Protection of Water Resources in Mining Sites in Northeast of Algeria



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Abstract Mining is a sector of activity essential in global economic development. These metals and minerals extracted by the mining industry are integrated in several consumer goods. Given the increase in the population and the demand for these goods, the mining industry is growing globally from a few decades.

This type of industry is responsible for several impacts during each phase of the mining process. In particular, it is during the exploitation phase that the natural ecosystems, located above the deposits, are destroyed by the elimination of soil and vegetation and the establishment of storage sites for discharge mining. Thus, the extraction of mineral resources has a definite duration, whereas the associated environmental impacts can be visible indefinitely if no corrective measures are taken. This is why, when extraction is complete, the restoration phase is just as important as it addresses these impacts by rebuilding new ecosystems and giving the site a natural look through revegetation. Responsible catering also ensures that the positive social and economic impacts of mining are sustainable for future generations.

Keywords Mining environment, Natural ecosystems, Restoration of mining sites

1 Introduction

The society is dependent on the mines that supply it with the minerals and metals needed to make things that we use every day, such as trucks, ATVs, boats, and homes. Mineral and metal products can easily be recognized in our daily lives.

Copper cabling in our homes, nickel in our stainless steel sinks, gypsum in our walls, silica in the windows of our windows, and the salt we use in our food, all come from the extraction of minerals and metals from the earth. In addition, various other metals such as zinc, silver, gold, platinum group metals, and rare earth elements are used in the production of many parts of our automobiles and electronic equipment components in our homes, like computers, stereos, and televisions.

Mining has been part of the life and economy of Aboriginal communities for generations. Aboriginal peoples did not just use the rocks as they were; they also extracted materials for a variety of purposes, including making tools, weapons, and decorative items.

Exploration and mining activities can make an important contribution to the prosperity and well-being of Aboriginal communities. For many indigenous communities, the exploitation of natural resources, including mineral resources, is the

main driver of socioeconomic development and diversification of the regional economy. Mineral exploration offers employment and skills development opportunities depending on the stage of the project. Well planned, a mine can generate benefits that will survive and strengthen the community's autonomy.

Without forgetting that the mining activities can have significant and long-lasting effects on the environment, there are many examples of good and bad mining operations and rehabilitation. Environmental damage associated with mineral extraction is having an increasing impact on the mining industry and the workforce it employs.

2 History and Current Situation of Mining Sector (According to the Ministry of Industry and Mines)

Before independence (1962), mining activity in Algeria was mainly oriented toward the exploitation of iron and lead-zinc deposits. Between the two world wars, Algeria was a major producer of iron ore in the world; its production contributed to the prosperity of the processing industries of several European countries, in particular France, Great Britain, and Germany.

During the 1950s, particularly during the National Liberation War, foreign mining companies accelerated the process of skimming deposits and limited or even stopped all investment in this sector.

After independence, foreign operators abandoned several mines after making the most of them; only "viable" mines remained in operation, such as phosphate, zinc, iron, barite, coal, and salt mines.

The nationalization of the mines, which took place on May 6, 1966, was followed on May 11, 1967, by the creation of the National Research and Mining Corporation (SONAREM) (http://www.mdipi.gov.dz/?PRESENTATION-DU-SECTEUR-DES-MINES).

It was from that date that the national mining activity was organized for research and exploitation of mineral substances until 1983, when SONAREM's restructuring took place.

During this period, major efforts were made by the state and led to a number of actions, in particular:

- The launch of major research programs to reopen abandoned mines, increase the reserves of active mines, and discover new deposits
- · The restoration of the production equipment
- The opening of new mines
- The training of qualified personnel

This plan for the recovery of the mining sector has made it possible to:

- Extend the life of several mines (iron, polymetals, and nonmetallic substances)
- Build several mining complexes (mercury, lead-zinc, and nonmetallic substances)

- Reconvert the activities of mines whose reserves were exhausted
- Conquer new external markets through the placement of a wide range of mining products such as phosphate, mercury, barite, iron ore, bentonite, kieselguhr, zinc, and lead concentrates.
- Establish a high-quality basic national geological infrastructure, accompanied by systematic exploration of the entire national territory, which has made it possible to inventory a large number of deposits and showings, some of which offer real development prospects.

From 1983 to the present day, the main highlights have been:

- The restructuring of the National Research and Mining Corporation (SONAREM) with the creation of six major mining companies: FERPHOS, EREM, ENOF, ENAMARBRE, ENASEL, and ENG.
- The creation of an industrial mining group MANAL Spa in 2010 bringing together all public companies in the mining sector.

2.1 Partnership in Mining Sector

Algerian mining resources offer significant investment opportunities through multiple partnership operations. Mining legislation now allows access to exploration, development, and exploitation of mining resources by private capital.

The targets of associations may be regions and districts to be explored, deposits to be evaluated for exploitation, or deposits already evaluated for development after feasibility studies have been carried out, as well as deposits currently underexploited such as phosphates, iron, gold, etc.

2.2 Development Axes in Mining Sector

Today, the country has a fairly well-developed geological infrastructure, numerous and high-quality previous works, geological engineers, and qualified miners.

For development, it should be recalled that the mining sector includes all mining activities intended to produce useful minerals or ores: metals and industrial and construction materials.

The main objective is therefore to stimulate a new development momentum in the mining sector so that it contributes substantially to economic recovery and plays a significant role in the national economy.

The development objectives envisaged include, among others, the following:

- The continuation by mining operators of efforts to modernize their production facilities
- The search for foreign partners with technical and financial capacities for the development of mining activities

- The implementation of projects to develop mining products such as phosphates, salt, marble, nonmetallic substances, gold, diamonds, etc.
- Increased export of mining products
- The intensification of mining research
- Partnership development of under- or underexploited mining resources

3 Acid Mining Drainage Training Process

3.1 Acid Mine Drainage

The term "acid mine drainage" (AMD) refers to a complex set of chemical reactions that occur when rocks containing sulfur are exposed to water and oxygen. In many ways, this process is similar to other natural processes such as weathering or rusting.

When oxygen and water come into contact with rocks containing sulfur, acid is produced. This acid can dissolve metals from surrounding rocks that will be released into the soil and surface water. High concentrations of metals and acid can be harmful to fish and other aquatic life.

