

Article

Volumetric Quantification and Quality of Water Stored in a Mining Lake: A Case Study at Reocín Mine (Spain)

Noemí Barral ^{1,*}, Raúl Husillos ¹, Elena Castillo ², Manuel Cánovas ³ , Elizabeth J. Lam ⁴  and Lucas Calvo ⁵

¹ Transport and Project and Process Technology Department, Universidad de Cantabria, 39005 Santander, Spain; raul.husillos@unican.es

² Geographic Engineering and Graphic Expression Techniques Department, Universidad de Cantabria, 39005 Santander, Spain; elena.castillo@unican.es

³ Mining and Metallurgical Engineering Department, Universidad Católica del Norte, Antofagasta 1270709, Chile; manuel.canovas@ucn.cl

⁴ Chemical Engineering Department, Universidad Católica del Norte, Antofagasta 1270709, Chile; elam@ucn.cl

⁵ Center for Hydraulic Research of the Technological University of Panama, Universidad Tecnológica de Panamá, Panamá 0819-07289, Panama; lucas.calvo@utp.ac.pa

* Correspondence: noemi.barral@unican.es

Abstract: This study deals with the potential use of water stored in a lake formed by Reocín's old zinc mine, which has become the second most important reservoir in Cantabria, with a flow of 1300 L s⁻¹. The methodology used is based on the hydrogeological and hydrochemical characterization of the area studied. A total of 16 piezometers were installed to monitor the amount and quality of water. Results obtained show a pH close to 8 and iron, manganese, zinc, and sulphate concentrations lower than 0.05 mg L⁻¹, 0.05 mg L⁻¹, 1.063 mg L⁻¹, and 1305.5 mg L⁻¹, respectively. The volume of the water stored in the lake amounts to 34 hm³. Measurements show that Fe, Mn, and Zn concentrations are below the limits acceptable for human consumption, according to the Spanish 0.2, 0.05, and 5.0 mg L⁻¹ standards, respectively, while sulphate greatly exceeds the 250 mg L⁻¹ limit accepted by the norm. Therefore, the water could be apt for human consumption after a treatment appropriate for decreasing the sulphate level by, for example, reverse osmosis, distillation, or ion exchange. Although industrial and energy uses are possible, the lake water could be utilized as a geothermal energy source. The management of the hydric resources generated when a mine is closed could improve the economic and environmental conditions of the zone, with all the benefits it brings about, thus allowing for compensating of the pumping cost that environmental protection entails, creating, at the same time, a new business opportunity for the company that owns the mine.

Keywords: abandoned mines; mine water; Reocín mine; water management



Citation: Barral, N.; Husillos, R.; Castillo, E.; Cánovas, M.; Lam, E.J.; Calvo, L. Volumetric Quantification and Quality of Water Stored in a Mining Lake: A Case Study at Reocín Mine (Spain). *Minerals* **2021**, *11*, 212. <https://doi.org/10.3390/min11020212>

Academic Editor: Teresa Valente

Received: 15 December 2020

Accepted: 14 February 2021

Published: 18 February 2021

Publisher's Note: MDPI stays neutral with regard to jurisdictional claims in published maps and institutional affiliations.



Copyright: © 2021 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (<https://creativecommons.org/licenses/by/4.0/>).

1. Introduction

The Reocín Zn-Pb mine is located on the Santillana Synclinal border in the Vasco-Cantabria basin at the north of the Iberian Peninsula, about 30 km southeast of Santander, Cantabria [1,2]. During its open-pit exploitation, a huge hole was made which, once the mine was closed, was gradually filled with infiltrated water mainly from the Saja River, through karstic materials, giving shape to the local geology. The water flow into the mine, 1100 to 1299 L/s, was a relevant problem for its exploitation [3,4]. Water infiltration from the Saja River amounts to 72%; the secondary sources are rainwater (26% to 27%) and the diapir (1% to 2%) [5–7], giving rise to a mining lake which is currently controlled. The presence of water in mining sites creates operational and stability problems. Consequently, it must be drained. Drainage quality depends on several geological and hydrogeological factors and the characteristics of the system, which are particular for each mine [8].

To avoid the Reocín mine flooding, it was necessary to pump water permanently, with an about 50×10^6 kWh/a energy consumption [5]. During the Reocín mine exploitation,

underground water was a potential risk of chamber flooding. Drainage costs are estimated to be 20% to 25% of the technical costs of the mining project [9,10], pumping $35 \times 10^6 \text{ m}^3$ of water in 1979 [11].

In March 2003, Reocín mine was closed after almost 150 years of continuous exploitation [12]. At present, pumping continues since there is no legal permit for ending the flooding process, the current water flood level being 45.69 m. To estimate the value of the potential use of this water, it is necessary to make a chemical characterization, which depends on the water origin. Different studies show three potential sources for the lake water, the most important being karstic materials, with pH 7.59 and 349 mS/cm conductivity [3–5]. Another source is diapiric, which flows through the faults, with pH 7.70 and 227 mS/cm electrical conductivity. The third source is rainwater, which is scarcely influential, except when heavy rains cause floods. This water contains a great quantity of solids in suspension, greatly affecting pumping [10].

Criteria used for mining lakes are particular for each territory and depend on authorities responsible for their regulation. To meet environmental requirements, Spain passed the Mining Law 22/1973 [13], that sets the juridical regime to study and use ore deposits and other geological resources, along with Royal Decree 975/2009 that provides directions for managing residues from extraction industries and protecting and rehabilitating spaces affected by mining activities [14]. The current legislation considers three basic restoration options: environmental and landscape integration, giving added value by using mining facilities, and finally, providing a choice of ludic, sports, and handicraft activities [15]. Mine voids are usually restored by integrating the landscape. This consists of filling the hole created during extraction with materials and then planting tree species and native vegetation in the empty area [16].

As to open-pit mines, the environmental conditions are more serious because the hole made for extracting minerals completely changes the land morphology, the landscape, and the site hydrology. In many cases, the solution is to flood the hole with runoff water or stabilize the phreatic level of the zone [17,18], thus forming a mining lake with great potential as a hydric resource. The water for flooding abandoned mines is often considered as an environmental responsibility bearing high economic costs [19] and urgently requiring alternative uses to reduce them [20,21].

Different strategies are used to address mine flooding. For example, Zwenkau lake in Germany is the result of post-mining; it is multifunctional, protecting against floods whilst providing suburban settlement, tourism, and sports activities [22]. Other open-pit mine restorations for recreational use include Cospuden lake in Leipzig, Germany [23]; Collie lake in the southwest of Australia [24]; and As Pontes mine (La Coruña), today an 8.7 km long lake with two artificial islands and an approximately 400 m quarry sand beach, which holds a huge dam with a 547 hm^3 water reservoir [25]. For decades, the water from the mine was used for heating and cooling [26]. Heat may be extracted from underground water by means of a heat pump. Using mine water as geothermal energy is an advantage because its temperature remains constant throughout the year, sometimes increasing by 1 to 3 °C every 100 m [27]. A large number of abandoned mines are used for this purpose: Springhill mine, New Scotland, Canada [28]; Florence mine, Cumbria, UK [29]; Henderson molybdenum mine, Empire, Colorado, USA [30]; Saturn coal mine, Czeladz, Poland [31]; and Barredo-Figaredo, Mieres, Asturias [32].

A mining lake is a complex system related to many factors that may influence water quality evolution. Among the most important factors are those connected with the watershed mineralogy, hydrology, and limnology. The water quality depends on slope and berm mineralogy and the surface exposed. For example, rocks with a high iron sulfide content may be oxidized with the presence of water and oxygen, thus producing lakes with high levels of sulphates and dissolved elements (Fe, Al, Mn, Cu, Zn, Pb, and Cd). As to Reocín, since the water is in contact with calcite or dolomite, it helps to neutralize the acidity that could form due to the reaction of sulfide, oxygen, and water naturally, thus improving the quality of the flooding water, whose pH ranges from 7 to 8. This was confirmed in

2009, when the authors also measured Na, K, Mg, Ca, SO_4 , Fe, Al, Mn, Zn, Co, and Ni concentration at different depths—0 and 90 m [33]. Concerning hydrology, it is necessary to determine the volume and chemical nature of the different inlets [34].

This study aims to provide the foundations for the future use of the flooded water of Reocín lake, according to its level of purity, to reduce associated risks and also give added value to this precious resource. Having an alternative plan for the final use of flood water before the post-closing phase will allow for a safer implementation from the environmental and social viewpoints. The alternative uses of water assessed in this study are human consumption and industrial and energy supply.

2. Materials and Methods

2.1. Study Area

This study was conducted at Spain's old Reocín mine, (Figure 1), one of the biggest and most well-known Zn-Pb ore deposits in Europe [1]. It was the biggest mine in Cantabria from 1856 to 2003 and has been Spain's biggest and most productive Zn-Pb ore deposit from an economic viewpoint, and the largest in Europe. The exploitation of the mine took place from 1856 until 2003 [35,36].

