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From Knowledge to Wisdom

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Spectrophotometric Determination of Hydrogen Molecule in Drinking Water with *o*-Phenanthroline in the Presence of Colloidal Platinum

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Abstract: A simple rapid method for the determination of hydrogen molecule in water is developed. This method is based on the redox reaction of ferric ion and hydrogen molecule in the presence of colloidal platinum. The released ferrous ion was developed with *o*-phenanthroline and spectrophotometrically measured at 510 nm. The suitable pH condition of redox reaction of ferric ion and hydrogen molecule is pH 2. And 1 mol of molecular hydrogen reduced 2 mol of ferric ion. The molar coefficient for hydrogen molecule is 2.25×10^4 $L \cdot mol^{-1} \cdot cm^{-1}$. The stability of hydrogen water was also discussed.

Key words: Molecular hydrogen, colloidal platinum, ferroine, spectrophotometry.

1. Introduction

Hydrogen water was known to be most effective wet cleaning of silicone surfaces [1] and used for nutrient solution of Komatsuna plants [2]. On the other hand, many studies have been made for influence of health. Ohsawa, et al. [3] reported that hydrogen water can efficiently remove active oxygen, therefore, hydrogen water can be expected for treatment of cerebral infarction. Shimouchi, et al. [4, 5] reported when 7 adults took hydrogen water and 40% hydrogen has been consumed by acting with hydroxyl radicals. Although hydrogen water has attracted attention in these ways, there are surprisingly few methods for easily measuring the concentration of hydrogen.

There are some methods for determination of hydrogen molecule concentration by amperometry [6], gas chromatography [7], methylene blue drop test [8]. However, no study has been made concerning spectrophotometric determination of hydrogen molecule in water. So, authors try to consider determining method of hydrogen. By methylene blue drop test method, it counts droplet of methylene blue solution till the solution changes to blue color. Disappearing of the color of the solution did not occur in the absence of colloidal platinum. The colloidal platinum is served as catalyzer for blue color of methylene blue to colorless of leuco methylene blue. However, the colorless solution changed to blue color after standing with oxygen in air. Therefore, the method is difficult to apply for spectrophotometric determination of hydrogen molecule in water directly. However, the catalyzer of colloidal platinum is one good idea to make hydrogen as increment of reduction power. Hydrogen molecule oxidation reaction on platinum nanoparticles was also reported [9, 10]. The present paper used colloidal platinum as oxidative catalyzer of hydrogen molecule for reduction of ferric ion to ferrous ion. The produced ferrous ion was developed with *o*-phenanthrorine and the complex (ferroin) formed was determined spectrophotometrically.

Corresponding author: Minori Kamaya, Ph.D., associate professor, main research field: analytical chemistry:

2. Experimental

2.1 Materials and Reagents

Spectrophotometer measurements were made with a Shimazu UV-1800 spectrophotometer using 1 cm glass cells. A TOA HM-30V was used for pH measurement. MAGICPOT hydrogen generator CCMP was used for preparation of hydrogen water using drinking water (total hardness 50 mg/L). The average of concentration of hydrogen molecule in this water is near 0.5 mg/L. And the concentration was measured using dissolved hydrogen meter KM2100DH.

All reagents were of analytical grade and the solutions were prepared with deionized water from a ElGA PURELABOTION-S type.

Ferric solution: Weigh 0.362 g of ferric nitrate enneahydrate and add 2.5 mL of 1 mol/L hydrochloric acid and diluted with water to 250 mL.

1×10^{-3} mol/L of platinum nanoparticle dispersion solution was prepared with diluting with water using 10 mM of platinum nanoparticle dispersion from Renaissance Energy Research Ltd..

2% *o*-phenanthrorine solution: 2 g of *o*-phenannthroline dichloride monohydrate was dissolved in 100 mL of water.

pH 6.15 buffer solution: 10.2 g of 2-morpholinoethanesulfonic acid monohydrate was dissolved in water and the pH was adjusted with sodium hydroxide solution and make up 250 mL with water.

2.2 Standard Procedure

Transfer 5 mL sample solution into volumetric flask. Add 0.5 ml of ferric solution, 0.15 mL of platinum nanoparticle dispersion solution, 0.5 mL of *o*-phenanthroline solution, 2 mL of buffer solution and diluted with water to 10 mL.

3. Results and Discussion

3.1 Influence of Colloidal Platinum

Hydrogen gas was not able to reduce ferric ion to ferrous ion. The dissociative adsorption of a hydrogen molecule occurs at platinum colloids [11]. The surface provides reaction field, and it suggests that it promotes redox reaction of ferric ion and hydrogen molecule. Fig. 1 indicates the influence of colloidal platinum solution on reduction of ferric ion. If the colloidal platinum is not present, the absorbance of the solution is same of blank solution. Increment of colloidal platinum introduced increasing of absorbance and more than 1.2×10^{-5} mol/L of colloidal platinum concentration indicates constant absorbance.