3.2 Acid Mine Drainage Formation

The natural mineralization of the subsoil is due to the circulations of the fluid that carries metal cations that will be trapped in the reducing horizons. Gold mining has or will abruptly change the oxidation-reduction conditions at the origin of the deposit by denuding the rocks and exposing them to oxygen in the air.

An exploited mine represents several kilometers of tunnels (a few hundred kilometers, sometimes several thousand). These are all conduits likely to bring water and oxygen in contact with the ore. Open pit and quarry materials, by definition, are subject to atmospheric conditions. AMD's are formed, either in the flooded galleries (Fig. 1) or by the percolation of water on the piles of excavated solids containing sulfides.

These materials extracted from the mine are of different types: sometimes containing sulphides (sterile franc) and minerals low in sulphides (halides, sterile selectivity) or reject treatment poor in precious metals but rich in sulfide.

When rocks containing sulfur are present in a rock formation, only small amounts come into contact with oxygen during natural weathering. Oxygen and water in the atmosphere react with exposed rock surfaces, inducing the production of small amounts of acid. The natural environment can often neutralize and/or dilute these small quantities.

During the mining activity, rock fragmentation and crushing exacerbate acid mine drainage as a result of the increased amount of rock surfaces exposed to oxygen and water in the atmosphere. The atmosphere has been observed to react



Fig. 1 Acid mine drainage formation [1]

with exposed rock surfaces, inducing the production of small amounts of acid. The natural environment can often neutralize and/or dilute these small quantities.

This phenomenon is accelerated by the presence of the bacterium *Thiobacillus ferrooxidans*, which considerably increases the speed of chemical reactions. *Thiobacillus ferrooxidans* cells grown on ferrous iron oxidized sulfite to sulfate at pH 3, possibly by a free radical mechanism involving iron and cytochrome oxidase.

The bacterium uses the sulfur present in the rocks as a source of energy, and, when the conditions are suitable, it can act as a real catalyst of the chemical reactions present.

The main chemical reactions that give rise to DMA are the oxidation of iron and sulfur in pyrite, the most common sulfide mineral. This reaction takes place in the presence or absence of bacteria according to the equation:

$$4\text{FeS}_2 + 15\text{O}_2 + 14\text{H}_2\text{O} \rightarrow 4\text{Fe} (\text{OH})_3 + 8\text{H}_2\text{SO}_4$$

This is of course only a balance equation: the oxidation process of the pyrite varies according to the evolution of the ph. The peculiarity of this reaction is to be auto-catalyzed, which allows the phenomenon of DMA production to propagate in a similar way to a fire: just as combustion produces heat that triggers the combustion of other materials, sulfide oxidation produces ferric iron, which causes oxidation of other sulfides.

The mechanism of DMA formation is related to the presence of sulfides (S^{2-} and S_2^{2-}), sulfur (S^0), or thiosulfate ($S_2O_3^{2-}$) with water and oxygen. The most common sulfide mineral present at mine sites is pyrite (FeS₂). The oxidation of pyrite is the main cause of acid mine drainage [2] (Fig. 2).

However, other sulfide minerals also participate in the DMA phenomenon, such as sphalerite (ZnS), galena (PbS), chalcopyrite (CuFeS₂), pyrrhotite (Fe₇S₈), and arsenopyrite (FeAsS). The oxidation of pyrite is governed by a set of reactions and takes place in three phases [3].

The first step, oxidation with oxygen, is an initiation step. It occurs in the presence or absence of bacteria. The pH is then greater than 4.5 and progressively acidifies.



The reaction is relatively slow, and the kinetics of the reaction decreases as the pH decreases. Both are essentially controlled by the availability of oxygen.

The second step, the oxidation of ferrous ion to ferric ion, is decisive. It becomes preponderant in the reaction with the progressive acidification of the medium: the pH becomes less than 4.5, which allows the ferric iron to remain in solution. The ratio Fe^{3+}/Fe^{2+} is still low and then increases gradually. The importance of this reaction lies in the fact that it produces ferric iron which will be able in turn to react in chain on the pyrite (Fig. 2).

4 Heavy Metals Pollution

The most studied metals in the field of the environment are generally arsenic (As), cadmium (Cd), chromium (Cr), copper (Cu), manganese (Mn), mercury (Hg), nickel (Ni), lead (Pb), and zinc (Zn) due to their abundance and toxic effects.

Naturally present in the geochemical seabed, metal pollutants can also be of anthropogenic origin. The extracted sediments can be compared to a polluting source [5].

The most important chemical processes influencing the fate and mobility of ETM are induced by transfer mechanisms between the solid and liquid phases [6, 7]. The availability of ETM depends considerably on the surface properties of particles, physic-chemical conditions of the environment such as pH and Eh, and salinity and biological processes [8]. The main constituents of soils and sediments likely to bind ETMs are clays.

EAU



Fig. 3 Schematic representation of a water-sediment exchange system [9]

Indeed, their negative charge makes them suitable for forming electrostatic bonds with any positively charged entity present in the liquid phase, such as metal cations (M^{2+}) . Other components of the solid phase also have an important role in the availability of heavy metals, such as carbonates, silicates, iron and manganese oxides, and hydroxides and organic matter.

It is often difficult, in the case of complex media such as soils and sediments, to predict the mechanisms responsible for the fixation and mobility of ETM and to describe these complex media in a "standard" way [8].

Nevertheless, the most important physic-chemical mechanisms involved in these transfers are: ionic exchanges (or nonspecific adsorption), specific adsorption on mineralogical phases (surface complexing), complexing by organic matter, and finally precipitation and coprecipitation phenomena (Fig. 3) [9, 10]. Depending on the physic-chemical conditions of the environment, one of the retention processes will always be predominant in a total interaction between contaminants, mineral species, and organic matter.

Our literature review was limited to these minerals, mercury (Hg), copper (Cu), lead (Pb), zinc (Zn), and iron (Fe).

4.1 Mercury (Hg)

Mercury is the element close to gold in the periodic table of elements and one of the alchemist's favorite. It has the particularity of being the only metal that is liquid at room temperature. It occurs naturally in the form of sulfide cinnabar and is used mainly for physics instruments and gold mining. Known since ancient times, mercury was very quickly used to amalgamate gold. It was referred to as lively silver from the sixteenth to the nineteenth century. Alchemists associated it with the planet Mercury, which explains its current name. The symbol Hg comes from the Greek hydrargyrum for "cash."