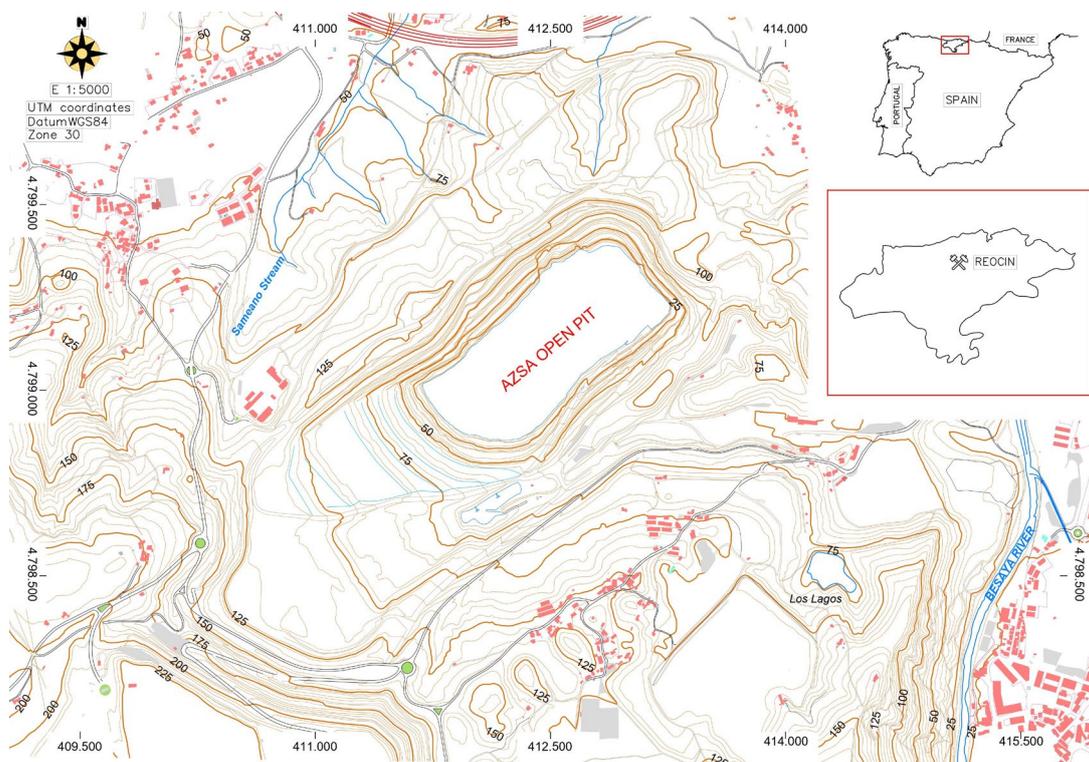


Figure 1. Location of the study area, Reocín mine.

During 147 years, more than 7 million tons of zinc concentrate over 60.5% ore grade and 0.7 million tons of lead concentrate were exploited [37]. The Reocín' ore deposit is proposed as one of Spain's geological places of interest on an international basis by the Spain Geological and Mining Institute due to its metallogenetic interest [38].

Reocín mine is framed within a karstic system that drains the whole watershed, increasing its volume as in-depth excavation progressed, with a watershed extent of about 44 km² [10,38].

In 1978, it was postulated that one of the potential sources of water infiltration was from the Saja and Besaya rivers (Figure 2). To support this hypothesis, Trilla [9] proved the existence of atmospheric tritium in the water from the mine galleries and, after geochemical and isotopic analyses, concluded that the water did come from both direct rain infiltration

and the Saja and Besaya rivers. The water was analyzed for dissolved materials and microscopic fauna. It was observed that at level 21, it contained sand, carbon vegetal material, pollen, leaves, spores, and residual wood quite similar to those obtained from the Saja River [39]. Then, it was determined that the water from the western part of the mine came from the Saja River, while the water from the eastern part (called Barrendera) came from rain water infiltration [40].

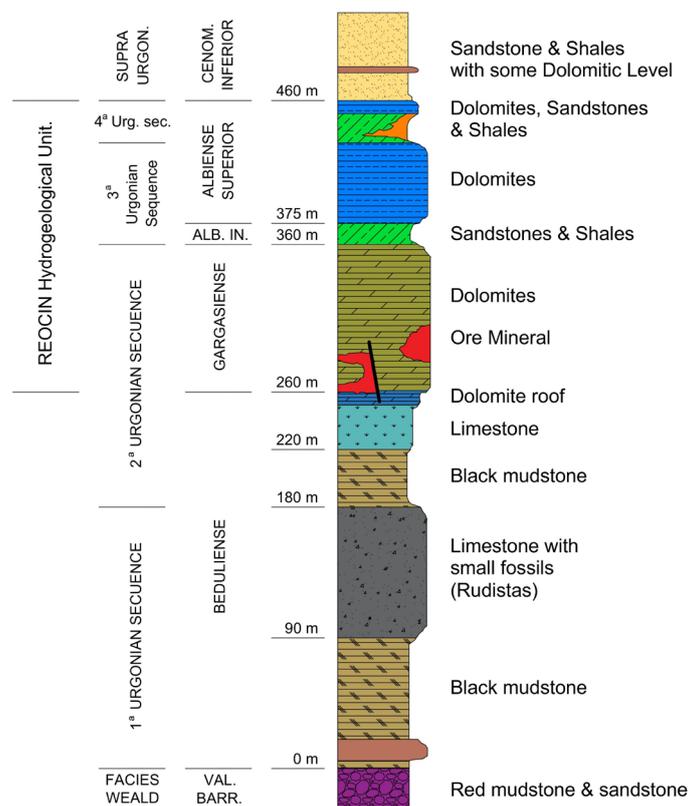


Figure 2. Stratigraphic column of Reocín mine. Modified from Pendás et al. [3].

Many studies have been conducted to determine the origin of the water causing this recharge, leading to the conclusion that the greatest volumetric contribution, corresponding to 100 L s^{-1} and with an 85% water supply, comes from the karstic system, the secondary sources being rainwater (14%) and, to a lesser extent (1%), diapiric water [8,40–42]. At present, the remnants of the open-pit exploitation are covered with water owing to the flooding of the watershed generated by mining activity, thus forming an artificial lake [43,44]. The starting level of the filling was -272 m . At present, the water is at level $+45 \text{ m}$. At the end of the filling process, the water will reach a level of $+60 \text{ m}$.

2.1.1. Climatology

The climate is a highly relevant research factor owing to its effects on floods. Cantabria province, and also the rest of northern Spain, is characterized by abundant rainfall during most of the year. Since the zone is located close to the coast, its climate is oceanic and, therefore, rainfall is abundant [10]. The annual mean rainfall amounts to 1080 mm, with a 63% loss due to evapotranspiration. So, effective annual rainfall amounts to 400 mm [8]. Considering the monthly balance, rainfall is scarce from June to September, while there is a surplus from November to May. There is no rainfall from July to September.

The temperature in the zone is characterized by a $14 \text{ }^\circ\text{C}$ annual mean. In winter, the mean temperature reaches $6 \text{ }^\circ\text{C}$ during the coldest months. In summer, the mean temperature is $23 \text{ }^\circ\text{C}$. The thermal amplitude is moderate, with a temperature difference

of less than 15 °C between the hottest and coldest months [8]. Humidity may reach over 75% [45].

2.1.2. Geology

Reocín mine is located on the western side of Santillana del Mar Synclinal, within a large hydrogeological system, where the Reocín subsystem is situated. It is bordered to the north and west by the Saja River, and to the south and east by a stratigraphic border consisting of a loamy limestone roof belonging to the Bedulian, showing low permeability during all its exploitation [46]. Sphalerite, marcasite, and galena forming at the Gargasian dolomites around Torrelavega were exploited [2].

On the roof, there is a 250 m layer from the Lower Cenomanian, alternating sandstone (impermeable and cemented) and black shale (impermeable) in very thick beds, providing impermeability to this level. The next layer belongs to the Upper Albian (with dolomite and sandstone of different thicknesses), followed by a layer from the Lower Albian, consisting of sandstone and shale of low thickness. Next, there is a layer from the Upper Aptian (Gargasian) consisting of dolomite and iron, beginning with 80 m thicknesses and then rapidly increasing as they advance to the north of Santillana Synclinal. Finally, there is a layer belonging to the Lower Aptian, with a 40 m thick layer formed of loamy limestone and another one formed of 40 m of black shale [9]. Figure 2 shows a representative stratigraphic column of the Reocín mine.

2.1.3. Hydrogeology

Santillana Synclinal is a structure that may contain water. There is an important recharge zone in the permeable materials from the Cenomanian. This feature is added to the immersion of the Synclinal to the east, defining a water accumulation area in the northern zone. The so-called Reocín aquifer, which is dolomitized around the ore deposit, may be located within this hydrogeological subsystem. The limestones are karstified and show high transmissivity, while the minimally karstified dolomite shows low transmissivity [1]. Hence, the water must enter the mine through the western zone, at the limestone zone of the aquifer, from the Saja River and as a recharge from the karstified outcrop [47].

Due to the column lithology, it may be concluded that, except for the upper zone, the set behaves as wholly impermeable [40]. Since it is an open watershed, pluviometry substantially affects the hydrogeological level of Reocín mine. Figure 3 shows the Reocín mine watershed map.

