au (J. Cui and Zhang 2008). FairPhone has also tested smelting to assess how much of the content of a FairPhone 2 could be retrieved. Among other metals, almost all of Ag, Au, Co, and Cu have been retrieved, at the expense of Al, Nd, and Pr (Nd and Pr being REE) (van Schaik and Reuter 2017).

Hydrometallurgy

Compared to pyrometallurgy, hydrometallurgy is a newer process that is being more and more used, thanks to its efficiency. Gold, uranium, and aluminium are typical metals extracted thanks to hydrometallurgy (Habashi 2019). With this process, the goal is to chemically dissolve valuable content out of the ores using acidic or alkaline solutions. Then the wanted metals are extracted from the solutions that have leached through several more and more refining steps (J. Cui and Zhang 2008). This process happens naturally when rainwater goes and leaches through spoils tips and landfills, taking with it some metals in a process named percolation. These metals can then percolate out and contaminate surrounding soils and water reserves (Ashiq, Kulkarni, and Vithanage 2019).

Hydrometallurgy is the usual process for recovering precious metals. The most common leaching solutions are strong acids: sulfuric acid, hydrochloric acid, nitric acid, aqua regia, or other compounds such as thiosulfate and cyanide. As so, no input of energy is needed during the process, on the contrary of pyrometallurgy (Ashiq, Kulkarni, and Vithanage 2019). The particle size affects the rate at which the solution will have contact with particles' surface: with large particles, there will only be a small surface (compared to the volume of the particle) that will react with the solution, as visible with the blue particle on Figure 9. In comparison, with the same volume, the surface in contact with the solution is increased by $2 * \pi R^2$ by breaking the particle in half. By doing so, all the atoms in the middle of the particle that were inaccessible to the solution are free to react, accelerating the process.

Volume = $V1 = \frac{4}{3}\pi R^3$ Volume = $V1$
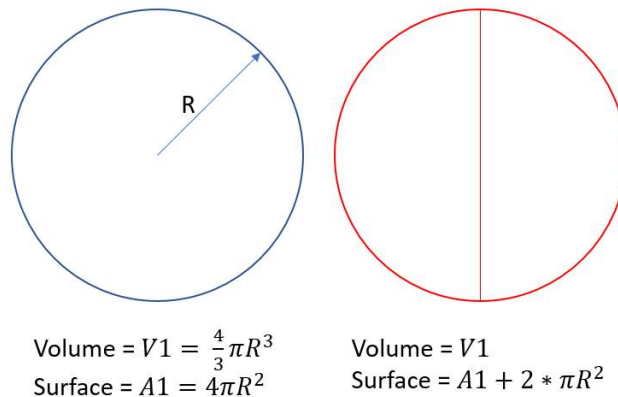Surface = $A1 = 4\pi R^2$ Surface = $A1 + 2 * \pi R^2$

Figure 9: Surface to volume ratio can be increased by having smaller particles (in red). The volume of the two small red particles together is the same as the big blue one, but the surface has increased by $2 * \pi R^2$. By increasing the available reaction surface, while keeping the same volume, the rate of reaction is increased.

Cyanide, molecular formula CN, is a powerful leachate for gold and copper. It is the only substance to solubilize gold, which is normally inert (Gail et al. 2011), making it the most used solution to extract gold. It solubilizes gold efficiently, even from very low-grade ores. Having strong negative impact on human, animals, and nature in general, fear of CN impacts prevented the opening of mines in the USA. It was also banned in the European Union for the same reasons. The trade-off of mining low-grade gold ores is the processing of large quantities of rocks to retrieve enough gold to be profitable (Laitos 2013). Once in solution, the metals

can be extracted through solvent extraction, electrodeposition, ion exchange and adsorption(Mineral Policy Center 2000).

Hydrometallurgy with e-wastes

To increase the rate of leaching, the scraps are first grinded to expose as much metals as possible to the lixiviants (acid or alkaline solutions) (J. Cui and Zhang 2008). The same lixiviants as for natural ores are used (such as cyanide, sulfuric acid, nitric acid and aqua regia) and the solution can then be purified to retrieve the wanted metals. However, the resulting wastewater are very toxic and difficult to salvage (Norgate, Jahanshahi, and Rankin 2007).

Cyanide can extract up to 1 to 3g of Gold out of 1 ton of waste, which is considered as effective, but the waste water is extremely toxic (Tuncuk et al. 2012).

Electrometallurgy

Electrometallurgy is considered as the newest type of metallurgical process as compared to the previous ones. The principle is to let an electrical current extract the wanted metals of aqueous solutions (Habashi 2019). The solubilized metals will then deposit on the electrodes because of redox potential. It is itself composed of several processes: electrowinning, electrorefining, electroplating, and electroforming (J. W. Evans 2003). This process is very specific, the drawback being the large quantities of electricity needed. As an example, the Hall-Héroult process needs 15 kWh/kg to separate the aluminium from the original alumina ore (Kvande and Haupin 2001; Gunasegaram and Molenaar 2015). Nowadays, aluminium, copper, and zinc are metals extracted with electrometallurgy (Habashi 2019).

Closing remarks on metallurgical processes

As visible on Fig. 10, these methods are not used in competition, but in synergy with one another to refine as much as possible the valuable metals (Habashi 2019). Aluminium for instance appears in both hydrometallurgy and electrometallurgy because it is a two-step purification.
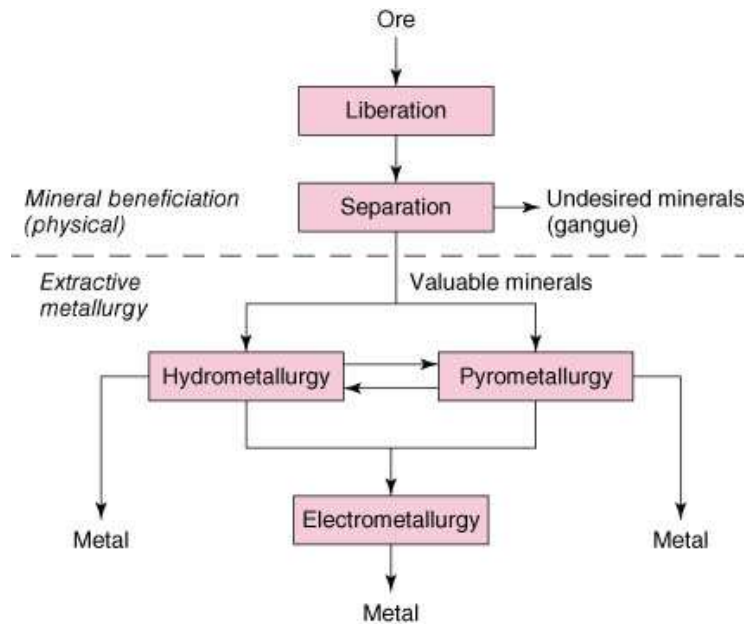
Figure 10: Sequential utilization of the different metallurgical processes. Illustration from (Habashi 2019)

To decrease the impact of by-products of these processes, and/or to increase the profits, the products are often recycled or stored for another usage. For instance sulfuric acids, ammonia, or catalysts, can be used to other steps in the chemical plant instead of being directly discarded (Habashi 2019). For very low concentration of metals, more exotic processes such as microwave assisted leaching can be used. It will specifically heat wanted metals and solubilize them, while minimizing gangue solubilization (Haque 1999).

1.4.3 Rare earth elements processing from natural ores

250 potential mineral species contain REE, but only twenty minerals contain them in valuable fractions of extractable REE, such as monazite, bastnaesite and xenotime (Corbett et al. 2017; Bru et al. 2015; Peelman et al. 2014). Ion adsorbed clay (mostly retrieved from south China) are more and more processed for how easy REE can be retrieved (Peelman et al. 2014). Mines from another ore exploitation (iron, copper, and gold) located in Sweden and Australia can contain quite a high percentage of REE, but they are not mined for it yet, as the prices of REE make these mines not yet profitable. Furthermore, the processing of REE is extremely complex and rely on several precise steps to achieve a high purity (Bru et al. 2015). Once extracted, the 0.05 to 10% REE ore is first crushed and concentrated until it reaches a concentration between 30 and 70%. They are then treated with hydrometallurgical process using acids (H_2SO_4), alkalis (NaOH), or electrolyte (NaCl); or with both pyrometallurgical and hydrometallurgical processes using high temperature acid roasting. Finally, solvent extraction is used to retrieve individual REE. However, as REE have chemical properties very close from one another, multiple steps are needed to separate them from one another (Navarro and Zhao 2014; Bru et al. 2015). As a consequence, extraction of REE is generating high loads of toxic by-products. For instance, the environmental trade-off of bastnaesite REE processing is

the production of fluorine that will leach out of the chemical plant and pollute surrounding areas (Peelman et al. 2014).