Mercury is a compound that can be found naturally in nature, in metallic form, as salts or in organic compounds. Mercury is not naturally present in food, but mercury can be found in food, as it can diffuse into the food chain through smaller organisms that are eaten by humans, such as fish. Mercury is a very toxic element for humans, regardless of the compound and the degree of oxidation. It binds easily in organic matter and metabolic processes. It is then found in methylated form. In addition, it is very mobile, as it is volatile at room temperature. Among its harmful effects on the body, it affects brain function and the kidneys. It could also be an endocrine disruptor and cause cancer. Mercury is also cytotoxic to stem cells in the central nervous system.

It enters the environment when minerals naturally break down in rocks and soil exposed to wind and water. The dispersion of mercury from natural sources has remained about the same over the years. However, the concentration of mercury in the environment is constantly increasing; this is due to human activity.

Most of the mercury released by human activities is released into the air through fossil fuel combustion, mining, smelting, and solid waste combustion. Some activities release mercury directly to land or water, such as the application of agricultural fertilizers and industrial wastewater discharges. All mercury released to the environment eventually ends up in soils or surface waters.

Acidic surface waters can contain a significant amount of mercury. When the pH is between 5 and 7, mercury concentrations in water increase because mercury is mobilized from the soil. Once mercury has reached surface waters or soils, microorganisms can transform it into mercury methyl, a substance that can be rapidly absorbed by most organisms and is known to cause nerve damage.

4.2 Copper (Cu)

Copper is relatively scarce on earth. It is present in 0.007% of the earth's crust (lithosphere) and 0.002% of the soil [7]. It is one of the few metals present in its native state in the environment. However, it is more frequently found in the form of sulfide ores such as chalcocite (Cu₂S) and chalcopyrite (CuFeS₂) [11].

The presence of copper in a given environment can be of natural origin, through erosion, volcanism, and vegetation. However, generally, the main contributions to the environment are anthropogenic and linked to the metallurgy industries.

In soils as well as in sediments, ETMs are distributed between the different carrier phases and/or fractions of the matrix according to the physic-chemical conditions governing the environment and the specific retention energies specific to each element. In these matrices, copper can be associated, complexed, precipitated, and adsorbed on six different carrier phases and/or fractions.

World copper production is still increasing. This means that more and more copper is entering the environment. Rivers deposit copper-contaminated sludge on their banks as a result of wastewater discharge. Copper enters the air mainly during the combustion of fossil fuels. It remains in the air for a long enough period before settling when it rains. It is then mainly found in the soil. As a result, soils can contain a large amount of copper after the copper from the air has settled.

Copper can be released into the environment from natural sources and human activities. Examples of natural sources include windblown dust, rotting vegetation, forest fires, and dispersed seawater droplets. Some examples of human activity contributing to copper dispersion have already been given; other examples are mining, metal production, wood production, and phosphate fertilizer production.

Since copper is dispersed by both natural and human processes, it is very widely distributed in the environment. It is often found near mines, industrial facilities, landfills, and garbage crushers. When copper is found in the soil, it binds strongly to organic matter and minerals. As a result, it does not travel very far and rarely enters groundwater. In surface waters, copper can travel long distances, whether suspended on mud particles or as a free ion.

Copper is not destroyed in the environment, and, as a result, it can accumulate in plants and animals when it is present in the soil. On copper-rich soils, only a limited number of plants are likely to survive.

4.3 Lead (Pb)

Lead is a soft metal that has had many applications over the years. It has been widely used since 500 BC in metal products, cables, pipes, but also in paints and pesticides. Lead is one of the four most harmful metals to health. It can enter the human body when ingesting food (65%), water (20%), or air (15%).

Lead is naturally present in the environment. However, most lead concentrations in the environment are the result of human activities. Lead cannot be destroyed; it can only change shape. Lead is a particularly dangerous chemical because it can accumulate in individual organisms but also the entire food chain.

4.4 Iron (Fe)

Since the Iron Age, there have been many iron mines around the world. Iron (Fe) is undoubtedly the most important metal, either because of its abundance in nature or because of the uses made of it. It is found in its native state, especially in the states of magnetite, oligist, limonite, siderite, and pyrite. Iron is rare in its native or pure state. Apart from a few large blocks found in Greenland basalt where iron is mixed with carbon, native iron is only found in meteorites or rocks that have fallen from the sky.

Iron can be found in its natural state in: magnetite (Fe_3O_4), oligist (Fe_2O_3), siderite ($FeCO_3$), and pyrite (FeS_2).

Iron (III)-O-arsenite, pentahydrate can be dangerous for the environment. Particular attention should be paid to plants, air, and water. It is strongly recommended not to allow the chemical to enter the environment because it persists in the environment.

Iron mines played an important role in the Industrial Revolution. Iron deposits in rocks are usually in the form of oxides, such as hematite. Production costs in the iron and steel industry are based on the distance between mines, steel mills, and blast furnaces. The case of the Boukhadra and Ouenza mines in the province of Tebessa and the Mittal Steelworks in Annaba.

4.5 Zinc (Zn)

Zinc is the third most widely produced transition metal (after iron and copper) and is best known for its good corrosion resistance, from industrial steels to roofs. Zinc has been known since ancient times, although it was not used in its pure form. Zinc has a much less chalcophilic character than lead and copper; we will speak of a more lithophilic character.

The most common zinc ores found in nature are however sphalerite (ZnS) and smithsonite (ZnCO₃). Sphalerite is fairly uniformly distributed in magmatic rocks (40-120 mg/kg).

Zinc deposits are of magmatic origin, known as primary or sedimentary, known as secondary. Zinc ores are often associated with lead, copper, and iron ores. The main zinc ore deposits are located in China and Australia.

In 1990, the deposits mined were also located in Peru, the United States (including the Red Dog mine in Alaska), Canada, Mexico, Russia (CIS), the Democratic Republic of Congo, Zimbabwe and South Africa, Japan, Morocco, Spain, Ireland, Sweden, Switzerland, Poland, and the Balkans, as well as Bulgaria. Their minimum contents were 40 kg per ton.

Zinc is one of the metallic trace elements that becomes a contaminant and a pollutant beyond the doses that make it ecotoxic (which vary according to the species and the context, e.g., it is more mobile and bioavailable in an acidic environment than in a basic one).