3.2 Effect of pH

The optimum pH condition of redox reaction of hydrogen molecule and ferric ion was investigated. The result is shown in Fig. 2. From this result, it was shown the maximum pH was pH 2. And higher pH more than pH 2, the absorbance was decreased. The recommended pH condition for ferroin formation is beyond from pH 4 to 6 [12]. Therefore the pH 2 is only the condition of redox reaction of hydrogen and ferric ion.

3.3 Calibration Curve for Hydrogen Molecule in Water

Linear calibration curve was obtained using a standard procedure (Fig. 3). Beer's law is obeyed in the range of 0 to 6.5×10^{-6} mol/L. The molar coefficient for hydrogen molecule in water was 2.26×10^{4} $L \cdot mol^{-1} \cdot cm^{-1}$ and exhibits an excellent linear correlation coefficient (0.9968). The molar coefficient is near twofold than ferroin, it means 1 mol of hydrogen molecule reduced 2 mol ferric ion. The detection limit of hydrogen in water is 6.96×10^{-7} mol/L (1.39×10^{-3} ppm, $n = 16$).

3.4 Stabilization of Hydrogen Water

Hydrogen gas is easily evaporated from the hydrogen water [13]. Stability of the hydrogen water on various temperature conditions was shown in Fig. 4. It indicates the stability of hydrogen water decreases depending on the temperature increased. The stability

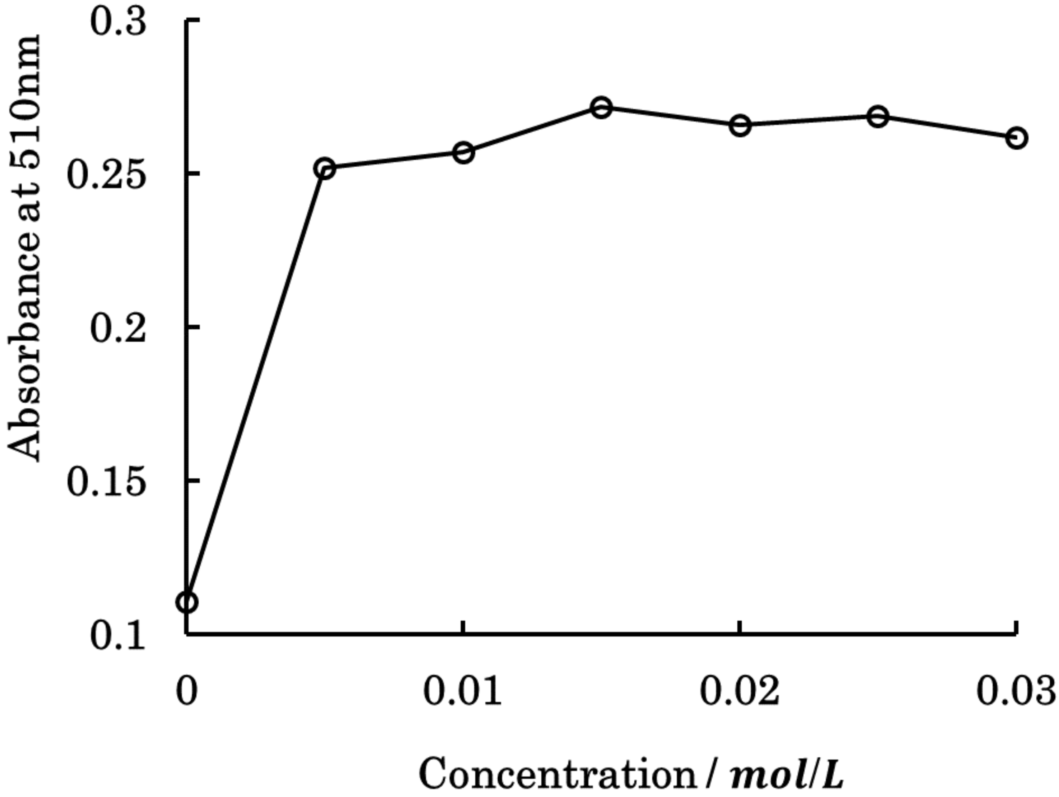

Fig. 1 The influence of concentration of colloidal platinum on reduction of ferric ion.