1.4.4 Rare Earth Elements retrieval from wastes

Overview

According to (Peelman et al. 2014), mine tailings and End-of-Life scrap can become great secondary resources. They are respectively materials that could not be processed after extraction of metal (leftovers) and manufactured objects that do not function anymore (that go from lamps and magnets to electronic objects). Recycling of these secondary resources offers several advantages: overcome supply risk for Europe, diminish pollution, and yield economical benefits if a successful process is found. However, less than 1% of REE was recycled in 2011 (Graedel, Allwood, Birat, Reck, et al. 2011), and it was mostly production losses not from End-of-Life products (Bru et al. 2015). The reasons are multiple: REE are often only present in very small quantity and in complex arrays, making them hard and costly to retrieve, and the necessity to handle many undesirable elements. Manufacturers then prefer to retrieve metals that have more value (gold) or are present in higher quantity (copper) and sacrifice the REE embedded in the compound (Graedel, Allwood, Birat, Reck, et al. 2011; Bru et al. 2015). To respect sustainable development, only End-of-Life or close to End-of-Life should be recycled. For instance, a wind turbine contains large quantities of REE (155 kg of Nd, 27.5 kg of Pr, and from 2.8 to 24 kg of Dy per MW), but only when it is close to its obsolescence that it should be discarded to make a new wind turbine even if it is more efficient, not before. This is an issue for the planning of the rehabilitation of new and large equipment (as wind turbines) which life expectancy is not known and expected to be long, hence not retrievable immediately and not able to satisfy the demand. This is less problematic for more usual items, such as consumer electronic, which has a shorter lifespan. For this kind of equipment, two problems arise: the inexistence of efficient collect points and the lack of information of the precise composition of such objects (ERECON 2015).

Potential sources of REEs

Examples of potential sources of REE are mine tailings issued from the phosphoric acid industry (Peelman et al. 2014) and red mud, the resulting waste of bauxite processing (Qu and Lian 2013). E-waste compose equally an interesting source of REES. Several studies worked on REE retrieval out of wastes using pyrometallurgical or hydrometallurgical processes. Potential sources are fluorescent lamp phosphor, permanent magnets, NiMH batteries and spent catalysts (Bru et al. 2015).

(F. Yang et al. 2013) as cited by (Peelman et al. 2014) recovered REE out of fluorescent lamp. Although some lamps needed low concentration of sulphuric acid (YOX needed 0.5M H_2SO_4) others needed a concentration of 18M, leaving highly corrosive leachates. (Lee et al. 2013) as cited by (Peelman et al. 2014) used H_2SO_4 to precipitate and HCl for solvent extraction of Nd out of NdFeB magnets.

Several companies are currently working on recycling of REE: Solvay/Rhodia, Umicore, Santoku, Hitachi, Shin-Etsu, Showa Denko, and Mitsubishi Materials, and organisations such as the European Rare Earths Competency Network (ERECON) give framework (Bru et al. 2015).

1.4.5 Incidence of waste

Primary wastes are coming from the mines (red mud, flumes, leachates, etc) and can pollute lands and water if not dealt with properly. Secondary wastes are coming from the electronical objects and that decompose in the environment (in open landfills). Both type of wastes cause health problems and are an economical burden. Most of the artisanal recycling activities are not official and unregulated, hence no protective measures are taken, leading to health and environmental harm (Ma 2019). Mostly because protective measures are costly and because these workers do not have the formation, nor the skills necessary to carry the recycling.

As it is nicely worded by (Kajitvichyanukul, Musikavong, and Phenrat 2019) the field of water treatment and pollutant removal is "*key for securing the present, correcting the past and sustaining the future*". Pollution is an economical, health and environmental burden. 785 million people cannot have access to basic water supply (WHO 2019), because of scarce water resources or of pollution. In the former, the availability of water can be deteriorated in case of deforestation, as soils cannot retain as much water. In the latter, sources of water can be contaminated by biological wastes (without any sewer systems) or by plastics and wastes from landfills. From an economic point of view, remediation of 217'000 contaminated sites in the USA could cost up to $187 billion, in 1996 dollars, with a time range of 10 to 30 years (US EPA 1997). However, this is also an incentive for the remediation industry, as it is a market, at least worth $187 billion in the US alone. In addition, the remediation of these sites would, by preventing health issues, save $54.8 billion in 2017 and redevelop areas (through tourism or local businesses) (US EPA as cited by (Kajitvichyanukul, Musikavong, and Phenrat 2019)).

1.4.6 Future *El Dorado* and their limitations

Large territories in Africa, Antarctica, deep ocean surface (Takaya et al. 2018; Wiltshire 2019) and extra-terrestrial surfaces (Moon, from the Apollo missions, asteroids) (Dallas et al. 2020) are considered to be future "El Dorado", future sites of economically viable mines. Metals extractable from deep sea surface are among others, cobalt, nickel, gold, and silver (Wiltshire 2019). Some asteroids could also contain platinoids in higher concentration than in Earth's crust, making these asteroids worth several trillions of dollars (Dallas et al. 2020). In the specific case of REEs, and to decrease the total control of China on the REE market, Western countries try to explore new type of REE-containing minerals, such as eudialyte and xenotime (Bru et al. 2015). It is assumed that deep sea floors have reserves of REE that could become profitable once the mining technology has matured, the legislation is made and the price high enough (Wiltshire 2019).

However, it will not resolve the problem of pollution due to the accumulation of wastes because of the manufactured products, nor space mining apart, the problem of pollution due to mining and metallurgy. Furthermore, it takes time before life can resettle in areas that have been disturbed because of sea mining (Wiltshire 2019). Finally, these mines will not handle the problem of inequal distribution of the mines, as only the countries able to extract metals from these locations will make profits. Even in the case of off Earth mining, only the countries or companies rich enough to finance a space program will mine in space while other countries will not share this wealth if the sustainable development framework is not followed (Dallas et al. 2020). It also must be stressed that the Golden Age for the economy and the society of the last century was made possible thanks to big cheap ores and oil. Without cheap energy and resources, a society cannot grow carefreely. Hence the need to find new ways of finding metals.

1.5.   Biohydrometallurgy

Aside the three metallurgical processes (pyro-, hydro- and electrometallurgy) come biohydrometallurgy. In general, this process is referred equally to biomining, bioleaching, bioextraction or biorecovery in the litterature, which are general terms englobing biological processes set to retrieve metals (Mishra et al. 2005). Biohydrometallurgy is a relatively recent process compared to the already implanted mining processes. It is nowadays considered as one of the most environmentally friendly process for the recovery of poor and refractory ores, as it requires low energy, and does not produce toxic gases or liquids (Jia et al. 2019; Priya and Hait 2017). In turn, it paved the way for the extraction of metals from low grade ores considered as non-economically viable until recently (Jia et al. 2019). The idea is to use microorganisms to extract metals. They were already used unknowingly by the Romans and Chinese two thousand years ago for the production of chrysocolla and copper by sedimentation (H. Watling 2016; Mishra et al. 2005). In a modern context, it was first observed that streams of water coming out of mines were acidic. These polluted streams are since named Acid Mine Drainage (AMD) and are a concern as environmental hazard. In 1947 (Colmer and Hinkle 1947) shown that the oxidation of ferrous iron in these waters due to the oxygen in the air was not enough to explain the acidity of these streams and that it was principally the doing of a bacterium: *Thiobacillus ferrooxidans* (since named *Acidithiobacillus ferrooxidans* (Kelly and Wood 2000)).

Most of the rich ores available today are already exploited and will be exhausted eventually. To satisfy global demand, poorer and/or more complex ores need to be used (Jia et al. 2019). As mentioned above, classical mining processes, such as pyrometallurgy, are costly and polluting, and are not well suited. Hydrometallurgical and electrometallurgical combined processes are more efficient (Anderson 2016). Biohydrometallurgy defines nowadays a subfield of hydrometallurgy, in which microorganisms are used as biocatalysts to separate more easily valuable metals from their surroundings (H. Watling 2016). Biological activities result in the dissolution of the metals of interest out of their gangues, then, and following

hydrometallurgical steps, metals are stabilized by complexation and finally enter refining steps (Mishra et al. 2005; Rohwerder et al. 2003). In this context, bacterial leaching, combined for instance with SX/EW (Solvent Extraction and ElectroWinning), offers a method of exploiting small ore bodies with a minimum of capital investment. Most commercial operations leaching copper from ore dumps are in the Southern hemisphere, Australia, Chile, and Peru, as well as Myanmar (Brierley 2010).

Several variations of this process are applied according to the metal and its geological origin. For instance, a process called biooxidation defines a biological process in which the metals of interest, imprisoned in a sulphide matrix, is liberated through the oxidization and solubilization of the latter. The metal is then concentrated in the solid remainder, enriching the ore (Mishra et al. 2005). For gold, this is done by solubilizing unwanted metals (such as iron) through the activities of dedicated microorganisms. The solid remainder is enriched and can be more easily processed (Rohwerder et al. 2003). In a recent trial, and without dissolution of the matrix, less than 50% of the gold was recovered, whereas up to 95% was recoverable thanks to biooxidation (J. Cui and Zhang 2008). Finally, biosorption is a passive absorption and accumulation of solubilized metals into organisms (J. Cui and Zhang 2008).