5 Mine Impacts on the Environment and Human Health

The use of metals and rare elements which accompany the development of human societies has led to mining, transformation, and waste elimination all of which are or can be a source of environmental contamination. The use of minerals, materials, and fuels which contain these elements, the intensification of underground water pumping, and other physical or chemical modifications of the soil also induce contaminations through transfers which add to the natural fluxes (alteration, volcanism, erosion) [12].

From the characteristics of use and the risk-related factors particular to each element, four elements stand out as particularly worrisome:

- Mercury is a dangerous contaminant of aquatic environments and even of the atmosphere. Its use is increasingly forbidden. However, the production of waste, the existence of old soil pollution, its considerable capacity for bioconcentration, and the increase in fish consumption are all risk factors. More consideration should be focused on sediments and water.
- Lead has great mobility in non-acid soils. The risk comes from former accumulation of important stocks within the soil surface layers, from which it does not get eliminated rapidly, and from continued deposits which are diminishing. However, some portions of the population remain affected, for example, by latent and irreversible effects on child development which are now well characterized. However, the worst risk is presented by the presence of old paint in older buildings and in old water pipes which distribute acidic water.
- Cadmium is mobile, and its applications are much more dispersive than in the case of lead. Contaminating quantities are much lower, but its toxicity is proportionally much higher. The risk it represents in soils necessitates particular vigilance.
- Arsenic is a naturally occurring and highly ubiquitous mobile element in the soil. Because it is rarely used, the risk mainly comes from water contamination due to circulation in the soil and underground. The recognition of its carcinogenic potential incites increased vigilance.
- The other elements are less problematic, because they remain rare in the soil (this is the case of tin, selenium, and other metals which are sometimes very toxic but have a specific use) or they are found in chemical forms which are only toxic at exceptionally high concentrations (this is the case for copper, zinc, nickel, which are essential trace elements, and even chromium).

5.1 Abandoned Mines

Thousands of abandoned mines are sleeping under the mountains. While they hold wonderful secrets, they also present many dangers, and that is why the government must condemn access and at the same time rehabilitate abandoned sites.

Taking the example of the United States and more precisely the West, an underground world testifies to the turbulent past of the once-promising far west. There are tens of thousands of abandoned mines, created at a time when everyone could take their chances and dig to the grave. However, once the coveted raw materials were extracted, the mines were simply left to fend for themselves without further consideration.

However, neither the closure of a mine nor the surrender of a mining title puts an end to a situation of physical and environmental risks. On the contrary, the risks associated with collapses, groundwater rise, floods, pollution, risks to the groundwater, gas risks (firedamp, CO, CO₂, radon and sometimes H₂S, mercury, sulfur gases, etc.), radiological risks, etc. will often persist over time and may even get worse.

As in the case of the Ismail mine, it ceased all activity in 2005, but unfortunately no rehabilitation operations were undertaken. Already, 12 years of closure and abandonment, but the pollution problem persists to this day. Traces of mercury have been detected on site, in soils and water. The iron mine of El Khanguet closed since 1966, located in Tebessa in northeast Algeria. The waste rock left in the mine site had a negative impact on the soil and water of the area [13].

5.2 Active Mines

Algeria has an interesting geological potential for investment and partnership in mineral exploration, development, and production of certain mineral substances. Despite this, the mining sector has remained very unproductive in relation to the potential of our country, which is particularly significant for nonmetallic useful substances such as phosphates, salt, marble, etc.

The disruptions in the world market for mineral raw materials and metals that have shaken the world economy dictate the implementation of strategies to mitigate the various shocks suffered by all countries, particularly developing countries, which hinder or delay their economic and social development.

Since independence, Algeria has striven to establish a mining sector that can respond to its concerns. In the mining sector, a major prospecting effort has been made over the past 30 years to develop the basic geological infrastructure and to inventory a large number of deposits and showings, some of which offer real investment prospects for their exploitation. It is on this basis that the Algerian state has decided to promote and develop this potential. As such, partnership formulas are offered to foreign investment, combined with incentives for both exploration and mining.

6 Case Study

6.1 History of Ismail Mercury Mine

The mercurial complex "Ismail" is located in Azzaba area; it is the only one in the country and the largest in Africa. This mercurial complex is composed of three deposits "Ismail, Guenicha, Mra sma" with a monometallic mineralization which forms cinnabar HgS. This complex was closed since 2005 without any rehabilitation operation. After 12 years of closure, the formation of mercury droplets in the factory compound has occurred so far due to climate change.

The name of the Ismail deposit is the name of a driver who found mercury in liquid form in northeastern Algeria for the first time in a long time (colonial period). Then, several polymetallic showings were reported in the North-Numidique zone. Others were highlighted during studies on the region's mercurial potential, carried out by the Soviets in the 1970s.

In 1971, the Ismail mercurial complex was installed and commissioned by ENOF to exploit the deposit. The majority of its production was destined for export to Germany, France, and other Asian countries. It also supplied the electrolysis process of the Skikda petrochemical complex.

Production was stopped in the second half of 2003 for a few months in order to rehabilitate the equipment of the mine and complex, as well as to strengthen work with the installation of a second furnace in order to restart production in January 2005.

Following the drop in production, a mercury pot produced in the 1970s and 1980s 300,000 while it produces 5,000 in recent years and due to its impact on the environment. The mine was closed under ministerial order in 2005 after 35 years of operation without any cleanup operations.

In 2006, following a visit to the site by a team from the Ministry of Environment, a decision was taken to start the cleanup work. As a result, studies have been carried out in collaboration with the French company GenCos in order to carry out rehabilitation work in the coming days. Something that has not been done is what prompted us to conduct this study.

6.2 Physical Setting of Study Area

The Ismail deposit is located 6 km southwest of the town of Azzaba province of Skikda on the left bank of the Fendek wadi valley and the north flank of the numidic chain. The mercurial complex of Ismail was located 2 km from Zaouia (Azzaba – Skikda) (Fig. 4).





Fig. 4 Geographical location of the Ismail mine and the industrial mining complex [14, 15]

The morphology of our study area, which is part of Azzaba, has two different areas:

- One is an elevated area forming the surrounding mountains.
- The other one corresponds to the Azzaba depression.

The relief of the region is very uneven; the most important orographic elements are part of the numidian chain. The east-west facing massifs extend from Ghedir Mountain in the West to Chbebik Mountain in the East.