The mine is located in Santillana Synclinal, surrounded by the Saja and Besaya rivers. At the zone studied, these rivers are fed by water from small streams, but they are exposed to floods and overflows during heavy rainfall. The Reocín aquifer shows heterogeneous permeability, being lower near the Saja River and higher in the mineralized zone [32]. Owing to mining activity, the Reocín aquifer was subjected to major infiltration with hydraulic connections and a large drainage network. Most of the drained water came from the Saja River, crossed longitudinal faults, and then entered the mine through cross-fractures resulting from mining activity [37].

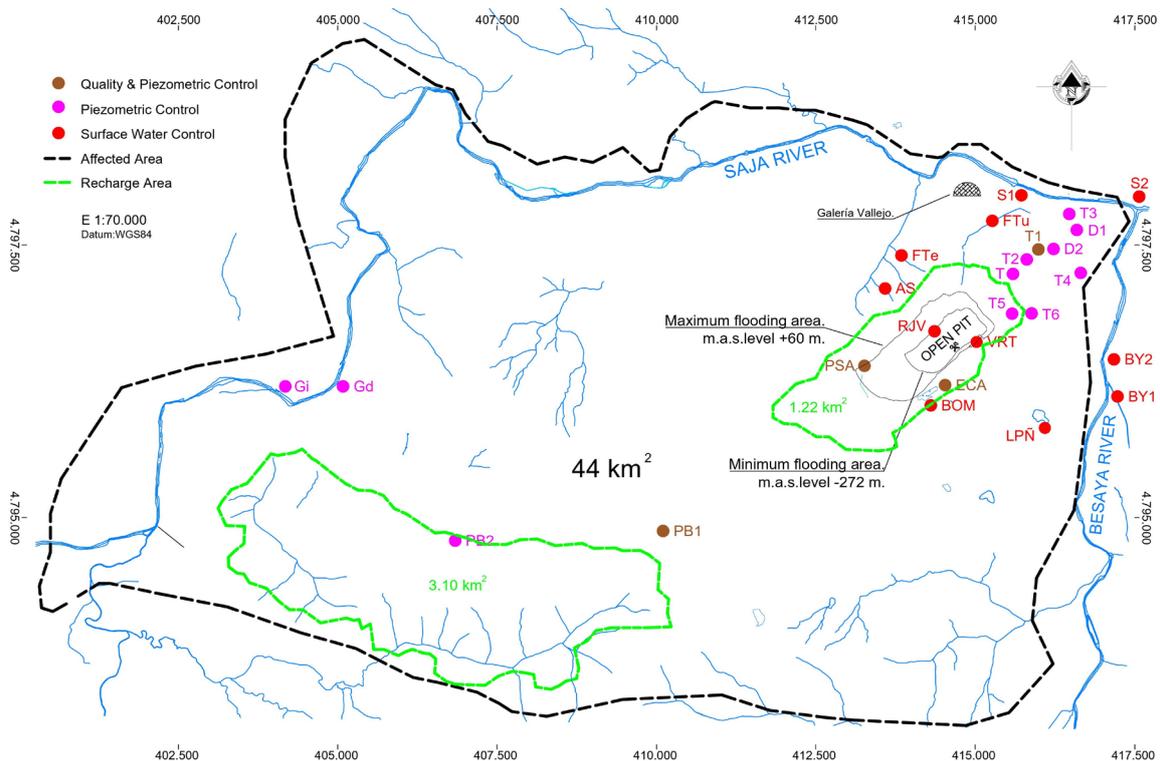


Figure 3. Reocín mine watershed map and piezometer distribution in the aquifer.

2.2. Methodology

The study included a hydrogeological and hydrogeochemical characterization of the area, and also the determination of physicochemical indicators related to water for human consumption. After analyzing the data, the affection area of the mine associated with the Reocín karstic aquifer was determined. To monitor possible water detraction in the Saja/Besaya hydrographic system during the mine void flooding, a piezometric control was made in the zone.

To monitor the Reocín aquifer, 16 piezometers were installed. They were distributed in different zones near the exploitation area. Their depths are shown in Table 1 and their location in Figure 3.

Piezometers GI and GD were installed on the left and right margins of the Saja River, respectively, to determine the role that the Saja River played in the Reocín aquifer and mine infiltrations. Piezometers SB1 and SB2 were installed at 1500 m from the Saja River to monitor the mine drainage. Most of the piezometers were located between the northeast zone of the mine and the Saja River because water leaks may occur here. The piezometers located next to Galería Vallejo, an old gallery situated at level +35, which collapsed and whose mouths are covered with clay, were intended to monitor an old mining gallery to ensure its sealing.

Table 1. Identification and piezometers depth.

ZONE	NAME	DEPTH (m)
WEST	Golbardo Izquierda (GI)	86
	Saja River under Golbardo bridge	85
	Golbardo derecha (GD)	98
	El Burco 1	217
	El Burco 2	203
	Pozo Santa Amelia (PSA)	108
EAST	Torres (T)	100
	Torres 1 (T1)	54
	Torres 2 (T2)	32
	Torres 3 (T3)	38
	Torres 4 (T4)	38
	Torres 5 (T5)	100
	Torres 6 (T6)	92
	Saja River under Ganzo bridge	29
Galería Vallejo	North (Vno)	56
	South (Vso)	56

2.2.1. Hydrogeochemical Karstic Aquifer Characterization

A hydrogeochemical study was conducted in the zone, focusing mainly on the mountain area separating the Saja River and Reocín mine on the northeast [11,41]. In addition, the flow pit filling was measured, estimating the maximum flooding level and using a linear correlation between the water rise and the water level.

The estimated watershed area is 44 km². A hydrological study on the Saja River was conducted to determine its influence on the mine flooding process. First, probable maximum flooding was estimated by using the Gumbel distribution, which is used for estimating extreme values [48]. The river flow and the water level were measured at Puente San Miguel station, located 1.5 km downstream with respect to the mine.

To determine the water quality, the pH, electrical conductivity, temperature, and metal concentration were measured using the APHA (American Public Health Association) standard methodology [49]. The pH was determined in situ and water samples from different zones were collected to analyze them at the lab, Caasa Tecnología Del Agua (Murcia, Spain). The flood water was analyzed at the open-pit exploitation (ECA), Santa Amelia well (PSA), pumping (BOM), Jorge Valdés ramp (RJV), and piezometers T1 and PB1. The surface water was analyzed at the Sameano stream (AS), Teja fountain (FTe), Turbera fountain (FTu), Saja River upstream (S1) and downstream (S2) Reocín aquifer, and Besaya River upstream (BY1) and downstream (BY2). Waste water was controlled at the open-pit exploitation, pumping, wastes (VRT), La Peña Lake (LPÑ), BY1, and BY2. A total of five samples/month were collected at the beginning of the flood (November 2004). From January to March 2005, three samples were collected monthly. From April 2005 to April 2010 the periodicity was twice monthly. From this date onwards, a monthly sample was collected. The temperature and electrical conductivity were measured with a YSI 3010FT equipment and the pH with a YSI 6010FT equipment (YSI Inc, Yellow Springs, OH, USA). The pH and electrical conductivity were measured continuously before collecting samples [49]. Sampling was done when their values stabilized for 15 min. To characterize water, the Zn, Fe, Mn, and Pb concentrations were measured using atomic adsorption spectrometry, while the sulfate concentration was measured with ion chromatography. The acceptable detection limits are 0.25 mg L⁻¹ for zinc, 0.05mg L⁻¹ for iron and manganese, and 0.002 mg L⁻¹ for lead.

2.2.2. Pluviometric Study

To assess the time delay from rainwater infiltration to pumping from the mine, the flooding process has been analyzed since it began on 1 November 2004. The vertical water

flow defined by the fracture resulting from mining activity was considered. Likewise, the flooding process was analyzed by relating infiltrated rainwater to rebound water during void filling [50]. By determining the average delay period of infiltration (50 days), the daily infiltration was estimated from the effective precipitation produced 50 days before. Daily infiltration during the flooding period represents the volume the deposit increased daily.

The flooding process is slow, considering the large amount of water—about 34 hm³—at the end of the flood. So, the water raises gradually, with water pumping alternating with periods in which the level remains constant. This is done in stages, alternating pumping and standstill periods to maintain a certain water level.

2.2.3. Potential Mine Water Uses

The methodology used was based on bibliographic data about the possible uses of abandoned mines [10,51–54]. As reported by Doupé & Lymbery [55] for water stored in mining dams, the following uses for Reocín Lake water were assessed: industrial supply, since there are large industries near the mine; supply for human consumption due to the strategic location of the water source at the center of the Cantabria Autonomous Community; hydroelectrical generation, considering the energy consumption required by nearby industries; and geothermal energy as a source of heat for nearby municipalities. The alternative uses of water will be assessed on the basis of the results of the physicochemical water analyses, which determine the quality of the water resource according to the current Spanish legislation on legal water requirements for human consumption established in Royal Decree 140/2003 [56].