1.5.1 Advantages and disadvantages of biohydrometallurgy

Biohydrometallurgy's pros and cons are listed by (Brierley 2010). The benefits of biohydrometallurgy has been summarized by Watling (H. Watling 2016): "*Looking to the future, this suite of well-developed and reliable biohydrometallurgical technologies can be applied, for example, to small deposits in remote locations perhaps with unfavourable terrain, to complex ores that are difficult to process, or to concentrates containing impurities that attract smelter penalties*". Additional advantages involve low cost of production, the use of little energy sources and low environmental impacts. By reducing the number of mining steps and the usage of smelters (and the related royalties) and by having an "autonomous" process (not relying on external acid supply for instance), the costs are also decreased. The second advantage of biohydrometallurgy is its usage on low grade and/or refractory (hard to recover) ores, at low cost. Complex ores are very difficult to process with the usual techniques, accumulating steps to extract the metal, making them not suitable (or at a prohibitive cost). This is a shame as some resources are voluntarily discarded, while still having recoverable material in relatively high concentration. This is particularly the case for e-waste and the retrieval of REEs, as these techniques would be particularly adequate (Peelman et al. 2014).

The main drawbacks of biohydrometallurgy are the slowness and the necessity to implement new facilities and processes (Jia et al. 2019; Priya and Hait 2017). Indeed, even though pyrometallurgy is polluting and energy demanding, its results are fast, the infrastructures are already in place and the technicians are formed. From this context, adding a new form of recovery technology is a risk to any mining company (Brierley 2010). Improving some of its key parameters (species involved, energy and nutrients consumption, etc) could allow it to

equal or maybe surpass old methods with optimisation (Breed and Hansford 1999). Other drawbacks include:

- The time needed between the research and the commercialisation of a method can go from ten to twenty years.
- The specificity to the site: a biological process may only be suitable for one site, because of the specific minerals involved and may not be transferred as such to another mine. This also means that a technician cannot transfer his skill from one site to another, complexifying the process of knowledge sharing.
- The risks: a new process is not accepted immediately, and its chance of success may be low, as it is always riskier to try something new than to continue with an existing technology.
- Capital investment, as it is a new project, the initial investment may also be higher than equivalent projects. Of course, the initial investment may also not be retrieved, in case of failure.
- Intellectual properties: apart of the question can we patent life, the mining companies are often reluctant to pay fees for a novel technology. It may be because the patent may not incorporate all the usage a site may need (all the ores may not be mines thanks to the purchased patent) or because the mining company does not want to share all its information ("production logs"). It can also be difficult because of the royalties that must be paid upon acquisition of a patent.
- The repeatability of the process: as a biological process, it is impossible to ensure that the yield and the products will be the same on the first and the twentieth time, there will be variability upon the results that are very difficult to predict.
- The lack of experienced scientists and technicians.
- The lack of validated model: there are many factors that are unknown and that merit investigation (need of aeration and at what rate, reason of sometimes low temperature during the leaching, etc). This could lead to a better understanding and an optimisation of the process, instead of trial and error.

1.5.2 Past and current usage

The most extracted metals by biohydrometallurgy are copper and gold (Brierley 2010). This process was used for two thousand years and is currently in operation in modern mines, such as the Rio Tinto mine (Spain), where stacks of copper wastes are left between one to three years to sediment its copper parts (Mishra et al. 2005). Other examples include the Kennecott Bingham mine (Utah, USA), the Lo Aguirre, Cerro Colorado, and Ivan-Zar mines (Chile) and the S&K Copper project (Myanmar) (Mishra et al. 2005; Olson, Brierley, and Brierley 2003). Most of these plants have been in operation since the 1990s. In Chile, biohydrometallurgy is used for the recovery of copper, accounting for 20% of world's production of Copper (Domic 2007). The processes developed are often site specific, meaning it is difficult to transfer a process developed in a mine in Chile into a mine in Australia for instance. It is therefore very difficult

to have a general process suitable to many substrates. However, a thorough knowledge of these individual processes could lead to understand and develop a general process for mixed substrates, such as mix of different e-wastes (Peelman et al. 2014; Helen R. Watling 2015).

1.5.3 Type of processes

Depending of the ore, several processes can be used for biohydrometallurgical purposes. Heap leaching is the simplest and cheapest form of leaching. It consists of letting water percolate through fragmented rocks to let microorganisms grow. These microbes will help to oxidize and solubilize metals contained in the rocks. They will then be transported with the water to be purified (J. Cui and Zhang 2008). Heap leaching is mostly used for low grade copper ores. The drawbacks of this method is the impossibility to monitor the different parameters and to keep the same optimal conditions throughout the entirety of the heap (Ojumu et al. 2006). For instance, there can be local areas that have a higher temperature due to increased bacterial activity.

More expensive, but also allowing more control on the conditions, are agitating tanks. They are used for the hard to recover metals (H. Watling 2016) that need specific conditions to help optimal activity from the microbes (J. Cui and Zhang 2008). Smaller, they also allow to control and keep optimal conditions in the whole process.

1.5.4 Microorganisms involved

Microorganisms involved in biohydrometallurgy processes include bacteria (*Acidithobacillus spp.* and *Leptospirillum spp.*), archaea (*Ferroplasma spp.*), algae and fungi (*Aspergillus spp.*) (Jia et al. 2019). Typically, these organisms can sustain hard living conditions. In nature, these organisms compose rich and robust ecosystems, made from a high diversity of acidophiles, showing a large variety of metabolisms. For instance, microalgae can tolerate harsher conditions by forming mats. Fungi can tolerate acidic or alkaline, high salt and high metal concentration, but cannot tolerate temperature higher than 60°C (Salwan and Sharma 2020).

Organisms living in harsh conditions are known as extremophiles, while organisms that bear such conditions (being not their optimal environment) are known as extremotrophs or extremotolerant (Salwan and Sharma 2020). Future usable microorganisms could be hyperthermophilic archaea, that have the advantage to work at higher temperature, and could therefore trigger some other kinds of metal recovery (H. Watling 2016). However, patentability of some organisms that have a better yield than others, because of the species or because of a specific mutation in the individual. This could prevent the share of some discoveries as it is commercially sensitive information (H. Watling 2016).

Nomenclature

Energy Source		Electrons Source		Carbon Source		Complete name
Chemical	Chemo-	Organic	-organo-	Organic	-heterotrophe	Chemoorganoheterotroph
				Inorganic	-autotrophe	Chemoorganoautotroph
		Inorganic	-litho-	Organic	-heterotrophe	Chemolithoheterotroph
				Inorganic	-autotrophe	Chemolithoautotroph
Light	Photo-	Organic	-organo-	Organic	-heterotrophe	Photoorganoheterotroph
				Inorganic	-autotrophe	Photoorganoautotroph
		Inorganic	-litho-	Organic	-heterotrophe	Photolithoheterotroph
				Inorganic	-autotrophe	Photolithoautotroph

Table 3 : Categories based on the energy, electron and carbon sources (Haug 2019)

Most bioleaching organisms are chemolithotrophs, and chemoorganotrophs (Srichandan et al. 2019). From Table 3, chemolithotrophs use inorganic material (such as iron and sulphur (Srichandan et al. 2019)) as energy and electron sources, whereas chemoorganotrophs use chemicals as energy source, but its electrons are coming from an organic source. Their capacity to use CO_2 as a carbon source makes them autotrophs otherwise, they are heterotrophs (Haug 2019). Chemolithotrophs can be separated in three categories, depending of their favourite temperature range (Srichandan et al. 2019; H. Watling 2016):

- mesophiles (20 to 40°C), like *Acidithiobacillus ferooxidans, Acidithiobacillus thiooxidans,* and *Leptospirillum ferooxidans*
- moderate thermophiles (40 to 60°C), like *Acidimicrobium* sp., *Ferromicrobium* sp., *Sulfobacillus* sp., and *Acidithiobacillus caldus.*
- extreme thermophiles (60 to 80°C), most are archaea, like *Sulfolobus, Metallosphaera, Acidanus* and *Sulfurisphaera*.

Chemoorganotrophs use organic material as energy and carbon sources (Srichandan et al. 2019), such as Fungi and cyanogenic microbes.

Typical microorganisms present in biohydrometallurgy processes
For bacteria, *Acidithiobacillus ferrooxidans* (*At. ferrooxidans*), *Acidithiobaillus thiooxidans* and *Leptospirillum ferrooxidans* (*L. ferrooxidans*) are the most present bacteria in mesophilic processes (Rohwerder et al. 2003; Brandl, Bosshard, and Wegmann 2001). Other bacteria also present in biomining activities are *Thiomonas cuprina*, *Acidiphilium spp.*, and *Acidocella spp.* (Jia et al. 2019). For fungi, *Aspergillus niger* and *Penicillium simplicissimum* are the most used (Brandl, Bosshard, and Wegmann 2001).