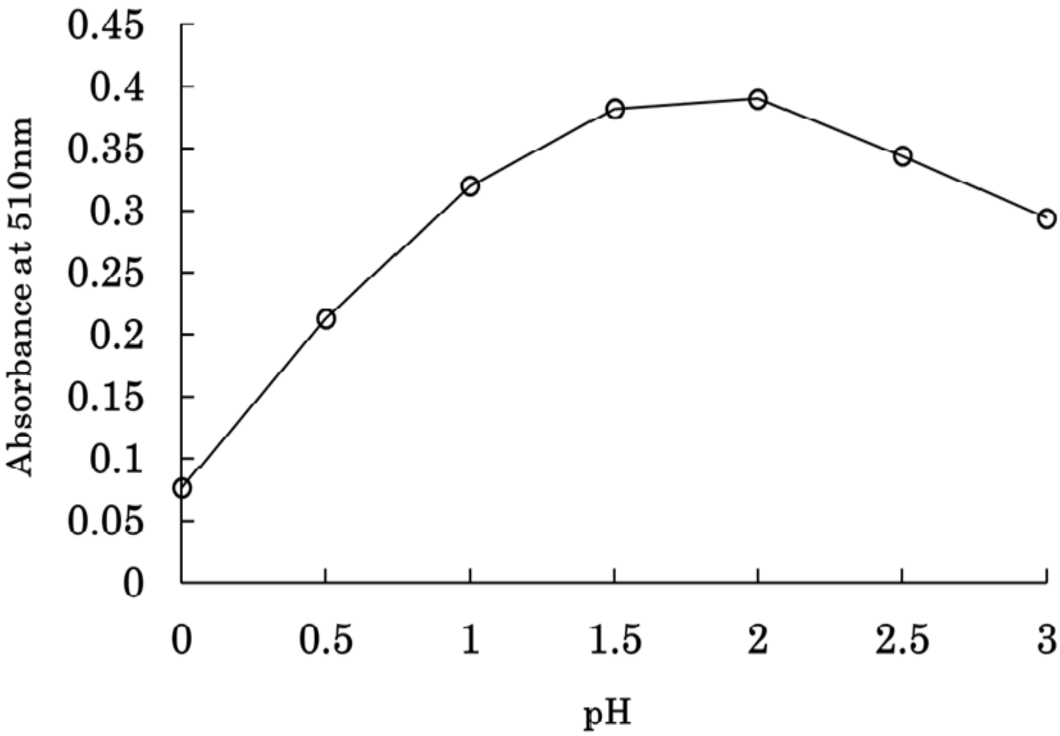

Fig. 2 The optimum pH condition of redox reaction of hydrogen molecule and ferric ion.

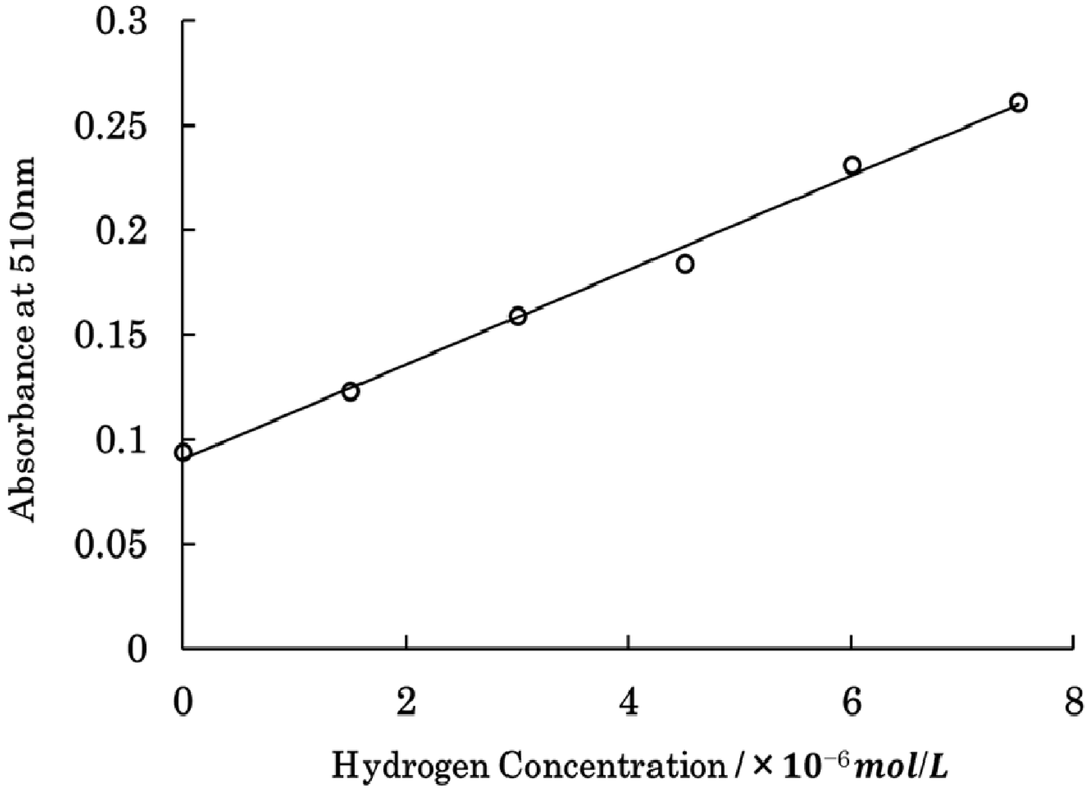

Fig. 3 Calibration curve for hydrogen molecule in water.