The highest ranges, Tengout Mountain and Saiafa Mountain reach 648 m and 496 m, respectively; they are reliefs of quartz sandstone or limestone sandstone covered with cork oak forests. To the east are the limestone and bare mountains, Mazeur mountain 473 m, Moulmdefa mountain 572 m, and Chbebik mountain 447 m, and finally in the center are the gneissic and schistose mountains peaking at 464 at Raout-Lessoued mountain.

The Azzaba low communicates in the West with Ramdane Djamel's at the Ras El Ma meridian and leads to the Fedzara low in the East.

- *Hydro-climatological Overview*, the Azzaba region has a relatively mild Mediterranean to subtropical climate. It is characterized by:
 - A hot and dry season spread over about 5 months, from May to September, characterized by an average monthly temperature of around 23°C. During this season, there are warm winds (sirocco) from the south.
 - A cold and humid season from October to April, characterized by a seasonal average temperature of around 14°C, with an average rainfall of around 82 mm.

As a result of these climatic conditions, typical vegetation has developed in the region. In the plain, there are mainly market gardening, cereals, as well as orangeries and vines. On the mountain slopes, a degraded forest cover develops with some groups of cork oaks and olive trees.

The inhabitants, who are mainly farmers, obtain excellent products in wheat, barley, corn, millet, melons, watermelons, etc.

In addition, this territory is generally wooded; cork oaks, holm oaks, ash trees, elm trees, and poplars are the most numerous species.

- *Hydrographic network* is not very dense; it is mainly composed of temporary wadi, namely:
 - In the mountains delimiting the slopes, thalwegs are ordered and form deep notches that facilitate the drainage of surface runoff.
 - In the plain, the wadi is few in number and shallow. The main wadi is
- Fendek wadi with a south to the north flow of water.
- The Adjoul Wadi is the collector of several small wadis and flows north-east.

These two wadis join the Mchekel Wadi in the northeast of Azzaba. They are characterized during dry periods by thin water drips, while during rainy seasons, the regime becomes turbulent. Mchekel wadi flows toward Kebir wadi, which flows into the sea to the east of Skikda (near iron cap) (Fig. 5).

• *Socioeconomic overview*, Azzaba town is a more or less developed urban center. It currently has a fairly large industrial expansion resulting in the depopulation of isolated areas, thus favoring a concentration majority of the surrounding population.



Fig. 5 Hydrographic network of the study area [14]

The Azzaba plain is essentially an agricultural region where market gardening and cereals are widely developed. The main economic resources of the region were mining and agriculture.

6.3 Geological and Mineralogical Study

The Ismail mining field contains three deposits: Ras El Ma, Ismail, and Guenicha. The geological structure of the study area and neighboring territory includes four (4) different units [16]:

- 1. The sub-Aboriginal unit of the Kabyle Ridge
- 2. The allochthone Kabyle unit
- 3. The allochthone flysch unit
- 4. The numidian unit

The sub-Aboriginal unit of the Kabyle Ridge forms a narrow zone (4–8 km), subdivided according to J.M. Vila into two (2) subzones, namely:

- The inner sub-area that borders the Kabyle unit to the north
- The external sub-area that borders the flysch units to the south [16, 17]

To the north and south of Azzaba [16], the flysch unit is more developed, it occupies an important place in the geological structure of the region, the outcrop of its formations which are limestone, sandstone, and clay breccias is in the form of a cover, and the correlation of some of its parts is difficult to establish (Fig. 6).



Fig. 6 Geological map of the Azzaba region [18]

So mercurial and polymetallic mineralization are separated over time. The formation of cinnabar is later than polymetallic mineralization, so the major control of mineralization is structural.

All the mercurial deposits exploited in Azzaba are subdivided into two mining fields:

- Ismail mining field (Ismail, Guenicha, and Ras El Ma)
- Mra sma mining field (Mra sma I, Mra sma II, Koudietsma)

Mercurial mineralization is expressed in the form of cinnabar, of which it is associated with another polymetallic mineralization consisting of galena, sphalerite, chalcopyrite, and pyrite. There are many alteration minerals such as malachite, azurite, iron oxide, and hydroxide, gangue is composed of barite, quartz, calcite, dolomite, gypsum, and kaolinite.

This mineralization is hosted in carbonate and sandstone formations, and it generally occurs in clusters; the mining method in all deposits is open-pit. Mercurial mineralization is in the form of cinnabar, of which it is associated with another polymetallic mineralization consisting of galena, sphalerite, chalcopyrite, and pyrite; there are many alteration minerals such as malachite, azurite, oxide, and iron hydroxide; gangue is composed of barite, quartz, calcite, dolomite, gypsum, and kaolinite. This mineralization is hosted in carbonate and sandstone formations; it generally occurs in clusters; the mining method in all deposits is open-pit.

Ismail The mineralized body is stratiform of medium dimensions: length 520 m, width 60 m, power 64 m; it forms two lenticular clusters [19, 20] (Fig. 7, Table 1).

Guenicha Consists of three mineralized bodies, of which bodies two and three are part of a single large cluster measuring 540 m long (Fig. 8, Table 2).



Fig. 7 Ismail's career [15]

Table 1	Perimeter coor	dinates of the Is	mail deposit [2	1]						
Pt	A	В	С	D	Е	F	G	Н	I	J
X	889,918	889,897	889,880	889,990	889,860	890,181	890,373	890,320	890,310	889,970
Y	385,133	385,110	385,465	385,678	385,678	385,661	385,480	385,380	385,210	385,099

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Fig. 8 Guenicha's career [15]

Mra sma I and II, the body is in the form of irregular pockets, 19 m long and 3-4 m (powerful), and appears in fine spread with a stratoid appearance of 47 m, sometimes in veins of metric length and width centimetric to decametric (Fig. 9, Table 3).

In the study area, the ore textures show two different aspects: friable and compact ore [20]; these two types are distinguished from the rock that holds them:

- Friable (powdery) ore, in the form of debris, isolated angular and rounded grains, it is associated with the following surrounding rocks: clays, clays, and dolomites.
- Compact ore occurs in clusters and disseminations and is associated with the following sedimentary rocks: quartzite sandstone, and detrital limestone (Fig. 10).
- In the study area, the ore textures show two different aspects: friable and compact ore; these two types are different from the rock that holds them.
- Friable (powdery) ore, in the form of debris, isolated angular and rounded grains, it is associated with the following surrounding rocks: clays, clays, and dolomites.
- Compact ore, it occurs in clusters and disseminations, associated with the following sedimentary rocks: sandstone, quartzite, and detrital limestone.
- The macroscopic and microscopic study allowed us to identify the following minerals and establish their paragenetic succession.