Archaea present in biohydrometallurgical processes are *Sulfolobus spp.*, *Acidianus brierleyi*, *Metallosphaera spp.*, *Ferroplasma spp.*, *Thermoplasma spp.*, and *Picrophillus torridus* (Jia et al. 2019).

Among these organisms, there is a broad spectrum of metabolisms, with some microbes able to carry several reactions (*At. ferrooxidans*) while others can only use some limited substrate (*L. ferrooxidans*) (Rohwerder et al. 2003). By having several routes to survive (for instance both aerobic and anaerobic pathways), the usage of *At. ferrooxidans* is also more robust (Rohwerder et al. 2003).

1.5.5 Bioleaching mechanisms of chemolithoautotrophs

Bioleaching of metals occurs through contact and non-contact mechanisms (Srichandan et al. 2019). They can be summarized into three major processes (Ojumu et al. 2006; Srichandan et al. 2019):

1. Ferric ions (Fe^{3+}) production: through oxidation of ferrous ions (Fe^{2+})
2. Protons (H^+) production: through oxidation of sulphur species (octasulphur (S_8), thiosulfate ($S_2O_3^{2-}$), hydrogen sulphide (H_2S) or polysulphides) into sulphuric acid (H_2SO_4)
3. Metal solubilization due to ferric ions and protons.

Dissolution mechanism: contact and non-contact mechanisms

It was first thought that the dissolution mechanism of the metal was carried out via direct and indirect contacts of the microbes to the ore (Ehrlich 2002). Now it is known that it is contact or non-contact mechanisms, both derived from the previous indirect pathway (Rohwerder et al. 2003).

Contact mechanism is the most used mechanism compared to the non-contact one (Rohwerder et al. 2003). The organism is in contact with the surface of the metal and will use Fe^{2+} as electron donor. The resulting ferric ion (Fe^{3+}) is a powerful oxidant that will oxidize other metallic ion in cations that will solubilize in the solution. In details, oxidation occurs spontaneously in high surface energy areas such as edges, cracks, and fractures, when enough redox potential is applied (Sun et al. 2015). Microbes will attach to these areas to benefit from these "easy to reach" energy surfaces, instead of plain surfaces (Jia et al. 2019; Srichandan et al. 2019). These areas are sensed by bacteria (by chemotaxis) as they often have a gradient of variable ions and molecules (ferric ions, thiosulfate, etc) (Rohwerder et al. 2003). Attachment is done thanks to electrostatic forces (Rohwerder et al. 2003) and to the production of "Extracellular Polymeric Substrate" (EPS) a network of multiple organic polymers 10 to 100 nm thick. It is linked to the "Bacterial Outer Membrane" (BOM) and serves multiple purposes, such as biofilm formation, defence mechanism, bacterial nutrition and signalling (Staudt et al. 2004). EPS is considered as a dynamic organ, as its production can be triggered upon attachment by the bacteria and its composition is dependant of the substrate the bacteria has been grown with (Rohwerder et al. 2003).

One of these polymers is a ferric ion (Fe^{3+}) – glucuronic acid complex. It is positively charged and allows the attachment of the bacterial cell to the metal surface while also taking out an electron out of the metallic substrate. This will reduce the ferric ion into a ferrous ion (Fe^{2+}) (Rohwerder et al. 2003). This ferrous ion will then go to the BOM and its electron will be transferred down the respiratory chain via different cytochromes (*Cyc2*, *Cyc1*) and a cytochrome oxidase (*Cox*). Oxygen will be the final electron acceptor. The passing down of this electron down the respiratory chain will fuel bacterial metabolism (Jia et al. 2019; Srichandan et al. 2019).

The non-contact pathway follows the same principle as for the contact pathway, at the difference that the microbe is not attached to the material and will oxidize ferrous ions that are in solution (Rohwerder et al. 2003; Srichandan et al. 2019).
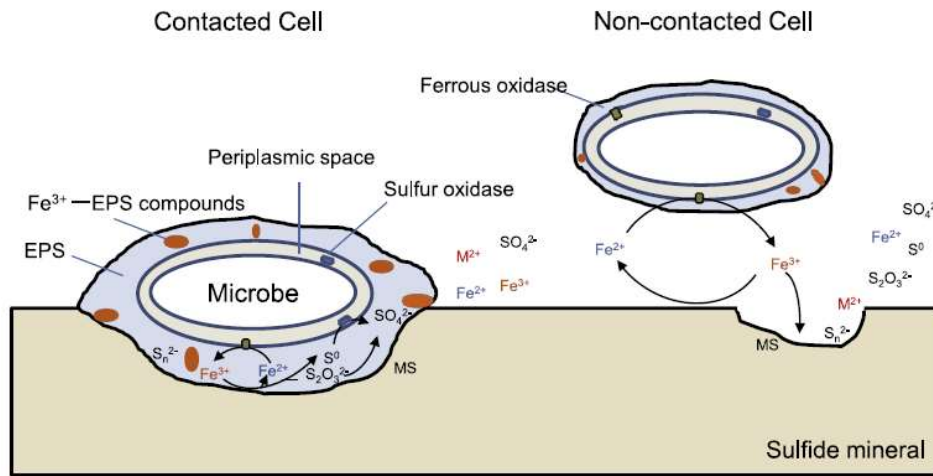

Figure 11: Mechanisms of the contact and non-contact pathways. Illustration from (Jia et al. 2019)
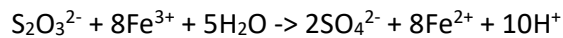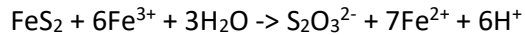
By observing the shielding role of the EPS to preserve bacteria and noticing also that most of the leaching processes occur while attached to the substrate, the contact mechanism should be chosen for further investigation over the non-contact mechanism. The non-contact mechanism can be avoided by growing the organisms with non-soluble substrates (if they were grown with soluble substrates, the production of EPS is severely hindered, as it is not needed, as well as attachment abilities).

Leaching pathways

Chemolithoautotrophs solubilize metals from ores through two pathways: the thiosulfate pathway or the polysulfate pathway. The valence of the mineral species is the most important parameter to know which pathway will be used. Metals sulfides that are acid non-soluble (valence bands are only due to the metallic atoms) will follow the thiosulfate pathways, while metal sulfides that are acid soluble (valence bands are a due to both mineral species) will follow the polysulfate pathway (Rohwerder et al. 2003; Schippers and Sand 1999).
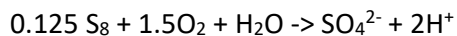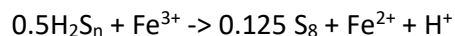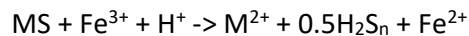
Thiosulfate pathway

In the thiosulfate pathway, only Fe(III) is used to dissolve metals insoluble in acid. Six ferric ions are needed to break the sulphur-metal bond and release the metallic cation and a thiosulfate, hence the name of the pathway (Rohwerder et al. 2003; Schippers and Sand 1999). Once Fe(III) have oxidized the metallic species, they are reduced to Fe(II) (Schippers and Sand 1999; J. Cui and Zhang 2008):

$$FeS_2 + 6Fe^{3+} + 3H_2O \rightarrow S_2O_3^{2-} + 7Fe^{2+} + 6H^+$$

$$S_2O_3^{2-} + 8Fe^{3+} + 5H_2O \rightarrow 2SO_4^{2-} + 8Fe^{2+} + 10H^+$$

Fe(II) serves then as electron donor for *Acidithiobacillus ferrooxidans* and *Leptosirilllum ferooxidans*. It will be oxidized into Fe(III), replenishing the quantity of Fe(III).

Polysulfate pathway

In this pathway, both Fe^{3+} and H^+ act to dissolve metals soluble in acid. When two H^+ attack the metal-sulphur bond, hydrogen sulphide (H_2S) is released, but will be immediately by oxidized by the powerful Fe(III), which leads to H_2S^+. This H_2S^+ can dimerize (H_2S_2), which can be further oxidized to polysulfides that can also be oxidized to give elemental sulphur, giving the eponymous name to the pathway (Rohwerder et al. 2003; Schippers and Sand 1999):

$$MS + Fe^{3+} + H^+ \rightarrow M^{2+} + 0.5H_2S_n + Fe^{2+}$$

$$0.5H_2S_n + Fe^{3+} \rightarrow 0.125\ S_8 + Fe^{2+} + H^+$$

$$0.125\ S_8 + 1.5O_2 + H_2O \rightarrow SO_4^{2-} + 2H^+$$

Where M stands for metal.