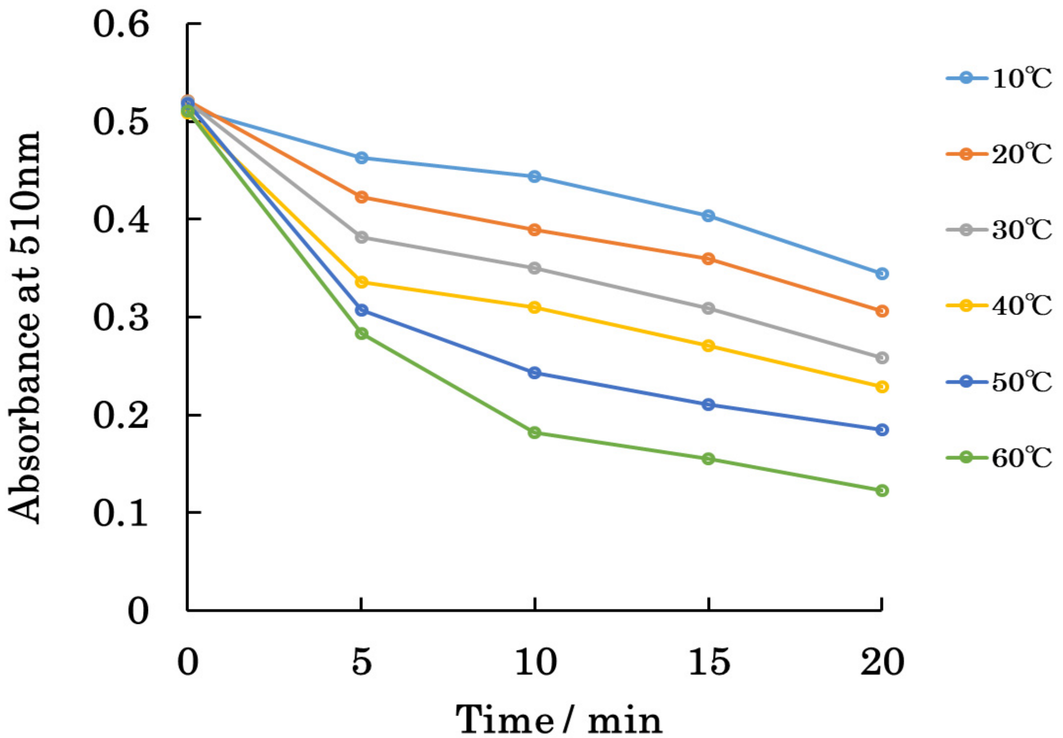

Fig. 4 Stability of the hydrogen water on various temperature conditions.