Table 2	Coordinates o	of the perimeter	of the Guenich	a deposit [21]							
Pt	Α	В	С	D	Е	ц	G	H		I	ſ
x	892,395	892,118	892,118	892,018	891,940	891,758	891,585	8	01,502	89,137,708	891,169
Y	386,940	386,635	386,445	386,465	386,527	386,540	386,435	38	36,435	386,407	386,700
Pt	K	L	M	z	0	Р		Ø	R		S
x	891,015	891,085	891,285	891,390	891,52	5 891	638	891,892	8	92,140	892,195
Y	387,075	387,365	387,293	387,365	387,38	5 387.	365	387,365	3	87,352	387,155

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Fig. 9 Mra sma I and II [15]

6.3.1 Primary Minerals

- Cinnabar (HgS, rhombohedral): (Fig. 11a–d) it is the main mineral of the deposit, is distinguished by its earthy red-brown color, and often presents two generations.
- In Ismail, it is found as small granular masses of dark red color, irregular shape (Guenicha), or as veinlets or breach cement, disseminated in Priabonian sandstones (Ismail).
- At Mra sma, it forms plasters and filonites that fill fine cracks in sandstones and quartzites.

Under a microscope, in polarized light, it exhibits a clear anisotropy with massive red internal reflections.

- Metacinnabar (HgS, cubic): is presented in the form of small black isometric grains and forms aggregates and coatings following the walls of the cracks, sometimes impregnated in the surrounding rocks; it is always in association with the cinnabar. Under a microscope, it is grey-white with a lower reflectivity than cinnabar; it is isotropic in polarized light.
- Galena (PbS): characterizes the Mra sma mining field; it occurs in two forms, in small crystals irregularly distributed in mercury ores or impregnation and crystal grouping.

Microscopically, it has a grey color and is characterized by triangular pullouts.

- Sphalerite (ZnS): occurs in sub-automorphic grains, with dimensions in the millimeter range; it appears as an impregnation of small crystals of greyish color and has internal dark red reflections.
- Pyrite (FeS₂): it is present in the form of small grains of isometric shapes, light yellow; it is also found in fine spread in the silicified gangue.

Table .	3 Perimeter co	oordinates of th	he Mra sma I	and II deposit							
Pt	А	В	С	D	Е	F	G	Н	I	J	K
x	897,110	896,755	896,617	896,865	897,530	897,530	897,682	897,690	897,305	897,237	897,180
Y	389,350	389,410	388,987	388,710	388,157	388,925	389,157	389,417	389,417	389,375	389,242

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Fig. 10 Flooded Mra sma II and Guenicha quarries, abandoned Ismail quarry [15]



Fig. 11 (a–d) Microscopic observation of the extracted ore [18]. (a) Cinnabar disseminated in the silicified gangue (ob ± 20 ,LP). (b) Cinnabar veinlet intersecting the silicified gangue (b ± 20 , LP). (c) An iron oxide vein intersects the shale (ob ± 20 , LN). (d) Association between barite and quartz (ob ± 20 ,LP)

- Chalcopyrite: it is more rarely found in comparison to other minerals, often disseminated in the gangue.

6.3.2 Secondary Minerals (Fig. C)

- Malachite: a secondary mineral due to the alteration of chalcopyrite, its color is greenish to glassy, often in the form of thin films in the barite veins.
- Azurite: less abundant, occurs in a large xenomorphic range bathed in silicified gangue.

- Iron oxide and hydroxide: represented by hematite, goethite, and limonite, and they are found in impregnation in the surrounding rock or in filling in the dissolution cavities, and the oxides underline the walls of the calcite veins.
- Native sulfur: occurs as yellow-greenish grains in the oxidation zone of mercuropolymetallic ore.

6.3.3 Gangue Minerals (Fig. D)

- Calcite (CaCO3): it is the most common mineral, it occurs in different forms, and it occurs in the ore body in small veinlets of variable color; sometimes it develops large rhombohedral crystals.
- Quartz: is frequently observed at the surface, easily recognizable to the naked eye, and has several generations and several shapes (geode, veinlet, compact mass, large crystals, well crystallized).
- Dolomite: which is less widespread than other gangue minerals, appears as small losanitary crystals, diffused in carbonate cement, as it can be found in large losanitary crystals in interstitial voids and quartz grain cracks.
- Barite: is widespread in the Mra sma deposit and very rare in the Ismail deposit, is in the form of flattened acicular crystals often grouped into massive lamellar masses in the gangue of the metalliferous vein, and it has a high density of 4.5.
- Kaolinite: a mineral with a cryptocrystalline structure of white to grey color, it is found in vacuoles and intragranular voids, sometimes in small discontinuous veins intersecting cinnabar filonets.
- Gypsum: transparent white, in lamellar and fibrous form, very abundant, and containing cinnabar (Fig. 11).

6.3.4 Textures

Three very common textures are marked in the ore:

- Disseminated texture: predominates over the others, the ore is in the form of small millimeter grains; this texture is often represented by cinnabar and pyrite crystals.
- Brecciated texture: results from the replacement of calcium cement in the breaches by cinnabar, it develops in highly crushed conglomerate breaches.
- Venous texture: observed in fracture zones and calcite and dolomite veins, cinnabar occupies the walls or fills the entire fracture.



Fig. 12 Ismail industrial mining complex [14]

6.4 Description of Ismail Mercurial Complex

6.4.1 Location

General observations had been made on the location of this complex, which led us to the following description:

- This site is occupied by several buildings and is traversed by several roads, the main one crossing it in an east-west direction.
- From the N coast of the main road, there is:

A huge landfill constitutes the warehouse of solid waste called "slag."

In two small lakes in which liquid waste was settled (called technical waters), the oldest and largest of these lakes is called "settling lake No. 1" or "lake No. 1" of Azzaba).

On the S side of this road, there is a long cylindrical chimney. (It is 112 m high from the ground and 2 m in diameter.) (Fig. 12)

6.5 Environmental Consequences of Exploitation of Ismail Deposits

A hydrochemical study was carried out on water and soil samples, to determine the impact of mercury on the water and soil of the Azzaba region.