For this pathway, ferrous ions are not strictly necessary for the advancement of the process, as it can be carried by the protons. In this context, sulphur oxidizing bacteria will oxidize H_2S and produce sulphuric acid (H_2SO_4). Sulphuric acid is crucial to provide protons as well as keep a low pH and therefore keep iron ions in oxidized state (Schippers and Sand 1999; J. Cui and Zhang 2008).
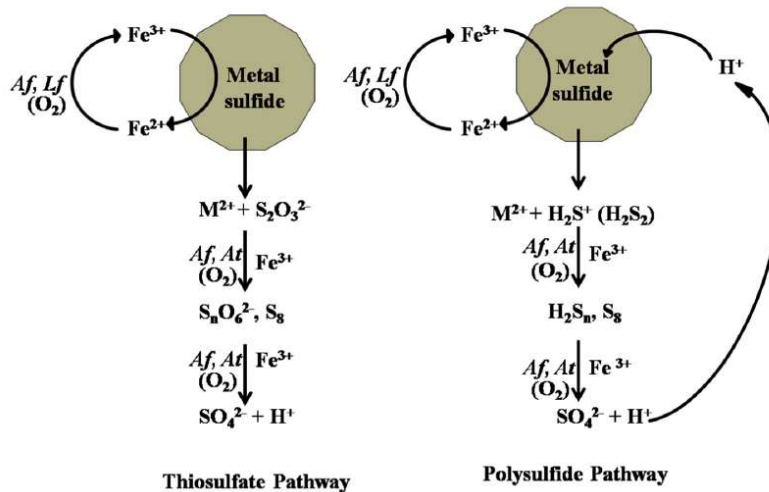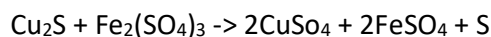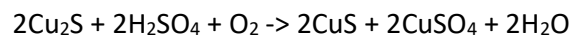
Figure 12: Illustration of the Thiosulfate and Polysulfide pathways. Af is for Acidithiobacillus ferrooxidans, Lf for Leptospirillum ferriphilum, At for Acithiobacillus thiooxidans and MS for Metal sulfides. From (Srichandan et al. 2019)

Closing remark

For both pathways, the metabolism of the organisms regenerates protons and ferric ion concentration. The Fe(III)/Fe(II) couple control the redox potential of the medium, allowing metal solubilization (Schippers and Sand 1999; J. Cui and Zhang 2008). This is illustrated by the leaching of chalcocite (Cu_2S), a mineral bearing copper, by protons and ferric ions (J. Cui and Zhang 2008; Olson, Brierley, and Brierley 2003):

$$2Cu_2S + 2H_2SO_4 + O_2 \rightarrow 2CuS + 2CuSO_4 + 2H_2O$$

$$Cu_2S + Fe_2(SO_4)_3 \rightarrow 2CuSo_4 + 2FeSO_4 + S$$

$$CuS + Fe_2(SO_4)_3 \rightarrow CuSO_4 + 2FeSO_4 + S$$

$CuSO_4$ is copper(II) sulfate, which can be further purified to pure copper through electrolysis (Parker and Muir 1981).

Knowing which pathway is involved is crucial as the products and their concentration are not the same. In the case of the thiosulfate pathway, 20% elemental sulphur can be produced while with the polysulfate pathway more than 90% can be produced, if there is no sulphur oxidizing bacteria (Rohwerder et al. 2003). The unknowing usage of the latter pathway instead of the former in a reactor can therefore lead to an accumulation of elemental sulphur that can be problematic for biomining processes, because of "sulphur layer", that cannot be oxidized abiotically in acidic conditions (Srichandan et al. 2019). This sulphur layer acts like a barrier and prevent optimal diffusion of ions and all the chemical species.

Furthermore, conditions within the heap or the bioreactor favours one or the other pathway, favouring also one species of bacteria over another, ultimately leading to efficiency differences (Rohwerder et al. 2003).

1.5.6 Other bioleaching mechanisms

Apart of sulfuric acid, which is the main pathway for metal leaching, other possibilities exist: acidolysis, complexolysis, redoxolysis, and the cyanide pathway (Srichandan et al. 2019; Asghari et al. 2013).

- *Acidolysis*

Acidolysis is the solubilization of metals through the action of protons (H^+), that will ionize metallic atoms, fragilize bonds and remove them from their surroundings. An example of acidolysis is the extraction of Nickel (Ni) out of its ore:

$$NiO + 2H^+ \rightarrow Ni^{2+} + H_2O$$
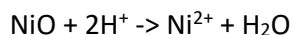
- *Complexolysis*

Complexolysis is a ligand-mediated mechanism. The organisms produce organic compounds that attach to the surface of the metal and change chemical bonding, resulting in metal detachment. Conversely organic compounds complex metallic ions in solution, rendering it more soluble and less toxic for the organisms (Asghari et al. 2013). One example of complexolysis is the nickel citrate production:

$$Ni^{2+} + C_6H_8O_7 \rightarrow Ni(C_6H_5O_7)^- + 3H^+$$

- *Redoxolysis*

Redoxolysis is based on exchange of electrons (an oxidoreduction reaction). As the oxidation state is paramount for the solubilization of most metals, understanding the exchange of electrons is therefore crucial. An example of redoxolysis is the reduction of the manganese ion:

$$MnO_2 + 2e^- + 4H^+ \rightarrow Mn^{2+} + 2H_2O$$
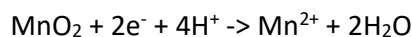
- *Bioaccumulation*

Bioaccumulation occurs when the metallic ions from the solution accumulate within prokaryotic or eukaryotic cells.

- *Cyanide pathway*

The cyanide pathway is mainly an aerobic pathway (Srichandan et al. 2019). Cyanogenic organisms (bacteria such as *Chromobacterium violaceum*, *Pseudomonas fluorescens*, and *Bacillus megaterium*, or fungi such as *Marasmius oreades*) produce cyanide (HCN) from Glycine. Cyanide can principally solubilize gold and other metals by binding to them and forming dicyanaoaurate [$Au(CN)_2^-$] or teetracyanonickelate [$Ni(CN)_4^{2-}$] for example. They are of great interest, as metal cyanides have a good solubility in water, are very stable, and are easily retrievable by chromatographic means or activated carbon (Faramarzi et al. 2004). Unfortunately, they are not interesting for Rare Earth Elements as they cannot form complexes with cyanide (Faramarzi et al. 2004). However, they may still be interesting by removing some metals and leaving only REE.

1.5.7 Parameters important for biohydrometallurgical processes

There are mainly four parameters that affect a bioreactor's rate of bioleaching: temperature, pH and the concentration of cations and anions (H. Watling 2016). Other parameters that are of importance in our specific case are the size of the powder, the nutrients given, the inhibitors within the substrate, and the system of the colonies (single strain or consortium).

- Temperature

Microorganisms can be separated depending of their growth temperature: psychrophiles (between 0 and 20°C), mesophiles (20 to 40°C) and thermophiles (40 to 120°C), based on their affinity for low, medium and high temperatures respectively (Srichandan et al. 2019; H. Watling 2016; Salwan and Sharma 2020). Outside of their optimum range, microorganisms may be slowing down or dye off, but if they survive, their bioleaching activities would be severely hindered. Several thermal categories of microorganisms can coexist in the same heap, as the temperature is not uniform throughout the pile (H. Watling 2016).

- pH

Most of known organisms involved in AMD are acidophiles, which are organisms living below a pH of 3 (Rohwerder et al. 2003). Each species has a range of pH tolerance, out of which their activity is drastically decreased, even though they can still be alive. Change of pH also affect the microbial diversity in a bioleaching process (Wang et al. 2018). But bacterial growth can also influence the pH in return. *A. ferroxidans* and *A. thiooxidans* decrease the pH, as they grow (Brandl, Bosshard, and Wegmann 2001). At a pH lower than 4, the oxidation of ferrous ion by the microorganisms is faster than the chemical oxidation (H. Watling 2016). Both are involved in the oxidations, but at different rates, depending of the pH. To date, only a few acidophiles were shown to grow at very low pH values (pH < 1): *Acidiplasma cupricumulans*, *Acidiplasma aeolicum*, *Picrophilus oshimae*, *Picrophilus torridus* and *Acidianus sulfidivorans* (H. Watling 2016).

It should also be noted that e-wastes lead to an increase of the pH, having an alkaline toxic effects on acidophilic bacteria (Brandl, Bosshard, and Wegmann 2001).

- Concentration of cations and anions

Anions, and especially those coming from the process water (such as chloride, nitrate, or fluoride), decrease microbial activities. This can be a problem if sea water was to be used for the leaching of heaps in some sites, because of the concentration of NaCl involved (H. Watling 2016). Anions are pH dependant. At low pH, fluoride is completely dissociated and can penetrate and attack the organisms. Whereas at neutral pH, most of the fluoride is undissociated.