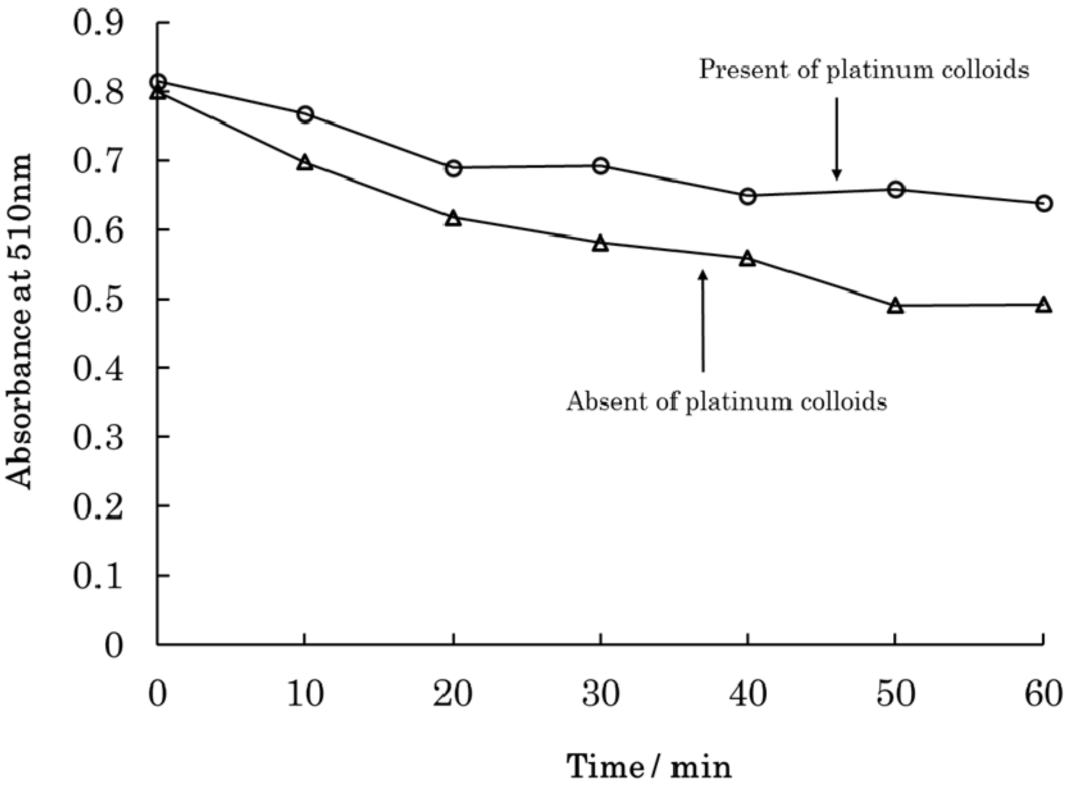

Fig. 5 The stability of hydrogen water in the absence or present of platinum colloids.

Table 1 Effect of diverse ion (amount added, 10 ppm).

Ions	Added as	Absorbance	Relative error (%)	Ions	Added as	Absorbance	Relative error (%)
None	—	0.327	—	None	—	0.302	—
Mg^{2+}	$MgSO_4 \cdot 7H_2O$	0.306	-6.4	Cl^-	KCl	0.290	-4.0
Mn^{2+}	$MnSO_4 \cdot 5H_2O$	0.308	-5.8	Br^-	KBr	0.305	+1.0
Ni^{2+}	$NiSO_4 \cdot 6H_2O$	0.320	-2.1	I^-	KI	0.628	+108
Cu^{2+}	$CuSO_4 \cdot 5H_2O$	0.317	-3.1	CH_3COO^-	CH_3COOK	0.274	-9.3
Zn^{2+}	$ZnSO_4$	0.306	-6.4	CrO_4^{2-}	K_2CrO_4	0.065	-78.5
				MnO_4^-	$KMnO_4$	0.071	-76.5
				CO_3^{2-}	K_2CO_3	0.268	-11.3
				NO_2^-	KNO_2	0.435	+44.0
				NO_3^-	KNO_3	0.264	-12.6

of the hydrogen water was also tested using addition of platinum colloids (Fig. 5). The stability of hydrogen water increased by addition of platinum colloids. It means hydrogen molecule adsorbs on the surface of platinum.

3.5 Influence of Diverse Ions

Influence of twenty amounts of various ions on the determination of molecular hydrogen was examined (Table 1). Oxidizing anions, such as dichromate, permanganate lead to negative errors. And iodide leads to positive error. These ions make redox reaction with ferrous or molecular hydrogen.

4. Conclusion

A simple rapid method for the determination of hydrogen molecule in water is developed. The suitable pH condition of redox reaction of ferric ion and hydrogen molecule is pH 2. And 1 mol of molecular hydrogen reduced 2 mol of ferric ion. The molar coefficient for hydrogen molecule is 2.25×10^4 $L \cdot mol^{-1} \cdot cm^{-1}$. Stability of hydrogen water was also discussed. The method influenced such as iodide, permanganate and chromate ions. The detection limit of hydrogen in water is 6.96×10^{-7} mol/L (1.39×10^{-3} ppm, $n = 16$).

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Study of Wastewater Treatment Plants in Operation with UASB Reactors in the Municipality of Juazeiro do Norte-Ceará

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Abstract: The indiscriminate release of effluents without any type of treatment, or previous treatment without adequate disinfection, can cause several inconveniences for the water body and society, including water-borne diseases. In the present study, the physicochemical and biological aspects of three WWTPs (Wastewater Treatment Plants) operated with UASB (Upflow Anaerobic Sludge Blanket) technology in Juazeiro do Norte were analyzed in order to verify the state of Ceará State legislation, compliance with standards for the release of domestic effluents into bodies' receptors. In the research, it verified that the stations did not meet the effluent release standards for TSS (Total Suspended Solids) and removal of *Escherichia coli* in several analyzed months. It also verified that the UASB stations need a post-treatment in order to assist in the process of removal of organic matter and pathogens.

Key words: Effluent, UASB, analyze.

1. Introduction

Sewage is defined as water supply to a community after its use in a variety of applications [1]. This wastewater contains approximately 99.9% water and the remaining fraction includes organic, inorganic solids, solvents, paper, plastic, detergents as well as microorganisms, and due to the degree of pollution, they must be treated properly before returning to the environment [2, 3].

The indiscriminate release of effluents without any type of treatment, or previous treatment without adequate disinfection, can cause several inconveniences for the water body and society, including water-borne diseases due to the contribution of organisms from the "coliform group" [3, 4].

The pollution of these water resources causes a number of problems, which tend to worsen over time because of misuse and anthropic activities developed along the river basin [5].