The assessment of surface water quality is based on the measurement of physicchemical and chemical parameters. These data can be supplemented by soil analysis (leachate) to show the degree of heavy metal pollution.

All these elements together make it possible to assess the degree of contamination of watercourses and their ability to purify themselves.

Our research is based on work that has previously attracted the interest of several authors on the impact of mercury mining in the Azzaba region.

After the closure of the Ismail mercury plant, several studies and research were launched on the area to see the vulnerability of the area to mercury; some works and their results are mentioned:

- Given the observation made on mercurial impregnation in the Azzaba region "Ismail" that the University Hospital research team has finalized a research project within the framework of the Work, Health and Development Research Unit of the University of Annaba. In this project, the hypothesis of this contamination was assumed, and the team developed an approach to verify it by studying the population of schoolchildren in the Azzaba region, comparing it to a control group in Annaba (Nezzal et al. 2004).

The results of this project showed that children attending school in the Azzaba region have an average concentration of mercury $(1.32 \ \mu g/g \ creatinine)$ significantly higher than that of the children in the Annaba region (0.81 $\ \mu g/g$ creatinine) showing impregnation chronic mercurial. Some children have reached a concentration of mercury in urine equal to 21 $\ \mu g/g$ creatinine. A WHO group report in 1980 indicates that the concentration of mercury in urine appears to be usually, in an unexposed subject, 0.5 $\ \mu g/L$ [22].

 The Ismail complex represents an important pollution area for the staff working there as well as for the population and the environment (Megueddem et al.) [23].

The workers in the complex are exposed in various ways. The most exposed group is treatment plant workers with a blood mercury concentration of 89.17 μ g/L, due to their direct contact with the mercurial fume [23].

- The high Hg levels in the water analyzes which were 80 μg/L are found in Oligocene formations, while the waters of the Eocene Paleocene groundwater have relatively low levels of Hg (<7 μg/L) (Benhamza 2007) [24].
- The industrial complex of Ismail is an extremely polluted area, and the areas encompassing the quarries are moderately to heavily polluted. By moving away from these areas, the degree of contamination is zero, except for mercury, where in some areas high concentrations are related to geochemical anomalies natural (Seklaoui 2015) [14].

6.5.1 Why Did Our Research Work Focus on Ismail Area?

The selected study area has been the subject of some research before our work in order to show the vulnerability of the Azzaba plain to mercury pollution due to the installation of the Ismail mercury treatment plant in the area.

In the vicinity of this area, there are also three cinnabar quarries that were abandoned after the closure of the plant; these can contribute to the contamination of this area. Following our field visits, water and soil samples were taken for analysis and to see the degree of pollution left by this complex.

6.6 Sampling

The sites where water samples are taken are four stations: settling basin (two samples), lagoon 1 (three samples), lagoon 2 (two samples), and Zebda wadi (three samples).

For the soil, three stations were selected: Stupp waste (two samples), main slag (two samples), and Zebda wadi (one sample).

The physic-chemical parameters such as temperature, pH, and conductivity were determined on the ground during April 2017 in the Azzaba area in the vicinity of the Ismail mercurial site using a Hanna multiparameter (HI 9829) (Fig. 13).



Fig. 13 Sampling plan of the study area [15]

6.7 Discussions of Results Obtained

Water and soil samples were analyzed at the UCEIV laboratory of the Littoral Opal Coast University Dunkirk, France.

The results obtained by ion chromatography show the presence of strong mineralization in our samples. This mineralization has been clearly noticed in the water samples taken from lagoons 1 and 2 with a high concentration of constituent elements (Cl-, So_4^{-2} , Na^+ , Mg^{+2} , Ca^{+2}).

The water samples taken from Zebda wadi show a high concentration of chlorides due to the origin of the water and/or the nature of the ground crossed. For water withdrawn from the settling tank is less loaded with these elements.

To determine the concentrations of mercury, zinc, and copper, atomic absorption with flame was used.

6.7.1 For Waters

The water withdrawn from the settling pond inside the plant has mercury contamination in the order of 20.89 ppb (Sample 1) and 17.41 (Sample 2) ppb. Samples from both lakes contain mercury levels ranging from 0.4597 ppb to 1.29 ppb with a maximum value in the six samples. The waters of Zebda wadi (sample 3, 4, 5) show no evidence of mercury contamination. Zinc is present at low concentrations in all samples with a maximum value of 0.0215 ppm (Sample 8); and for copper, no concentration was found in all stations.

6.7.2 For Soil

Taking soil samples inside the factory shows high mercury contamination, with very high levels of 6,904.15 ppb (sample 1) and 11,749.3 ppb (sample 2). Soil samples which were taken from the main slag also show high mercury contamination also with values of 4,077.57 ppb (sample 6) and 1,252.39 (sample 7), slightly different values compared to samples taken in the factory.

A soil sample which was taken near Zebda wadi shows mercury contamination (5.1823 ppb). Zinc is present with low concentrations with a maximum of 0.0608 ppb (sample 07). Copper was absent in our soil samples.

6.8 Interpretation of Physic-Chemical Results by Statistics Methods

6.8.1 For Water Samples

The distribution of individuals on the F1–F2 plane shows that along the F1 axis, which includes elements with the same chemical facies (Hg, Cu, Zn, Ca2+, Mg2+, Na+, K+, Cl-, Cl-, SO4 2-) at Zebda wadi and the settling basin. Elements with the same chemical facies group along the F2 axis, reflecting a high concentration of elements (So4⁻², Na⁺, K⁺, Mg⁺², Ca⁺²) in the two lagoons (Fig. 14).

To confirm the presence of these high concentrations of the major elements obtained, the diagram software was used to determine the different chemical facies present in the waters of the two lagoons.

According to this diagram, the chemical facies of the waters show the existence of three types of waters:

- Highly calcic chlorinated waters
- High calcium sulfate waters
- Chlorinated and sulfated waters and calcium and magnesium

These chemical compositions obtained reflect the strong mineralization of the waters of the two settling lagoons located near the plant; this mineralization is due to geological formations and the climate that contributes through high precipitation and evapotranspiration.

The dissolution of carbonate rocks (calcite, dolomite, gypsum) reflects the chemical facies obtained in the study area.