As previously shown, the main product of a biohydrometallurgical process are cations, the metallic form allowing metal solubilization. However, at high concentration the cations can become toxic for the organisms. The key then is to find the equilibrium between leaching an

optimal amount of metals and the having the least lethal effect on the organisms. This aspect will be further analysed in the next section (pulp density). Furthermore, the main reactants of the bioleaching reaction, ferric ions and sulfate ions, have toxic effects on planktonic cells when their concentrations are greater than 30 and 75 g/l, respectively.

- Pulp density

Pulp density correspond to the ratio between the solid material to be leached and the fluid media supporting life of the organisms involved in the process. If this ratio is low, the rate of the process is expected to be low equally. However, even if higher amounts of material can be retrieved by having high pulp ratio, the trade-offs are numerous: low gas (O_2 and CO_2) exchange, abrasive conditions and high shear stress on the bacterial cells leading to higher metabolic stress as well as rapid production of toxic leach products that accumulate in the liquid medium (Ahmadi et al. 2011). (Brandl, Bosshard, and Wegmann 2001) showed that a concentration around 5 to 10 g/L scraped waste was optimal for *T. thiooxidans* and *T. ferrooxidans* to leach more than 90% of the metals (Al, Cu, Ni, and Zn) embedded in electronic wastes in a one-step process.

- Rate of medium replacement

By replacing the medium and taking out products of leaching, toxic compounds are also taken away. Fresh supply of medium also allows nutrients to be given, and the microorganisms can work optimally. The downside is that microbes are also washed away if the rate of medium replacement is too high. Trade-off consists in a careful liquid replacement and optimization of the bacterial growth in presence of reduced amounts of leached products.

- Stirring mechanisms

A good stirring mechanism is necessary to have optimal and homogenous contact between the microorganisms and the substrates. If the rate of stirring is too low, only part of the substrate will be in contact with the leaching mechanisms. At the same time, if the rate of stirring is too high, there will not be enough time for the chemical reaction to take place. Furthermore, if this rate is too high, the mechanism could apply shear stress on the microorganisms. In addition, many chemicals are produced, such as elemental sulphur, that can accumulate in a sulphur layer and prevent an efficient process (Srichandan et al. 2019).

- Reduction potential

As bioleaching processes are based on the exchange of electrons, the reduction potential dictates which metals can be solubilized or not. Furthermore, by applying a current to the medium, bacterial growth and activity is increased (Ahmadi et al. 2011). Above +850 mV, *At. ferrooxidans* cannot oxidize Fe(II) into Fe(III). For *L. ferrooxidans*, the potential can go up until 950 mV (Rohwerder et al. 2003).

- Contact mechanisms with the metals

Organisms are exposed to the substrate via different mechanisms: one-step, two-step and spent medium bioleaching.

With the "one-step bioleaching", the organisms, the substrate and the medium are put together at the same time (Srichandan et al. 2019). The advantages of this method are its fastness, as the reaction starts immediately. The downside is a large number of organisms may be inhibited because of the toxicity of the substrate and the products in large concentration.

With the "two-step bioleaching", first the bacteria are grown, then the substrate is added once either enough level of oxidants or enough number of microbes is reached (Srichandan et al. 2019). This allows to first have a sufficient number of organisms that may survive the deleterious concentration of metals and that can trigger the bioleaching.

With the "spent medium bioleaching", only the medium in which microbes have grown is mixed with the substrate (Srichandan et al. 2019). As the microbes are not in contact with the e-wastes, this method kills no microbes. Only chemicals will be allowed to solubilize metals of interest out of their surroundings. There will be no pathways to further solubilize the metals nor further production of leachants once there are depleted. In other words, this is simply a hydrometallurgical process.

According to (Brandl, Bosshard, and Wegmann 2001) spent medium bioleaching (or "two-step bioleaching" in their text) offers several advantages: e-wastes and microbes are not in direct contact and higher concentration of scraps can be obtained compared to one-step process. The former allows easier and differentiated processing of the fluxes, enabling specific recycling or purification. The latter allows better yields and efficiency, as higher concentrations are reached, more scraps can be processed during the same time.

- Type of material

Several types of materials can be processed by biohydrometallurgy: natural ores, electronic wastes, old catalyst (from the petroleum industry for instance), or remainder of other processes (Srichandan et al. 2019).

- Size of powder

To increase the rate of leaching (i.e. to speed up the process), a simple way is to grind the scrap material to an adequate size. Indeed, with large parts, the chemicals secreted by the microbes or the microbes themselves will take more time to erode the material completely. On the contrary, by having fine powder, the reactions are accelerated as the surface/volume ratio is increased and the microorganisms have direct access to as much possible material as possible. Contact zone ratio increases with a decrease of the size of the particles. As an illustration, on a plane surface, bacteria prefer cracks on the surface, as more surface is available for a contact mechanism of dissolution. Like the microvilli of the intestine, cracks allow a bigger surface for the same volume. However, by decreasing too much the size of the

material, EPS production can be inhibited (Rohwerder et al. 2003). Furthermore, with a too small size, the solubilization rate can become so rapid that the concentration of cations in solution can become quickly toxic for the microbes.

- Aeration

Archaea are strictly anaerobe (Salwan and Sharma 2020), meaning a process based on archaea will not work in the presence of oxygen. On the contrary, other organisms need oxygen as the final electron acceptor, as visible with the equation (Ojumu et al. 2006):

$$4Fe^{2+} + 4H^+ + O_2 \rightarrow 4Fe^{3+} + 2H_2O$$
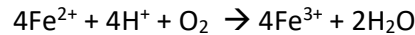
Alternating between aerobic and anoxic conditions can enhance metal recovery (Helen R. Watling 2015). In complement, enriching air with CO2, will help autotrophs grow more (Srichandan et al. 2019).

- Carbon source

Acidithiobacillus spp. and Leptospirillum spp. are strict autotrophs, meaning their carbon source is only CO_2. While *Acidiphillum acidophilum* and *Acidimicrobium ferroxidans* can grow heterotrophically in the presence of glucose, autotrophically without and mixotrophically if every substrate is available (Rohwerder et al. 2003). For heterotrophs, several carbon sources can be used (such as sucrose, maltose or glucose), each having an effect on the growth of the organisms (Kim et al. 2016).

- Catalysers and inhibitors

Catalysers act on the substrate to make it more easily available to the oxidant or attack the substrate to make complexes easier to work on by the oxidant (Srichandan et al. 2019). Citric acid was used by (Choi et al. 2004) as a complexifying agent. Without, only 37% of copper remained in solution, while more than 80% remained in solution in the presence of citric acid. By increasing the solubility of leached metal ions, more ions are available to further processing and retrieval (J. Cui and Zhang 2008). Inhibitors will decrease the efficacy of the process or the activity of the organisms or their growth. Glycine has been shown to have a inhibitory effect on bioleaching rate, but it is still unclear why (Fathollahzadeh et al. 2019).

- Type of cells

As shown before, the type of cell (bacteria, archaea, eukaryotes (fungi, algae)) and its metabolism will influence the conditions of the process (its pH, temperature, etc). Hence also influencing its yield.

- Single strain or consortium

It was first thought that the inhospitable environment of ore waste (due to low pH, high concentration of heavy metals and low concentration of nutrients) would give a very limited number of species. On the contrary, the diversity of microbes living in these hostile

environments is remarkably high (Rohwerder et al. 2003). Single strain qualification is easier to assess than a consortium, but it is a situation that does not happen often in nature and it is also more fragile. Indeed, an ecosystem with several strains, is more resilient as some species can use the metabolites ("wastes") of another organism and transform it back into substrates (Cavaliere 2017, Evans 2017). Furthermore, it has been shown that in harsh (with less nutrients) environment, bacteria tends to be more cooperative and mutualistic (Hoek et al. 2016).

The composition of the species can change with time, depending of the nutrients available in the medium, its pH, its temperature, and the metals present in it. One can imagine that some species can be added not at the start, but later in the timeframe of the process to increase the rate of extraction. For instance, thermophiles can be added after a reactor has reached a certain temperature.

- Number of cells

The optimal concentration of cells according to (H. Watling 2016) is 10^5 cells/ml. Below this number, the population may not be able to trigger the reactions of metal extraction or they would be washed by the change of medium. Above this number, there would be competition for resources, or the nutrients would be depleted before any reactions could have taken place efficiently. These numbers are can vary from one study to another. (Fathollahzadeh et al. 2019) stated that 10^6cells/ml is ideal. In addition, in this study, they took the bacteria in the exponential growth phase.

- Production of a biofilm

The production of a biofilm and/or of an Extracellular Polymeric Substrate (EPS) protects the bacteria from the toxicity of the medium and can enhance extraction rate (Nemati et al. 1998).

Rare Earth Elements retrieval based on these parameters
Often in the different studies, the aforementioned parameters were treated individually, instead of using systemics, which is how these parameters influence each other. With an increase of temperature, REE's solubility decreases (Lee et al. 2013) as cited by (Peelman et al. 2014). Therefore, even though the leaching rate (the speed at which REE can be leach out) is decreased at room temperature, it is preferred as more REE can be leached out.