Consequences of water pollution affect ecological, social or economic fields [4, 5]: (1) Damage to the human supply, making it a vehicle for the transmission of diseases; (2) Damages to multiple uses of water such as recreation, industrial, fishing; (3) Worsening problems of good quality water scarcity; (4) Elevation in the cost of water treatment, therefore, the increase of the tariff paid to the population; (5) Injury to fish and other aquatic organisms, with ecological imbalance; (6) Excessive algae proliferation (eutrophication); (7) Reduction of the average life of the population; (8) Higher incidence of diseases; (9) Increased hospital costs; (10) Increase in infant mortality and (11) Reduced productivity at work.

Over a period of 9 years (2001 to 2009), diseases such as diarrhea and dengue, which are related to lack of sanitation, were responsible for more than 93% of hospitalizations in Brazil [6].

In the Garulhos region, in the city of São Paulo, Brazil, in 2005 and 2006, they reported that cases of diarrhea in

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children were 15 times more frequent for populations with precarious housing and lack of adequate access to basic sanitation [7]. The mortality from this disease is a pointer to be considered in Public Health, given the responsiveness of various changes in conditions of access to adequate sanitation, food quality and behaviors of an individual in a community [8].

Juazeiro do Norte is located in the southern state of Ceará, with a population of 249,939, the climate is tropical hot with average temperatures of 25 ºC [9]. The hot climate is ideal for adoption of UASB (Upflow Anaerobic Sludge Blanket), technology due to the development of organisms in the anaerobic phase at temperatures above 20 ºC, and the reactor heating process is unnecessary [2, 10-13].

This type of reactor was created in the 1970s by teacher Lettinga and his team from the University of Wageningen—Netherlands, characterized by a three-phase separation system: solid, liquid and gaseous. Sewage with high concentrations of pollutants, being applied in domestic wastewater with low concentrations of organic matter from the middle of 1995 [4, 10, 14]. A great diversity of organic effluents, even those that previously were not believed to be possible to treat anaerobically, are now treated using UASB [15].

In the 1980s, feasibility studies of the UASB reactors were started, which were highlighted in the operational cost, high rates of sewage treatment, possibility of energy production for methane gas and attractive cost. However, improper use, without great knowledge about this type of technology, has eroded its image in front of us and several sanitation companies [16].

The UASB reactors can be a good option for small Brazilian municipalities when compared to other technologies, mainly due to the low cost of construction and maintenance, besides the possibility of the energetic use of the biogas generated [17, 18]. Among the main advantages and disadvantages of UASB type reactors, it is possible to highlight in Table 1.

The Resolution COEMA (State Environmental Council) No. 02/2017 Article 12 governs launch standards for domestic sewage [19].

According to the Public Services Regulatory Agency and Delegates of the State of Ceará, ARCE [20], the wastewater system of Juazeiro do Norte consists of five WWTPs (Wastewater Treatment Plants): (1) WWTP Malvas—2 Anaerobic Lagoons + 2 Facultative Ponds + 1 Maturation Lagoon; (2) WWTP Vila Três Marias—UASB + Contact Tank with Chlorination + Sludge Drying Bed; (3) WWTP Tenente Coelho—2 UASB + 2 SAFs (Submerged Aerated Filters) + 2 Decanters + Chlorination + 2 Sludge Drying Beds; (4) WWTP Mutirão—2 UASB + 5 Contact Tanks + 4 Mud Drying Beds; (5) WWTP Prourb - 8 Septic Tanks + 8 Anaerobic Filters + Chlorination.

Information obtained from the National Sanitation Information System [21], showed that in Juazeiro do Norte in the period from 2006 to 2016, 26,801.71 m³ of sewage was collected and treated. The Water and Sewage Company of Ceará (CAGECE) is the concessionaire responsible for the collection and treatment of sewage in the municipality. Juazeiro do

Table 1 Characteristics of UASB reactors [1, 10].

Positives	Negatives
1. Lower power consumption.	1. Possibility of emanation of bad odors and corrosive gases.
2. Lower production of biological sludge.	2. Longer starting period for biomass development required.
3. Less need for nutrients.	3. It may require additional treatment by an aerobic treatment process to meet effluent emission standards.
4. Production of methane, energy source.	4. It does not allow the biological removal of nitrogen and phosphorus.
5. Lower reactor volume.	5. Very sensitive to the negative effects of low temperature.
6. Elimination of air pollution by exhaust gases.	6. Low system capacity to tolerate toxic loads.
7. Satisfactory removal of BOD and COD (Chemical Oxygen Demand), in order of 65 to 75%.	7. May require addition of alkalizing agent.

Norte has 21.99% of collected sewage, being among the 15 worst municipalities of the 100 surveyed, in investments in the area of sanitation [22].

In view of the above, the objective was to verify the environmental suitability, removal of COD and compliance with the state legislation of treated effluents from stations that use UASB reactors as a type for the treatment of domestic effluents from Juazeiro do Norte.