3. Results and Discussions

3.1. Hydrological Study

The piezometer analysis throughout the mine flooding process provided data for determining how far it actually affected the Saja and Besaya rivers. The observation of the piezometer behavior led to the conclusion that the Saja River was a positive barrier, preventing mine water drainage from extending to its left margin. Therefore, the Reocín mine drainage affected the whole of the Saja River's right margin, having practically no influence on the left margin. Figure 4 shows that the water level in piezometer GI, located on the left margin, remains over the Saja River level; meanwhile, the water level of piezometer GD on the right margin of the river is over the level during rainfall seasons and under it during dry seasons. So, the Saja River acts as a barrier and, therefore, has no influence on the flooding process. Figure 4 shows that the piezometer GI always remains over the Saja River level, oscillating between +77.44 m and +82.01 m. The piezometer at the Saja River shows an oscillation between +74.12 m and +76.00 m, while piezometer GD oscillates between +66.47 m and +81.44 m. The river shows smaller oscillations, while the piezometer closer to the mine (GD) shows greater oscillations. Thus, the barrier effect defined for the river is confirmed, highlighting the hydraulic gradient existing between the river and the aquifer toward the mine. Therefore, the river has no influence on the flooding process.

Figure 5 shows a hydrological threshold in the northeast zone, where most of the piezometers were located. When filling mining voids (September 2007), the water level of all the piezometers was over the Saja River level.

In the northern zone, where Galería Vallejo is located (+35 m), the water level in the piezometers has remained over the gallery level (32.60) since the flood began. So, the gallery sealing can be ensured (Figure 6).

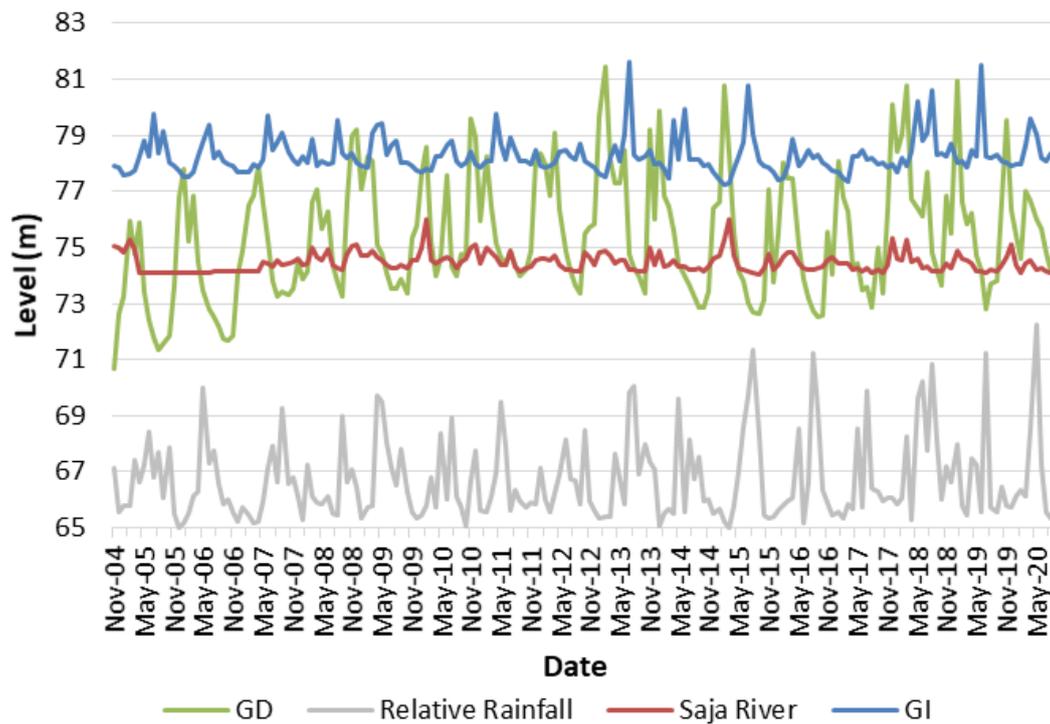


Figure 4. Western piezometry.

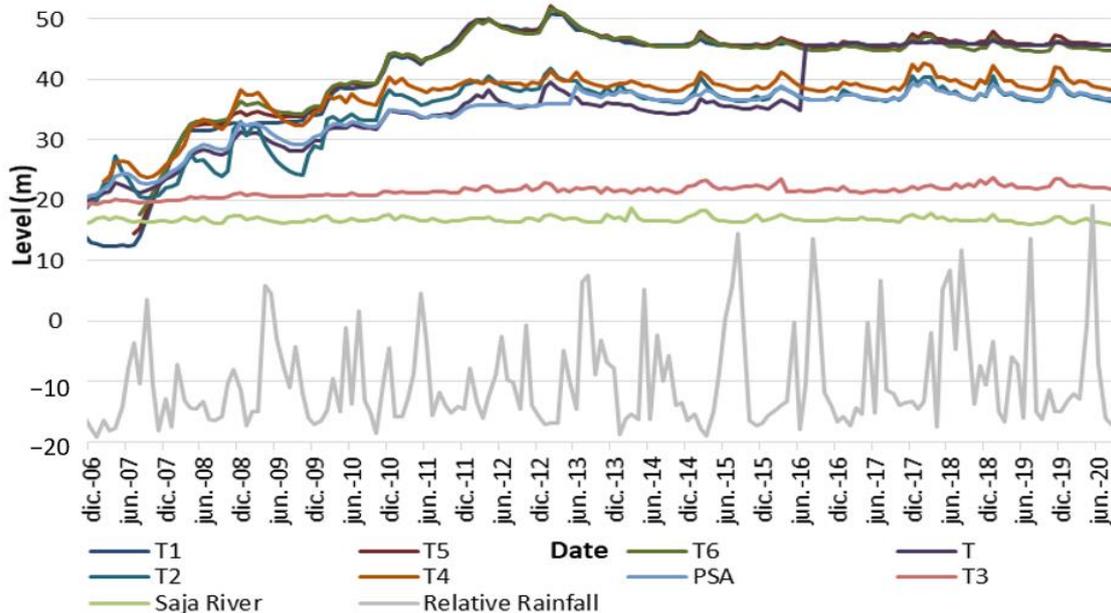


Figure 5. Eastern piezometry.

As to the quality of surface water, there are two stations at the Saja River; one of them is over the Gargasian Albian outcrop (S1) and the other is downstream (S2) (Figure 3). There are also two stations controlling the discharge at the Besaya River, one over the filling discharge (BY1) and the other one downstream (BY2) (Figure 2). At the Saja River, the concentrations of all the parameters measured are of the same order: ($[Fe] < 0.05 \text{ mg L}^{-1}$, $[Mn] < 0.05 \text{ mg L}^{-1}$, $[Zn] < 0.013 \text{ mg L}^{-1}$, and $[SO_4] \approx 26.50 \text{ mg L}^{-1}$), indicating that the water quality is not affected by the flooding process. At the Besaya River, the most different

parameter between the stations is the sulfate concentration (upstream, the concentration is 76.78 mg L^{-1} , while downstream, it is 207.78 mg L^{-1} , indicating a certain influence of the open-pit water pumping [57]. The discharge of the water pumped into the Besaya River increases its flow, temperature, and solid content, both dissolved (related to electrical conductivity and salinity) and suspended (related to turbidity) [49]. The Besaya River's average annual flow is $14.13 \text{ m}^3/\text{s}$, with a $6.22 \text{ m}^3/\text{s}$ minimum during summer and $25.41 \text{ m}^3/\text{s}$ maximum during rainfall periods. The average flow pumped at level +45 m is $0.23 \text{ m}^3/\text{s}$; that is, 1.62%. However, there are no significant changes in the pH, its value remaining at 8, in Fe, Mn, Zn and sulfate concentrations.

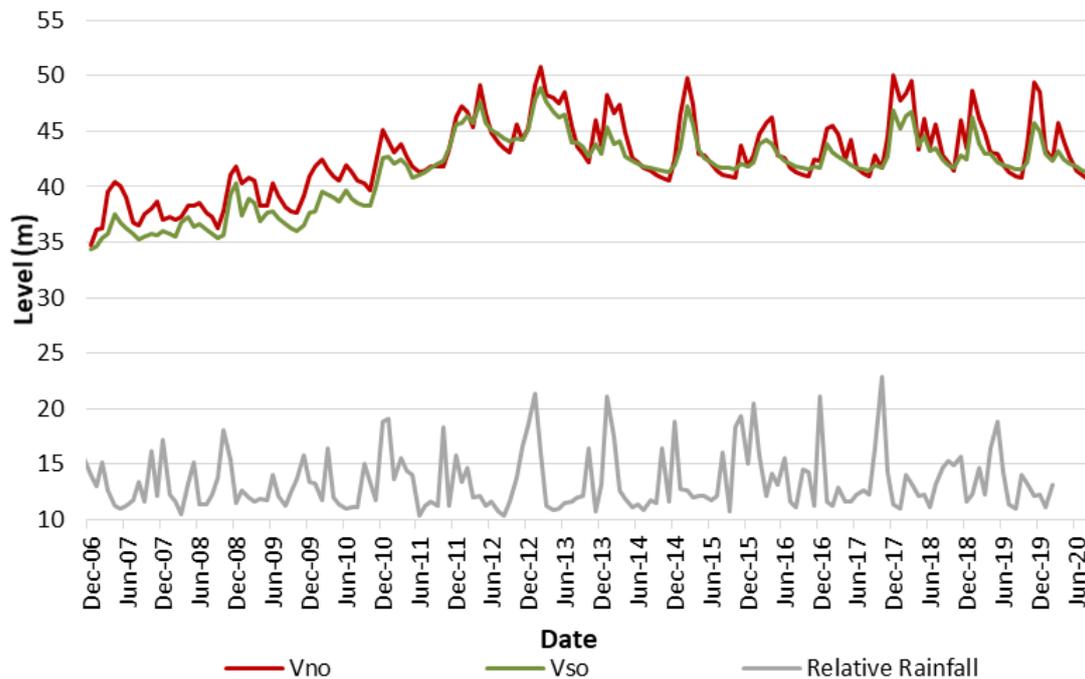


Figure 6. Galería Vallejo piezometry.