Fig. 14 Piper diagram and correlation circle of the main component analysis for water samples [15]

6.8.2 For Soil Samples

The projection of individuals according to the F1–F2 plane shows that the F1 axis group elements with the same chemical facies S02 and S06 (Hg, Cu, Zn, Ca²⁺, Mg²⁺, Na⁺, K⁺, Cl⁻, SO₄²⁻) and groups in a point cloud the individuals with high Hg contents, despite their samples from different locations. It can be said that the main slag S06 and the stupefied waste S01 have the same chemical composition (Fig. 15).

From the analyses and results obtained, it was found that our samples show strong mineralization with heavy metal contamination. The main source of this contamination is Hg; it comes from the HgS cinnabar, as it is the first ore used for mercury production previously in the plant.

The correlation between mercury and calcium (-0.6281) is explained by the gangue which consists of calcite CaCO₃. The strong correlation with Mg is expressed by the presence of dolomite in the gangue also CaMg(CO₃).

Our soil samples show mercury contamination in the order of 11.2 ppm as a maximum value in the plant enclosure (S02) and a maximum value of 6.9 ppm in the



Fig. 15 The correlation circle of the analysis as a main component of soil samples



Fig. 16 The trajectory of mineral-rich waters [15]

main slag. The mercury values in the soil decreasing near the Zebda wadi (0.005 ppm). This decrease in concentration is due to the distance from the plant.

Soil contamination (Stupp waste; main slag) will cause water contamination during periods of heavy rainfall; the water will transport these heavy metals in dissolved form to the settling lakes, as the land has a slope that facilitates the transport of water loaded with these metals. Indeed, the waters of the lakes will be saturated, and the excess will flow once again toward Zebda wadi according to the slope shown in the figure.

Rainwater also generates another very important phenomenon, which is "mercury recycling." The mercury residue in the capacitors will be vaporized under the effect of high temperatures during periods of high temperatures; heavy rains with low temperatures will condense the mercury into small droplets, which is observed on site during the field visit (Fig. 16).

These droplets will be transported by rainwater to Zebda wadi, which is the receiver according to the direction of flow in the region. Zebda wadi is a tributary of Fendek wadi [24], the latter supplies the Oligocene groundwater table, so that this table will be contaminated.

In the metal trace elements (MTE) analyzed according to the different stations and in the vicinity of the site, the following order of abundance or contamination is recorded:

Hg > Zn > Cu [15].

The results obtained are alarming and show that at the plant level the problem of mercury pollution still persists. The rehabilitation operation of the site is strongly requested in order to protect the environment.

7 Suggested Solutions to Clean up the Ismail Site

- As with any therapeutic approach, it is desirable to provide clear and objective information to the public and professionals on the dangers of mercury. To this end, national documents should be produced and widely disseminated.
- The availability of accurate mercury emission inventories is an important first step toward controlling major sources of pollution. Good knowledge of these sources will facilitate the development of cost-effective emission control policies.
- The first phase of depollution involves a waste classification process followed by an assessment of the impact of different disposal methods.
- The decommissioning and dismantling of treatment facilities and equipment are mandatory. These installations must be cleaned and then melted.
- Canals must be empty, equipment cleaned and sold, and buildings must be reused or demolished.

7.1 Solution 01

- Remove the surface layer of the soil (up to 20 cm deep) on which the treatment plant is located.
- Thermal desorption of the removed layers and recovery of mercury in a gaseous state (Fig. 17).
- Tailings and waste rock management techniques include the use of thermally desorbed soils to close pits (Guenicha and Mra-Sma) as backfill.

If the soil is not treated (polluted soil), these pits must be insulated from the outside with a polymer waterproofing geomembrane. The use of a thin layer of topsoil as a growing medium for future vegetation.



Fig. 17 Schematic diagram of thermal desorption [18]

- Physical stabilization of the soil by reforestation
- The storage of hazardous waste in specialized sites
- Pumping and recycling of water from the settling basin, lakes 1 and 2

7.2 Solution 02

"Venting" is the extraction of volatile pollutants using air injection. Also, preliminary work may be necessary such as lowering the groundwater table (Fig. 18).

Containment (after venting) consists of installing an underground watertight partition to prevent the migration of pollutants to the groundwater table (Fig. 19).



Fig. 18 Schematic diagram of the venting principle [18]



Couverture pour collecter les émanations gazeuzes

Fig. 19 Surface isolation – containment by covering and sealing [18]

It is a reliable method, but the pollutants are not destroyed and remain in place (heavy metals).

- Physical stabilization of the soil by reforestation
- Storage of hazardous waste in specialized sites
- Pumping and recycling of water from the settling basin, lakes 1 and 2
- Finally, it is recommended that a monitoring program be put in place to assess the effectiveness of the remediation measures and identify any corrective measures that may be required.
- Regular water quality monitoring in wadi and well

8 Conclusions

When an operation is completed, the site must be prepared for future use. The management of waste from mining activities and tailings and waste rock usually represents an undesirable financial burden for operators.

Generally, the mine and ore processing plant are designed to extract as many marketable products as possible, and tailings and environmental management as a whole is then designed as a consequence of the mining stages.

The choice of tailings and/or waste rock management method to be applied depends mainly on an assessment of three factors:

- The cost
- Environmental performance
- The risk of accidents

The aim will therefore be to leave as few traces as possible.

9 Recommendations

Mining operations generate wastes that can be harmful to the environment if they are disposed of without adequate treatment. For example, some of the waste generated by mining contains significant amounts of sulfide minerals that oxidize when exposed to water and air. In the short and long term, metals are known for their effects on human health. In humans, as in other living organisms, the toxicity of metals varies according to the metallic elements, their mode of penetration into the organism, and their chemical form (speciation).

Monitoring of an abandoned or active mine site is mandatory. This monitoring is aimed at preserving the environment and especially natural ecosystems. Therefore, studies must be carried out, whether ad hoc and local or recurrent and national, to measure the levels of metal deposits. These studies measure the deposition either directly (by placing collectors close to the ground) or indirectly (by accumulation in soils, sediments, living organisms). The implementation of a program allows an estimate, in background situations, of metal deposits (iron, mercury, nickel, lead, arsenic, zinc). This program has the following objectives:

- Monitor the variations of metal deposits in the natural environment.
- Evaluate the extent of contaminated areas by using the ArcMap application.
- Identify the local origin of the sources of emissions.
- Set up a rehabilitation plan for closed or abandoned sites.
- Monitor improvements resulting from the application of rehabilitation plans to reduce the impact of metal emissions.

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