The pH range is more flexible. Monazite ores have been processed at a pH of 7, with bacteria (among others, *Bacillus megaterium* and *Pseudomonas aeruginosa*) and fungi (*Aspergillus niger, Aspergillus tubigensis* and *Penicillium sp*) (Corbett et al. 2017). In another study, still with monazite, *A. ferooxidans* was used with a pH of approximatively 3.3 (Fathollahzadeh et al. 2019). However, e-wastes scrap lead to an increase of the pH. Therefore, non-acidophilic organisms should be considered. (Qu and Lian 2013) emitted the hypothesis that autotrophic acidophiles are not suitable for alkaline medium (red mud in their studies), and heterotrophic microbes should be preferred. The reasons are their tolerance for alkaline conditions and

their excretion of metabolites able to complexify toxic compounds of the medium, hence protecting the organisms. For their studies, (Qu and Lian 2013) used a fungus, *Penicillium tricolor* RM-10.

A thorough knowledge of chemistry and composition of the wastes can also facilitate the understanding of the dissolution of REE out of them. For instance, a Pourbaix diagram (a potential-pH diagram), shows stability regions for some metals. (Takeda, Uda, and Okabe 2014) as cited by (Peelman et al. 2014) showed that Nd^{3+} and Fe_2O_3 are stable in a pH range between 1 and 7, meaning a leaching with 0.02 HCl extracted 99% of Nd, but also more than 50% of Fe as a by-product. After roasting (6h at 900°C) less than 0.5% of Fe was leached. Even if this example comes from hydrometallurgical and pyrometallurgical processes, it shows that proper pre-processing of the wastes can improve the efficacy of biohydrometallurgical processes too.

A pulp density of 10% (W/v) gave the best yield with red mud and Penicillium tricolor RM-10 (Qu and Lian 2013). The usage of thiourea as a catalyser prevents oxidation of Ce^{+3} to Ce^{+4}, allowing it to leach with other REE by using HCl. Otherwise, in the Ce^{+4} form, cerium cannot leach properly (Yörükoğlu, Obut, and Girgin 2003) as cited by (Peelman et al. 2014).

1.5.8 Bioleaching mechanisms of e-wastes: examples
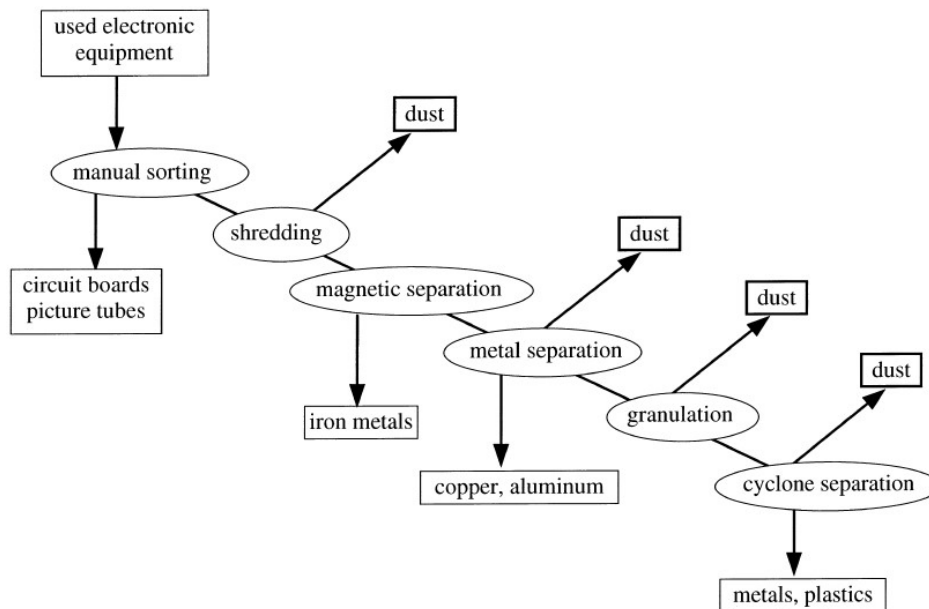*First preparations of e-wastes*

Figure 13: Preparation of the e-wastes before metallic retrieval. Illustration from (Brandl, Bosshard, and Wegmann 2001)

The initial steps leading to the preparation of the e-waste for bioleaching are included into the whole recycling process. These steps consist in the retrieval of elements (plastics, metals,

ceramic and glass particles) that can be easily recycled using already existing recycling efficient processes. These steps equally reduce considerably the initial volume of the waste, leading to the production of homogenous raw material. An example is displayed in Figure 13. After shredding, conductive metallic fragments are removed by magnetic separation, followed by the removal of other metals using electromagnetic separation. Plastic, silica glass components can be removed easily by physical separation (Reck and Graedel 2012). The most difficult fractions are the dust fractions and the metal-plastic fragments. Dust fractions (size below 0.5 mm) must be discarded or incinerated as classical processes cannot recycle them, even though they carry valuable metallic content in non-neglectable concentrations (for instance 237 g/kg for Al and 80 g/kg for Cu) (Brandl, Bosshard, and Wegmann 2001). As such, for these fragments, biohydrometallurgy can be used.

Bioleaching and copper solubilization

For this study, (Hong and Valix 2014) grown *A. thiooxidans* (ATCC8085) for 14 days at 30°C with elemental sulphur and harvested the produced sulphuric acid, which was then put in contact with crushed PCB wastes (size between 40 – 104 μm), to recover copper in particular. They first used abiotic conditions to find the critical parameters resulting of optimal copper dissolution. The parameters found during this first step were the temperature, the acid pH, the period of leaching, and the pulp density. They then fixed some parameters, while varying one. The ranges assessed were for the temperature of the reaction between 30 to 90 °C, the pulp density between 10 to 100 g/L, and the time between 0.5 to 24h. It was observed that at very low pH (pH < 1) the efficiency of copper dissolution was increased, certainly by getting rid of the passivation layer. For the pulp density, the more it increases, the less copper was recovery, with a plateau at a concentration of 50 g/L, meaning that there are abiotic reasons behind the decrease of efficiency and that it is not only due to toxic effects on the organisms. Then, they compared bioleaching and hydrometallurgy, by putting bacteria and sulphuric acid respectively in contact with the wastes at a concentration of 10 g/L at a temperature of 30°C and 90 °C once the pH of the medium reached a pH of 1. While at 30°C the results were not very different (less than 10% copper recovery after 120 hours), at 90 °C predictably abiotic leaching was much better than bioleaching (100% vs 60% recovery after 8 hours).

The reaction in place was the oxidation of elemental sulphur into sulphuric acid by *A. thiooxidans*:

$$S^0 + 1.5O_2 + H_2O \rightarrow 2H^+ + SO_4^{2-}$$
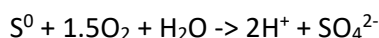
The protons being then able to solubilize the solid copper out of the e-wastes (Nandeesh and Sheshadri 1988):

$$2Cu^+ + O_2 + 4H^+ \rightarrow 2Cu^{2+} + H_2O$$
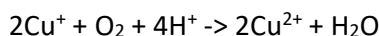
Finally, copper ion Cu^{2+} will react with sulphate ion SO_4^{2-} to give copper(II) sulfate, which can be further purified to pure copper through electrolysis (Parker and Muir 1981).

Another explanation of the solubilization of copper was made by (Choi et al. 2004). In this process, copper is oxidized thanks to $Fe_2(SO_4)^{2-}$:

$$Fe_2(SO_4)_3 + Cu \rightarrow Cu^{2+} + 2Fe^{2+} + 3SO_4^{2-}$$
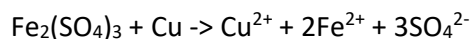
Bioleaching and gold solubilization

The goal of the experiment of (Faramarzi et al. 2004) was to retrieve gold out of PCB using *Chromobacterium violaceum* (*C. violaceum* DSMZ strain 30191), a cyanogenic bacterium (bacterium able to produce cyanide). They cut 5 mm by 10 mm pieces of PCBs, that was estimated to contain 10 mg of gold (gold has a concentration of 20 mg/kg in PCBs) and manually sorted valuable and non-valuable parts. As cyanide is a direct product of glycine, the authors also had to assess the optimal concentration of glycine, which was found to be between 8 and 10 g/L. After 4 days, the growth of *C. violaceum* reached a plateau and after 7 days the concentration of dicyanoaurate [$Au(CN)_2^-$] also reached a plateau at 0.8 mM. The efficiency of their experiment was therefore of 14.9% dissolution of gold embedded in waste PCBs. Unfortunately, the effect of the size on the dissolution rate was not assessed. In comparison, dust of electronic wastes of less than 0.5 mm were leached by *T. thiooxidans* and *T. ferrooxidans* and more than 90% of Al, Cu, Ni, and Zn were recovered (Brandl, Bosshard, and Wegmann 2001). Even though these are not precious metals, this experiment shows that the size of the fragments plays a non-neglectable part on the rate of recovery.