3.2. Pluviometric Study

The rain water infiltration delay period was estimated during 50 ± 10 days, comparing the maximum drainage points with useful precipitation peaks [58]. From the 2006-to-2007 hydrological year, the infiltration coefficient increased from 14% to 24% owing to the filling of the underwater mining voids, considering constant input ($12960 \text{ m}^3 \text{ day}^{-1}$) from the Saja River. Therefore, pumping must continue in periods without rainfall. To determine the delay period, a hyrogram was devised to schematize the essential parameters to be considered triangularly, noting the relationship between the maximum drainage and the peak of useful rainfall. The time elapsed since the peak of the useful rainfall until it is changed into a maximum of drained flow was determined. The infiltration coefficient was obtained by relating the useful rainfall to the infiltration determined from the pumped flow. By increasing the water level in the mine and the aquifer, the pumped flow decreased significantly (from $1.2 \text{ m}^3/\text{s}$ at the beginning of the flooding to $0.23 \text{ m}^3/\text{s}$ at the present level of 45 m), thus increasing the infiltration coefficient.

Equation (1) [54] shows the relationship between effective rainfall and infiltration

$$\text{Infiltration (m}^3/\text{day)} = 0.24 \text{ effective rainfall (m}^3/\text{day)} + 12960 \text{ m}^3 \quad (1)$$

The effective rainfall average, 250 L s^{-1} , is distributed in a 96 L s^{-1} infiltration and 154 L s^{-1} runoff. The water infiltrated through the mine voids and the surface runoff are drained toward the Saja River. The infiltration from the underground mine comes

from rainfall (96 L s^{-1}) and the Saja River (789 L s^{-1}), thus agreeing with the average amount pumped (885 L s^{-1}). This relationship was established for 1.5 years, obtaining the conceptual model of hydric balance.

3.3. Void Volume Estimation

The void volume produced by mining exploitation and the resulting galleries and access ramps were considered. To estimate the void volume, the underground mine exploitation phase was analyzed by work plans [37]. The lowest level reached during mining activity was -332.50 m (-568 m deep from the surface) in the western zone. From that depth up to level $+60 \text{ m}$ —the level at which the open-pit mine overflows— 13.1 million m^3 of voids have been created, most of which are already filled. The exploitation area was 1800 m long, 600 m wide, 280 m deep at the most, and elliptical in shape. To estimate the void volume to be flooded, a coefficient was assigned, depending on the filling method (cemented, pneumatic, and debris in pit), that is, 3% , 5% , and 5% , respectively [42].

To compare these values, the voids were calculated from the volume occupied by the infiltrated water, using daily rainfall during the flooding process and considering daily evapotranspiration to obtain useful rainfall. Once the infiltration delay period was determined (50 days), the infiltration corresponding to the useful rainfall precipitated 50 days before was considered for each day, according to the infiltration equation.

The daily infiltration during flooding represents the volume the dam receives daily. The void volume at each level is obtained by representing the daily accumulated volume and determining the temporal flood level. Figure 7 shows a comparative analysis between the mine void volume filling and the flooding time.

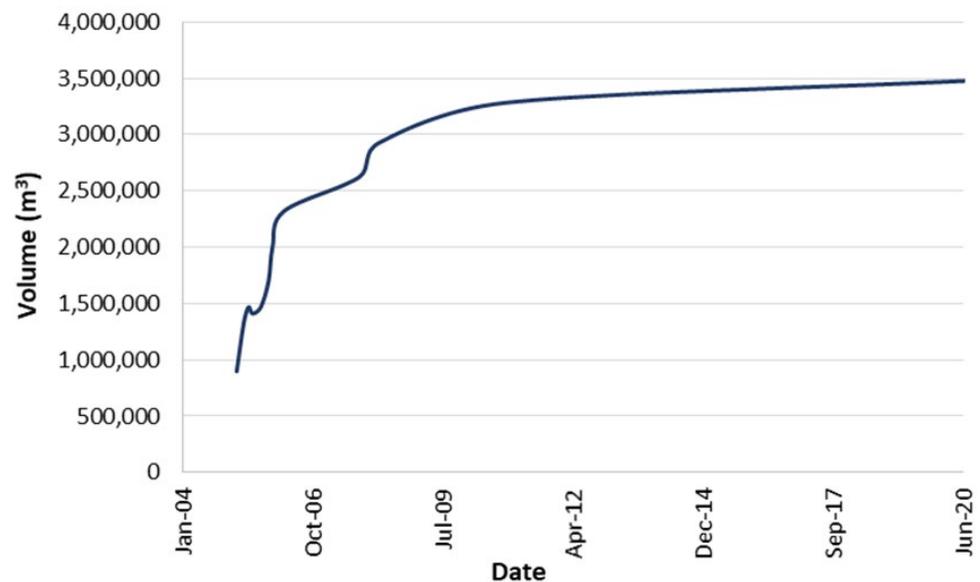


Figure 7. Temporal void filling volume variation during flooding.

Likewise, it is important to determine the level at which equilibrium is reached [59]. To do this, the velocity of the water rise per level was observed, estimating that the maximum level of filling during the flooding process should be reached at level $+60$, as shown in Figure 8.

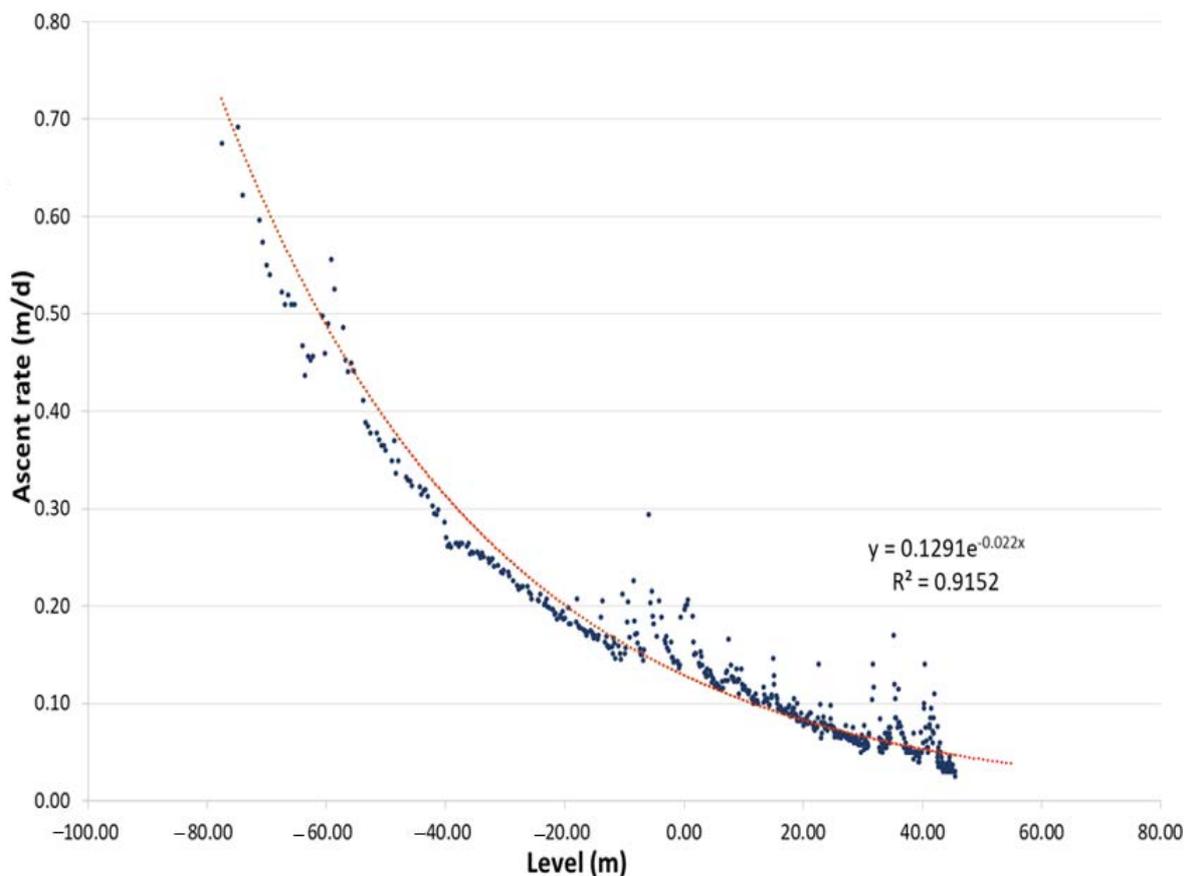


Figure 8. Daily water increase, according to level.