2. Material and Methods

The study was carried out based on documentary research and data from the inspection reports of the State Regulatory Agency of Ceará, responsible for the supervision of water and sewage services in Juazeiro do Norte. The research considered the data (pH, COD, TSS (Total Suspended Solids) and *E. coli*) of the effluents treated in the WWTP Vila Três Marias, WWTP Tenente Coelho and WWTP Mutirão na (Fig. 1) due to the importance of these parameters in the operational control as well as a greater frequency of analysis of these parameters by the concessionaire, benefiting a greater credibility of the information analysis.

According to the Sampling Plan for Sewage Quality Monitoring [23], for anaerobic reactor type technologies, with and without post-treatment, monthly analyses of the raw sewage are carried out and only treated for the COD parameter, thus making it impossible to evaluate the efficiency of other physicochemical and biological parameters of the seasons.

2.1 Description of the UASB Reactors in Juazeiro do Norte

2.1.1 Vila Três Marias

The Vila Três Marias WWTP, receives contributions from Vila Três Marias community, the effluent sent to a lifting station equipped with railing, sandbox with Parshall gutter, suction well with self-priming pump and generator set power. After the preliminary treatment, the sewage is sent to the contact tank where chlorine is applied for disinfection and the final destination is the Salgado River [20]. The quality of the Salgado river is compromised, an important fact, given that the waters of this river will be used for the transposition of the São Francisco river [24].

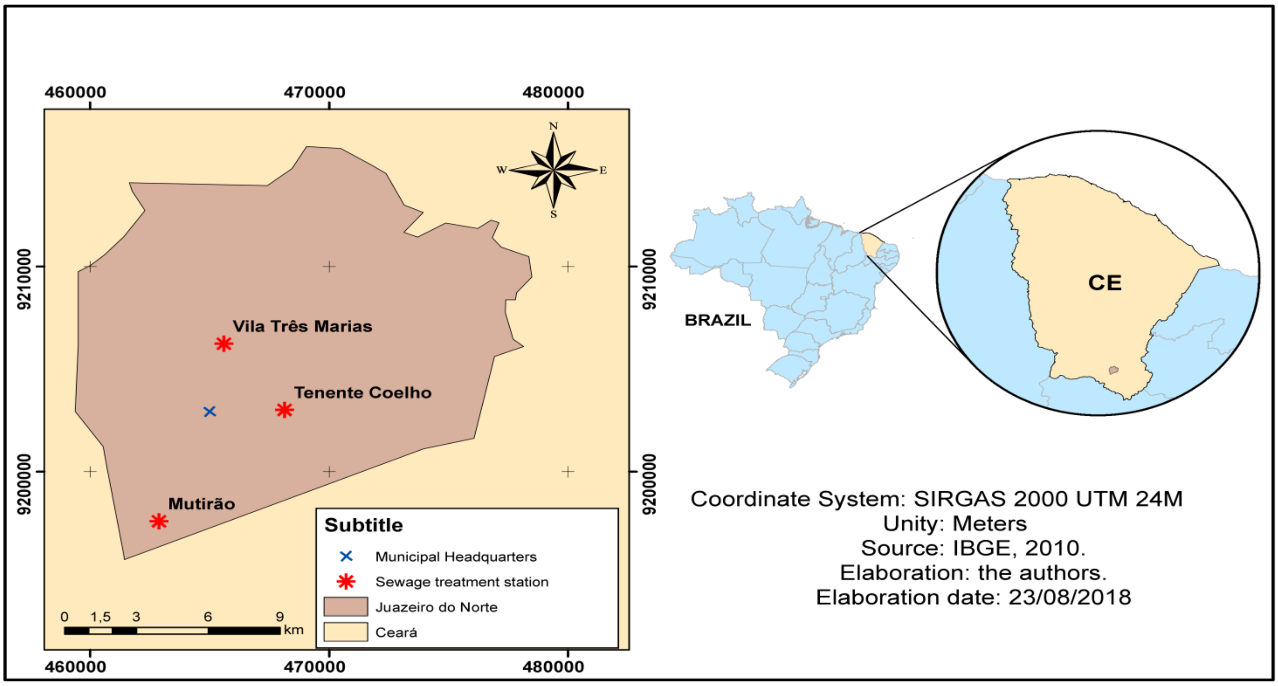

Fig. 1 Location of the UASB stations in Juazeiro do Norte.

2.1.2 Tenente Coelho

The station receives an exclusive contribution from Tenente Coelho residential condominiums through a condominial collection network that drains the effluents, soon after it sent to the preliminary treatment with railing and sandbox with flow measurement in the Parshall gutter. This preliminary treatment is essential to preserve the pump motor assembly, which then sends the primary treatment sewer to two UASB reactors. The improvement of UASB effluent quality at the secondary level will be achieved through the application of a fixed film aerobic biological reactor, in this case an SAF was used as secondary sewage treatment. In practice this type of unit constituted of a tank, where in its interior there will be a filling (half support). As the filler does not retain the biomass, it is necessary to decant downstream of the reactor [4]. To do so, the ASF effluent will pass through a settling unit obtained with the use of parallel plates, called the SD (Secondary Decanter). After this process, the effluent will be sent for disinfection with chlorine and will pass into a contact tank. Finally, the final destination is the Salgado River [20].