Specific case of biohydrometallurgy for REE

(Auerbach et al. 2019) utilized *A. ferrooxidans, A. thiooxidans,* and *L. ferrooxidans* at pH 2.2 or 1.8, 10 g/L of magnet powder (MQU-F sintering powder, at unknown sizes) at different temperatures for 14 days and in 40 ml of media. An up-scaling of the operation was also tested in a 3.5 L bioreactor for 3 days. To purify the REE bioleached, several techniques were used (precipitation with oxalic acid to separate from Fe, Liquid/liquid extraction with H_2SO_4, etc). It was shown that abiotic controls (with sulphuric acid) were less efficient at leaching than microorganisms leaching. 91% of Nd and 100% of Pr were leached thanks to *L. ferrooxidans*, and 86% Nd and 100% Pr with *A. ferrooxidans* (without mentioning more common metals such as Al and Cu).

(Qu and Lian 2013) worked with a fungus (*Penicillium tricolor* RM-10) and Red Mud (bauxite tailings, as previously seen). What is interesting here is the usage of a fungus and the working pH of 12.9, alkaline. A pH in which acidophiles cannot survive and in which other chemical reactions might occur. Furthermore, as e-wastes are alkaline, this fungus is a good candidate to work with. Lastly, 2% red mud pulp density seemed to have a stimulating effect on the growth of the fungus, also decreasing its lag phase. Growth should normally be maximal at 0% red mud pulp density, according to the authors.

Example of commercial application of biohydrometallurgy: BioCOP™ process

The BioCOP™ process, developed by BHP Billiton, is used at the Chuquicamata mine in Chile and produces 20 kilotons per year (Batty and Rorke 2006). It uses thermophilic archaea at 80°C to leach copper sulphides, without liberating toxic compounds, such as arsenic. Copper

is then purified using Solvent Extraction and ElectroWinning (SX/EX). Unfortunately, the species of the archaea was not specified in the study.

Several difficulties arose: archaea have no cell wall and therefore are very sensitive to shear stress. In consequence, only 2% pulp density was possible with low agitation. In addition, at a temperature of 80°C, partial pressure of oxygen is reduced by one third, forcing to use enriched oxygen gas (at least 90% v/v oxygen).

2. Recommendations and Conclusion

2.1 Increasing the efficiency of biohydrometallurgy

2.1.1 Present considerations

To increase yields and speeds of biologically-based metal extraction processes, several conditions must be fulfilled. Only the reactions that dissolve wanted metals should be promoted and all other reactions not directly linked to it or organisms' survival should be prevented. For instance, the ferrous ion oxidation provides only 30 kJ/mol of energy (Rohwerder et al. 2003). If the organism has a better way of replenishing its energy (thermodynamically more favourable), the ferrous ion oxidation will not be favoured (Haug 2019) and solubilization of metal will be severely decreased. A second important aspect to consider is the density of the pulp, or the ratio of between solid particles and the culture medium. To have the highest yield, one would saturate with maximum waste concentration the culture medium. By doing so however, the toxicity and physical stress on the microbes is high. Inhibiting growth and the pathways that are useful for the bioleaching process. To circumvent this problem, one can lower the pulp density until and/or wait for enough cellular density before putting scraps to have a higher proportion of surviving organisms. The third aspect that is a corollary is the rate of change of the medium. By regularly supplying fresh medium, toxic compounds are eliminated, while having a steady supply of nutrients. Furthermore, by recycling the medium often the yield would also be higher by taking out the product, as the equilibrium would be displaced towards the reactants (Le Chatelier's principle). Finally, e-wastes should be pre-treated to lower its toxicity and increase the efficiency of the process. It can be done mechanically to get rid of most of the plastic parts that can only hinder the process and to decrease the size of the scrap to accelerate the process.

2.1.2 Future advances

A better comprehension of the pathways involved, both chemical and physical, could help optimize biomining processes (Rohwerder et al. 2003). Genetic selection is already made to select the organisms that adapt the best to the process (Batty and Rorke 2006). Therefore, the next step could be, thanks to biotechnology, genetic manipulation to enhance resistance or bioleaching properties of some microbes and further increase the efficiency of the process.

Unfortunately, laboratories could patent such organisms and prevent exchange of data to improve the processes in place (Brierley 2010).

2.1.3 Proposition to retrieve Rare Earth Elements

From all these parameters, for our experiment to retrieve Rare Earth Elements, we should focus on low temperature. Otherwise, at higher temperature the solubility of the REE decreases. The question of pH is more complex. Electronic scraps are alkaline (Brandl, Bosshard, and Wegmann 2001), therefore alkaliphiles organisms are maybe more suited to handle high pH processes and detoxify wastes (Qu and Lian 2013). Most papers (J. Cui and Zhang 2008; Srichandan et al. 2019; Jia et al. 2019) studied acidophiles and the protocols are already in place and robust. Same comment goes for the bioleaching mechanisms (ferrous ion oxidation, thiosulfate and polysulfate pathways) that were extensively studied. However, biohydrometallurgy being a young science, both should be compared to gather valuable information. Organisms or consortia growing in mines in which REE are retrieved can be candidates for REE bioleaching, as they already can bear such conditions.

Proposition of process

Every parameter should be fixed as much as possible to optimize them, before generalizing this method. As such, first the type of e-wastes should be defined. Smartphones would be a good choice as the amount of common metals and REE is low, concentrated and almost constant. Then pure plastics, pure metallic parts and fragments containing both should be manually sorted. Only the latter should be studies and grinded to different sizes to study its effect. Then REE should targeted at low pH, first abiotically to measure the effect of pH on chemical properties of REE retrieval (creation of a passivation layer, modification of the Redox potential, etc.). Several bioleaching steps could be made, by targeting first one kind of metal (copper or gold, as the examples in the literature is already abundant) and then targeting REE. This way, the remainder after the first extraction is already more concentrated in REE and should be easier to recover. All these reactions should occur at standard conditions of temperature using a growth medium which was already optimized for the culture of the selected organisms and slurry density at ca. 10 % (W/v).

In a second time, high pH, complexifying agents, size of powder, time duration can be studied, following the same steps, as well as physical or chemical preparations of the samples before bioleaching.

2.2 Conclusion

It has been shown that landfills contain more material than naturally occurring ores, giving it the name of "urban mines" (Kuroda and Ueda 2011) and accentuating the value of waste recycling, instead of mining new areas. Furthermore, ores containing REE are available only in a few locations and can be retrieved after extensive extraction, preventing easy retrieval (Corbett et al. 2017; Bru et al. 2015; Peelman et al. 2014). While e-wastes may contain 10

times more REE than natural ores (Cesaro et al. 2017). Therefore, this is also a way to "shift power" from a few countries owning large amounts of valuable material to a fairer distribution, as these wastes could be valorised directly where they were produced, bearing in mind also that the demand for REE will not decrease in the short term. In 2016, REE consumption was expected to grow 5% per year until 2020 (Ayora et al. 2016). At the level of Europe or the United-States, it would even have a geostrategic advantage to retrieve valuable metals out of their own wastes, as they would not be dependent on a restricted number of producers anymore. In addition, to decrease dependency on fossil fuels, countries rely on renewable energy (solar panels and wind turbines). The trade-off of the latter solution being large metal consumption (Hertwich, de Lardel, and Suh 2016). (Jacobson and Delucchi 2011) calculated that more than 3.8 million of 5 MW wind turbines are needed to reach the COP21 ambitions. Knowing that each MW needs 155 kg of Nd, 27.5 kg of Pr, and 2.8 to 24 kg of Dy (Bru et al. 2015) will trigger tensions over these resources as each country will want to secure its supply of REE to be able to ensure sufficient energy supply to its society. One way to increase the likelihood of recycling initiatives is to make them affordable: cheap and easy to do. Biomining once its processes have been thoroughly researched and understood can fulfil these requirements. Furthermore, compared to other recycling processes such as pyrometallurgy and hydrometallurgy, it is "almost without exception more environmentally friendly" (Rawlings 2002) and is therefore a good solution to meet sustainable development requirements. In addition, the burden of mining is unfairly shared: most pollution and health issues resulting of mining sites and landfills are bore by low income countries. Finally, Earth is a finite resource system. The richest ores are becoming depleted and processing poorer ores will become more and more challenging, hence forcing society to secure another supply chain. Going from a linear to a circular economy in close loop (Voulvoulis 2018) would not decrease the standards and the quality of life.

The area needed for bioleaching processes can be adaptable and modulable. Bioreactors of 300 m^3 are used for copper biomining (Batty and Rorke 2006). One of these bioreactors could be used at the scale of a small country or a region and process its e-wastes to create wealth and jobs. Switzerland that has a good transport system, a functioning organization and qualified workers, recollection and gathering of the waste could be easy. As it was done in Japan for the making of the medals using used phones for the next Olympic games. A company could do it and even import waste from the neighbouring countries to create wealth.

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4. References

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