3.4. Potential Mine Water Uses

Some parameters important for the mine flooding process were analyzed. First, the use of passive deperation systems was considered; however, owing to the large river flows, it was necessary to build a water treatment plant using lime as a reagent. The water quality improved with initial washing and, therefore, there was a treatment plant shutdown [37]. This chemistry improvement is due to mining work, water infiltration from the aquifer that dilutes the salts and dolomite neutralizing acid waters [32].

In the exploitation zone (ECA), the electrical conductivity stabilized at 2000 $\mu\text{S}/\text{cm}$, the pH being close to 8. Fe concentration decreased below 0.05 mg/L, Mn below 0.05 mg/L, Zn by 1.063 mg/L, Pb below 0.002 mg/L, and sulfates by 1304.5 mg/L. The Pb concentration remained below 0.008 mg/L throughout the flooding process, at a present concentration lower than 0.002 mg/L. Figures 9 and 10 show the variation of sulfate and Zn content since the beginning of the flood and the favorable evolution of both concentrations according to the watershed filling.

Using the sanitary criteria for the quality of the water for human consumption in Spain, established by R.D. 140/2003, stating 0.2 mg/L maximum concentration for Fe, 0.05 mg/L for Mn, 0.01 for Pb, and 250 mg/L for sulfates, the water stored would meet all the requirements, except for sulfate content, which is above the 250 mg/L allowed [56]. Therefore, to supply water to the neighboring communities, a series of treatments, such as reverse osmosis, distillation, or ion exchange must be made to decrease the sulfate concentration.

The Saja River quality at Torres was not affected by the flood due to the low permeability of the rocky massif between the mine and the river, which does not let enough water pass and change the river chemistry. Chemical tests during the flooding process control showed that the massif dolomite reacts with water at a pH below 7 [42], resulting

in metal precipitation and facilitating the water deperuration process. The open-pit water temperature varies between seasons. The minimum and maximum values observed were 13 and 24 °C, with a 17.5 °C mean temperature.

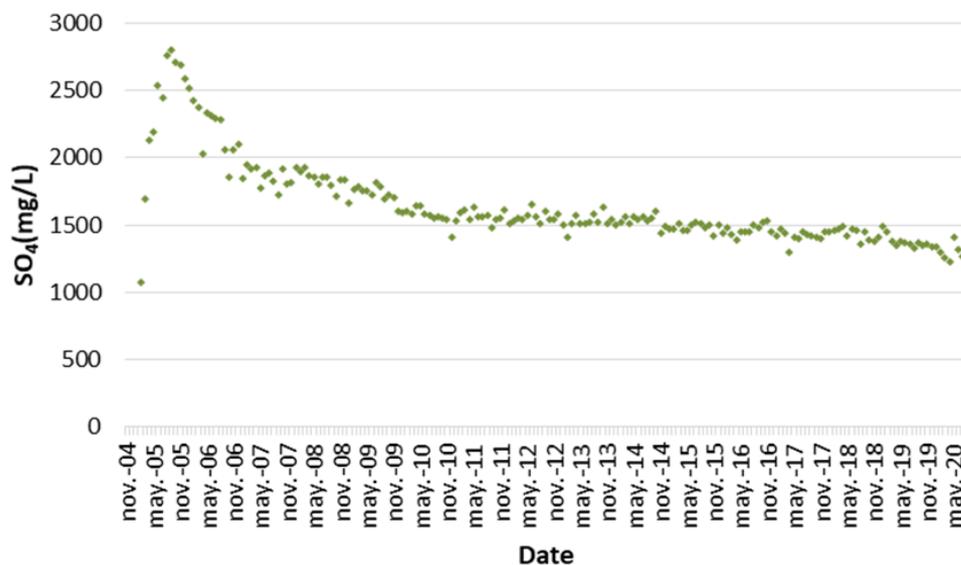


Figure 9. Sulfate concentration evolution in ECA.

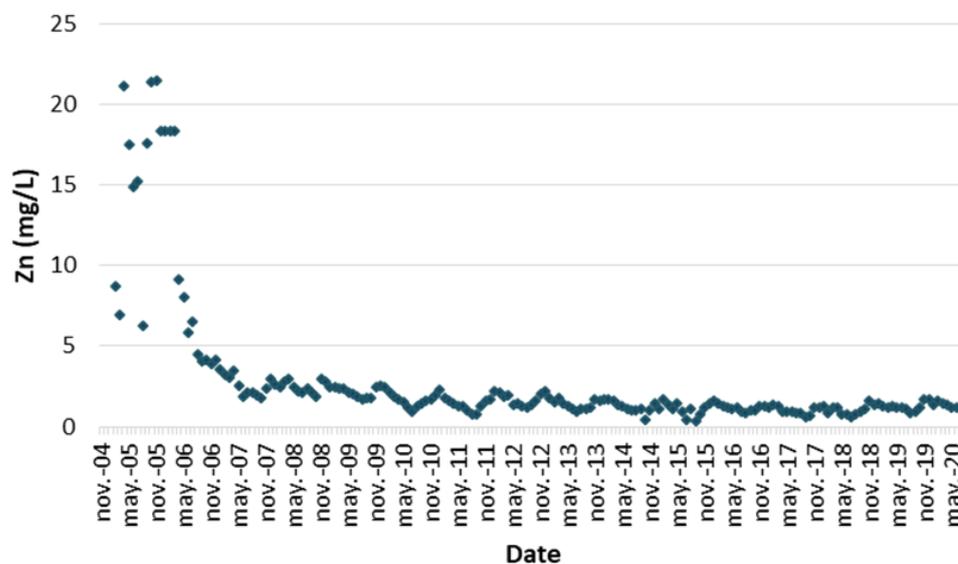


Figure 10. Zn concentration evolution in ECA.

Since the mine is located almost at the center of the Cantabria Autonomous Community, surrounded by industries, and at a few kilometers from the second most populated nucleus of the community, three possible sustainable uses are: a water supply for both human and industrial consumption, geothermal energy, and hydroelectric generation.

At the end of the mine flooding, the resulting dam could be used for supplying water to Torrelavega zone since there is a 9.7 hm³ underground capacity at the 34 hm³ open-pit mine and a 7 hm³/year recharge, considering the water pumped during 1.5 years. These amounts may be enough to supply water to Torrelavega population, whose density is 51.687 inhabitants (considering a 161L/inhabitant/day consumption at Cantabria Autonomous Community) [60].

There is an important source of energy in the underground water of the shallow aquifers, whose extraction and use may be quite economically profitable [61]. To assess

profitability of mine water use, data on the aquifer depth, flow, temperature, and water chemistry were considered [62]. The analysis of the parameters controlled during the flooding allows the conclusion that a pump working 1700 h/year may produce 47.80 GW of thermal energy and consume 6.7 GW h of electric energy. Therefore, the mining dam could be used for reducing electric energy consumption in the Torrelavega zone.

The mine water could also be used for developing renewable energy by building a hydroelectrical power plant [63–65]. To assess the efficiency of this type of use, several factors, such as the mine location, geometry, underground properties, the type of mining activities while in use, and the desired energy production, must be considered [66]. In addition, the underground water flows and water capacity stored underground mitigate the possible differences in the water height of the dam, reducing the operational ranges of pumps and turbines, thus improving their efficiency [65]. By calculating the power produced, the mean production of the mini-hydroelectric power plant may be calculated by multiplying this value by the work hours.

4. Conclusions

Depending on the origin of the mining lake water and its potential use, it is necessary to set design parameters and use mixed water purification technologies that best adapt to the project and water use. The volume quantification and the geochemical parameters of the mining lake water allows for optimizing the efficient use of hydric resources, thus reducing costs and conditioning the mine flooding process. So, it is necessary to conduct a controlled closure and post-closure to ensure the correct use of the stored water.

Following the Reocín mine closure in 2003 after 147 years of exploitation, a mining lake was formed in the open-pit exploitation zone. Due to its capacity, it may be considered Cantabria's second largest dam. Its strategic location at the center of the region opens a large range of possibilities, from industrial and domestic use to hydroelectric energy and as a heat pump. From a geological viewpoint, the zone where the mine is located is thoroughly dolomitized, changing into limestone in the western zone. These materials—limestone and dolomite—show different hydrogeological behaviors. Thus, water enters the mine mainly through the limestone zone on the west, being also fed by the Golbarido River and the recharge on the outcrop zone. On the east, the water inlet is minimal because of the low massif transmissivity.

Considering the voids formed during the exploitation, a 43.7 hm³ void volume and some 94 to 184 hm³ in Reocín subsystem reserves were formed. Fe, Mn, and Zn concentrations are below the limits acceptable for human consumption according to the Spanish norm, while sulfate considerably exceeds the acceptable limit. Therefore, the water could be apt for human consumption after an adequate treatment to reduce the sulfate content by, for example, reverse osmosis, distillation, or ion exchange.

On the other hand, the mine water bears a huge geothermal potential throughout the year since the water stored is between 13 and 24 °C, with a 17.5 °C annual mean, pumped flows being high. So, it could reduce the use of other alternative energies.

Finally, the management of the hydric resources could improve the economic and environmental conditions of the zone, with all the benefits it brings about. Hence, what was previously a challenge for Spanish mining, is today a chance to use the hydric resource as a business opportunity.

Author Contributions: Conceptualization, N.B., R.H. and E.C.; methodology, N.B., R.H. and E.C.; investigation, N.B., R.H., E.C., M.C., E.J.L. and L.C.; data curation, N.B., R.H., E.C., M.C., E.J.L. and L.C.; writing—original draft preparation, N.B., R.H., E.C., M.C., E.J.L. and L.C.; writing—review and editing, N.B., R.H., E.C., M.C., E.J.L. and L.C. All authors have read and agreed with the published version of the manuscript.

Funding: This study received no external funding.

Data Availability Statement: Not applicable.

Acknowledgments: Authors thank Asturiana de Zinc S.A. (AZSA) for providing invaluable information.

Conflicts of Interest: The authors declare no conflict of interest.

References

1. Velasco, R.F.; Herrero, J.M.; Yusta, I.; Alonso, J.A.; Seebold, I.; Leach, D.L. Geology and geochemistry of the Reocin zinc–lead deposit, Basque– Cantabrian Basin, northern Spain. *Econ. Geol.* **2003**, *98*, 1371–1396. [[CrossRef](#)]
2. Symons, D.T.; Lewchuk, M.T.; Kawasaki, K.; Velasco, F.; Leach, D.L. The Reocin zinc–lead deposit, Spain: Paleomagnetic dating of a late Tertiary ore body. *Miner. Depos.* **2009**, *44*, 867. [[CrossRef](#)]
3. Pendás, F.; Cienfuegos, P.; García, R.; Cueva, J.M.; Pelayo, C.; Loredó, J. Consequences of pumping cessation at Reocin Mine, Cantabria (Spain). In *Water in Mining Environments, Proceedings of the IMWA Symposium, Cagliari, Italy, 27–31 May 2007*; Cidu, R., Frau, F., Eds.; IMWA: Cagliari, Italy, 2007.
4. Fernandez-Rubio, R.; Del Olmo, A.G. Mining drainage and water supply under sustainable constraints. In Proceedings of the IMWA: Water resources at risk, American Institute of Hydrology, Denver, CO, USA, 14–18 May 1995.
5. Plata-Bedmar, A. Investigation of the origin of the water discharging at the Reocin Mine using isotope techniques. Isotope techniques in the study of the hydrology of fractured and fissured rocks. In Proceedings of the Advisory Group Meeting, IAEA, Vienna, Austria, 13–17 March 1989.
6. Plata, A. Parameters of carbonate rock aquifers from tracer methods. Hydrogeological Processes in Karst Terranes. In Proceedings of the Antalya Symposium and Field Seminar, Antalya, Turkey, 7–17 October 1990.
7. Finlayson, B.; Sauro, U. International cooperation in research on karst environments. Hydrogeological Processes in Karst Terranes. In Proceedings of the Antalya Symposium and Field Seminar, Antalya, Turkey, 7–17 October 1990.
8. Fernandez-Rubio, R.; Lorca, D.F. Mine water drainage. *Mine Water Environ.* **1993**, *12*, 107–130. [[CrossRef](#)]
9. Trilla, J.; López, C.F.; Peón, A. Sobre el origen y dinámica de las aguas fluyentes de las explotaciones minerales de Reocin (Santander, España). In Proceedings of the Water Mining and Underground World Congress (SIAMOS-78), Granada, Spain, 18–22 September 1978; pp. 293–307.
10. Fernández, G.; Reinoso, J.; Fernández, G. El karst de la mina de Reocin: Un problema hidrológico. In *Jornadas Sobre Tecnología del Agua en la Minería*; IGME: Madrid, Spain, 1992; pp. 31–54.
11. Fernández-Rubio, R. Investigations about the origin of water inflow at Reocin Mine (Santander, Spain). In Proceedings of the 1st International Mine Water Congress, Budapest, Hungary, 19–24 April 1982; pp. 101–120.
12. Reutilización turística del patrimonio minero de Cantabria. *Cuadernos de Turismo* **2009**, *23*, 69–88.
13. Ley de Minas 22/1973, por el que se Establece el régimen jurídico de la Investigación y Aprovechamiento de los Yacimientos Minerales y demás Recursos Geológicos. BOE 176. Available online: <http://www.cma.gva.es/admon/normativa/legislacion/legis/001001000360.html> (accessed on 17 February 2021).
14. Real Decreto 975/2009, de 12 de junio, Sobre gestión de los Residuos de las Industrias Extractivas y de Protección y Rehabilitación del Espacio Afectado por Actividades Mineras. BOE 143. Available online: <https://www.boe.es/buscar/doc.php?id=BOE-A-2009-9841> (accessed on 17 February 2021).
15. Juncosa, R.; Delgado, J.; Padilla, F.; Rodríguez-Vellando, P.; Hernández, H. Improvements in Mero River Watershed Water Supply Regulation Through Integration of a Mining Pit Lake as a Water Supply Source. *Mine Water Environ.* **2016**, *35*, 389–397. [[CrossRef](#)]
16. *Manual de Restauración de minas a cielo abierto*; Asociación Nacional de Empresarios fabricantes de Áridos ANEFA, Gobierno de La Rioja. Consejería de Turismo, Medio Ambiente y Política Territorial, Dirección General de Política Territorial: Logroño, Spain, 2006.
17. Sena, C.; Molinero, J. Water Resources Assessment and Hydrogeological Modelling as a Tool for the Feasibility Study of a Closure Plan for an Open Pit Mine (La Respina Mine, Spain). *Mine Water Environ.* **2009**, *28*, 94–101. [[CrossRef](#)]
18. Fontaine, R.C.; Davis, A.; Fennemore, G.G. The comprehensive realistic yearly pit transient infilling code (CRYPTIC): A novel pit lake analytical solution. *Mine Water Environ.* **2003**, *22*, 187–193. [[CrossRef](#)]
19. Banks, S.B.; Banks, D. Abandoned mines drainage: Impact assessment and mitigation of discharges from coal mines in the UK. *Eng. Geol.* **2001**, *60*, 31–37. [[CrossRef](#)]
20. McCullough, C.D.; Lund, M.A. Opportunities for Sustainable Mining Pit Lakes in Australia. *Mine Water Environ.* **2007**, *25*, 220–226. [[CrossRef](#)]
21. McCullough, C.D.; Schultze, M.; Vandenberg, J. Realizing Beneficial End Uses from Abandoned Pit Lakes. *Minerals* **2020**, *10*, 133. [[CrossRef](#)]
22. Czegka, W.; Junge, F.W. Zwenkau: The genesis from a lignite open cast mine to a recreation lake. Hydro- and geochemical impacts. *SDGG* **2007**, 81–83.
23. Schultze, M.; Geller, W. Filling and management of pit lakes with diverted river water and with mine water—German experiences. In *Mine Pit Lakes: Closure and Management*, 1st ed.; ACG Australian Centre for Geomechanics: Nedlands, Australia, 2011; pp. 107–120.
24. Hinwood, A.; Heyworth, J.; Tanner, H.; McCullough, C.D. Recreational Use of Acidic Pit Lakes—Human Health Considerations for Post Closure Planning. *J. Water Resour. Prot.* **2012**, *4*, 1061–1070. [[CrossRef](#)]
25. Juncosa, R.; Delgado, J.; Cereijo, J.L.; Muñoz, A. Hydrochemical Evolution of the filling of the Mining Lake of As Pontes (Spain). *Mine Water Environ.* **2019**, *38*, 556–565. [[CrossRef](#)]

26. Preene, M.; Younger, P.L. Can you take the heat? Geothermal energy in mining. *Mining Technol.* **2014**, *123*, 107–118. [[CrossRef](#)]
27. Banks, D. *An Introduction to Thermogeology: Ground Source Heating and Cooling*, 2nd ed.; Wiley: Chichester, UK, 2012; pp. 133–149.
28. Raymond, J.; Therrien, R. Optimizing the design of a geothermal district heating and cooling system located at a flooded mine in Canada. *Hydrogeol. J.* **2014**, *22*, 217–231. [[CrossRef](#)]
29. Banks, D.; Steven, J.; Berry, J.; Burnside, N.; Boyce, A. A combined pumping test and heat extraction/recirculation trial in an abandoned hematite ore mine shaft, Egremont, Cumbria, UK. *Water Resour. Manag.* **2019**, *5*, 51–69.
30. Watzlaf, G.R.; Ackman, T.E. Underground mine water for heating and cooling using geothermal heat pump systems. *Mine Water Environ.* **2006**, *25*, 1–14. [[CrossRef](#)]
31. Malolepszy, Z.; Demollin-Schneiders, E.; Bowers, D. Potential use of geothermal mine waters in Europe. In Proceedings of the World Geothermal Congress, Antalya, Turkey, 24–29 April 2005; pp. 24–29.
32. Loredó, J.; Ordóñez, A.; Jardón, S.; Álvarez, R. Mine water as geothermal resource in Asturian coal mining watersheds (NW Spain). In Proceedings of the IMWA Congress 2011 Mine Water—Managing The Challenges, Aachen, Germany, 4–11 September 2011; Rüdé, R.T., Freund, A., Wolkersdorfer, C., Eds.; IMWA: Aachen, Germany, 2011; pp. 177–181.
33. López-Pamo, E.; Sánchez-España, J.; Santofimia, E.; Reyes, J.; Martín-Rubí, J.A. *Limnología físico-química del lago formado Durante la Inundación de la Corta de Reocín, Cantabria*; Unpublic Report; Instituto Geológico y Minero de España (IGME), Ministerio de Ciencia e Innovación: Madrid, Spain, 2010.
34. Eary, L.E. Predicting the effects of evapoconcentration on water quality in mine pit lakes. *J. Geochem. Explorat.* **1998**, *64*, 223–236. [[CrossRef](#)]
35. Boente, C.; Martín-Méndez, I.; Bel-Lan, A.; Gallego, J.R. A novel and synergistic geostatistical approach to identify sources and cores of Potentially Toxic Elements in soils: An application in the region of Cantabria (Northern Spain). *J. Geochem. Explorat.* **2020**, *208*, 106397. [[CrossRef](#)]
36. Hamdi, E.; Du Mouza, J.; Fleurisson, J.A. Evaluation of the part of blasting energy used for rock mass fragmentation. *Fragblast* **2001**, *5*, 180–193. [[CrossRef](#)]
37. Fernández, P. Propuesta de Valorización del Patrimonio Minero de Reocín, Cantabria. Master's Thesis, University of Cantabria, Cantabria, Spain, June 2016.
38. Fernández, J.R.; Alonso, J.A.; Loredó, J.L. La inundación de la mina de Reocín. In *Investigación y Gestión de los Recursos del Subsuelo*; López-Geta, J.A., Loredó, J., Fernández, L., Pernía, J.M., Eds.; IGME: Madrid, Spain, 2008; pp. 389–405.
39. Rouch, R.; (CNRS, Paris, France); Gourbault, N.; (CNRS, Paris, France). Etude de la Derive des Animaux dans les eaux de la mine de Reocín (Torrelavega-Santander-Espagne). Personal communication. 1980.
40. Fernández, R.; (FRASA Ingenieros Consultores, Madrid, Spain). Estudio Hidrogeológico del Sinclinal de Santillana (Cantabria) Relacionado con el cese de Bombeo del agua de la mina de Reocín. Personal communication. 2004.
41. Ford, D.C.; Williams, P.W. *Karst Geomorphology and Hydrology*, 2nd ed.; John Wiley & Sons: Chichester, UK, 2007.
42. Fernández, R.; Baquero, J.C.; Lorca, D.; Verdejo, J. Hidrogeología de la mina de Reocín. In *Investigación y Gestión de los Recursos del Subsuelo*; López-Geta, J.A., Loredó, J., Fernández, L., Pernía, J.M., Eds.; IGME: Madrid, Spain, 2008; pp. 423–455.
43. Castro, J.; Moore, J. Pit lakes: Their characteristics and the potential for their remediation. *Environ. Geol.* **2000**, *39*, 1254–1260. [[CrossRef](#)]
44. White, W.B. Karst hydrology: Recent developments and open questions. *Eng. Geol.* **2002**, *65*, 85–105. [[CrossRef](#)]
45. Pisabarro, A.; Pellitero, R.; Serrano, E.; Gómez-Lende, M.; González-Trueba, J.J. Ground temperatures, landforms and processes in an Atlantic mountain. Cantabrian Mountains (Northern Spain). *Catena* **2017**, *149*, 623–636. [[CrossRef](#)]
46. Bruschi, V.M.; Bonachea, J.; Remondo, J.; Gómez-Arozamena, J.; Rivas, V.; Méndez, G.; Cendrero, A. Analysis of geomorphic systems' response to natural and human drivers in northern Spain: Implications for global geomorphic change. *Geomorphology* **2013**, *196*, 267–279. [[CrossRef](#)]
47. Grandia, F.; Canals, À.; Cardellach, E.; Banks, D.A.; Perona, J. Origin of ore-forming brines in sediment-hosted Zn-Pb deposits of the Basque-Cantabrian Watershed, Northern Spain. *Econ. Geol.* **2003**, *98*, 1397–1411. [[CrossRef](#)]
48. Yue, S.; Ouarda, T.B.M.J.; Bobée, B.; Legendre, P.; Bruneau, P. The Gumbel mixed model for flood frequency analysis. *J. Hydrol.* **2000**, *228*, 3–4. [[CrossRef](#)]
49. APHA. *Standard Methods for the Examination of Water and Wastewater*, 20th ed.; American Public Health Association; American Water Works Association; Water Environment Federation: Washington, DC, USA, 2005.
50. Álvarez, R.; Ordoñez, A.; De Miguel, E.; Loredó, C. Prediction of the flooding of a mining reservoir in NW Spain. *J. Environ. Manage.* **2016**, *184*, 219–228. [[CrossRef](#)]
51. Hrdinka, T. Typology and potential utilization of anthropogenic lakes in mining pits in the Czech Republic. *Limnol. Rev.* **2005**, *7*, 47–53.
52. Nixdorf, B.; Lessmann, D.; Deneke, R. Mining lakes in a disturbed landscape: Application of the EC Water Framework Directive and future management strategies. *Ecol. Eng.* **2005**, *24*, 67–73. [[CrossRef](#)]
53. Gammons, C.H.; Harris, L.N.; Castro, J.M.; Cott, P.A.; Hanna, B.W. Creating lakes from open pit mines: Processes and considerations, with emphasis on northern environments. *Canad. Tech. Rep. Fish. Aq. Sci.* **2009**, *8*, 1–106.
54. Ordoñez, A.; Jardón, S.; Álvarez, R.; Andrés, C.; Pendás, F. Hydrogeological definition and applicability of abandoned coal mines as water reservoirs. *J. Environ. Monit.* **2012**, *14*, 2127–2136. [[CrossRef](#)]

55. Doupé, R.G.; Lymbery, A.J. Environmental risks associated with beneficial end uses of mine lakes in southwestern Australia. *Mine Water Environ.* **2005**, *24*, 134–138. [[CrossRef](#)]
56. *Real Decreto 140/2003, por el que se Establecen los Criterios Sanitarios de la Calidad del agua de Consumo Humano*. BOE 45 (Sec. 1). pp. 7228–7245. Available online: <https://www.boe.es/boe/dias/2003/02/21/pdfs/A07228-07245.pdf> (accessed on 17 February 2021).
57. Akcil, A.; Koldas, S. Acid Mine Drainage (AMD): Causes, treatment and case studies. *J. Clean. Prod.* **2006**, *14*, 1139–1145. [[CrossRef](#)]
58. Valenzuela, P.; Domínguez-Cuesta, M.J.; Meléndez-Asensio, M.; Jiménez-Sánchez, M.; de Santa María, J.A.S. Active sinkholes: A geomorphological impact of the Pajares tunnels (Cantabrian range, NW Spain). *Eng. Geol.* **2015**, *196*, 158–170. [[CrossRef](#)]
59. Unsal, B.; Yazicigil, H. Assessment of Open Pit Dewatering Requirements and Pit Lake Formation for the Kışladağ Gold Mine, Uşak, Turkey. *Mine Water Environ.* **2016**, *35*, 180–198. [[CrossRef](#)]
60. Instituto Nacional de Estadística. Demografía y Población. Available online: http://www.ine.es/dyngs/INEbase/es/categoria.htm?c=Estadistica_P&cid=1254734710984 (accessed on 15 June 2020).
61. Hamm, V.; Sabet, B. Modelling of fluid flow and heat transfer to assess the geothermal potential of a flooded coal mine in Lorraine, France. *Geothermics* **2010**, *39*, 177–186. [[CrossRef](#)]
62. Rybach, L. Geothermal energy: Sustainability and the environment. *Geothermics* **2003**, *32*, 463–470. [[CrossRef](#)]
63. Pujades, E.; Orban, P.; Bodeux, S.; Archambeau, P.; Erpicum, S.; Dassargues, A. Underground pumped storage hydropower plants using open pit mines: How do groundwater exchanges influence the efficiency? *Appl. Energy* **2017**, *190*, 135–146. [[CrossRef](#)]
64. Wessel, M.; Madlener, R.; Hilgers, C. Economic feasibility of semi-underground pumped storage hydropower plants in open-pit mines. *Energies* **2020**, *13*, 4178. [[CrossRef](#)]
65. Pujades, E.; Willems, T.; Bodeux, S.; Orban, P.; Dassargues, A. Underground pumped storage hydroelectricity using abandoned works (deep mines or open pits) and the impact on groundwater flow. *Hydrogeol. J.* **2016**, *24*, 1531–1546. [[CrossRef](#)]
66. Kitsikoudis, V.; Archambeau, P.; Dewals, B.; Pujades, E.; Orban, P.; Dassargues, A.; Erpicum, S. Underground pumped-storage hydropower (UPSH) at the Martelange Mine (Belgium): Underground reservoir hydraulics. *Energies* **2020**, *13*, 3512. [[CrossRef](#)]