2.1.3 Mutirão

It receives the contribution of the housing complex Frei Damião, where it passes through an elevation with well sand, railing and suction well with submersible pumps. Subsequently, the effluent is repressed to an equilibrium tower for the purpose of breaking the pressure so was not to cause operational problems in the UASB reactors which soon follow after the tower. After the anaerobic treatment in the UASB, the first one is directed to the five contact tanks, where it was disinfected with chlorine, and finally, the final destination is disposed of in a soil near the station [20].

2.2 Launch Patterns

Regarding the launching standard, the final quality of the WWTP effluent was evaluated in compliance with the standards established by the SEMACE (State Environmental Authority, Ceará), contained in the COEMA no. 02, dated February 21, 2017, which on standards and conditions for the discharge of liquid sources (Table 2).

2.3 Efficiency of Removal of Organic Compounds

In order to calculate the efficiency of COD removal at the stations studied [3], Eq. (1):

$$E = \left(\frac{A_C - E_C}{A_C} \right) \cdot 100 \tag{1}$$

where:

"E" is removal efficiency (%);

"E_c" is efluent concentration in mL;

"A_c" is afluent concentration in mL.

The same methodology was used in other studies on effluent treatment [12, 25, 26].

3. Results and Discussion

3.1 COD Removal Efficiency

The efficiency of COD removal at the stations that operated with UASB in Juazeiro do Norte, is observed according to Fig. 2, that from March to November of 2017, the station Mutirão, although the WWTP did not obtain an aerobic treatment to guarantee the improved

Table 2 Standard of release of domestic effluents from state legislation [19].

Resolution standards No. 02/2017 art. 12, COEMA		
Parameter	Unity	Maximum value
pH	-	5.0-9.0
COD	Not specified	
TSS	mg/L	100.0
E. coli	Number of CFU (Colony Forming Units)/100 mL	5,000

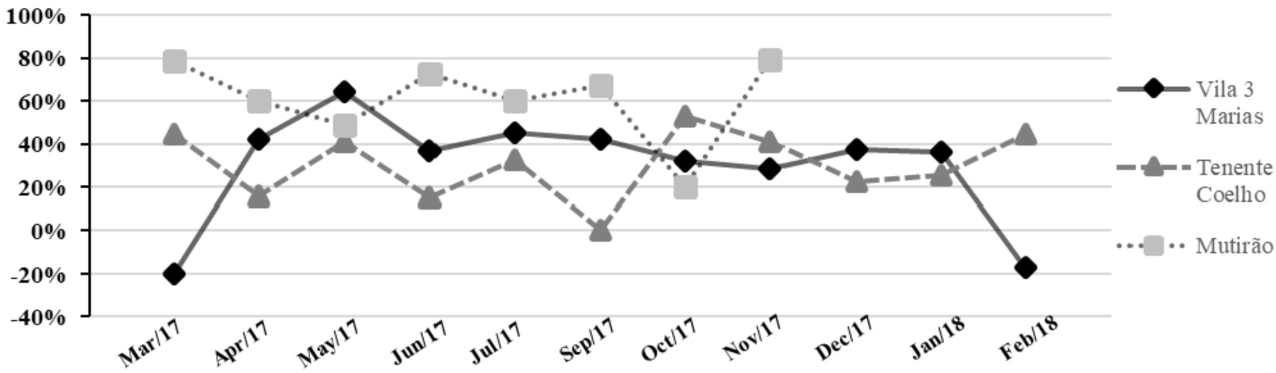

Fig. 2 Efficiency of COD removal at UASB stations in Juazeiro do Norte.

quality of the effluent, it was the one that had higher removal rates of COD, against WWTP Tenente Coelho and WWTP Vila Três Marias. However, in the months of December (2017) to February (2018) the CAGECE due to operational problems, did not carry out analyses of the quality of the effluent in this station. In addition, in September 2017 no analyses were carried out in two stations.

It is also verified through Fig. 2 that in the months of March/2017 and February/2018, there was negative efficiency of organic matter removal at Vila Três Marias station, that is, the organic load of the sewage dumped in the Salgado River is greater than organic load of raw sewage affluent to the season.

This fact can be explained by the occurrence of a possible overload of oils and greases in the reactor, thus causing the adsorption of fat in the bacterial sludge, causing a drag of solids and, therefore, influencing the organic matter removal in the reactor [13].

The average COD removal efficiencies are consistent with the values presented in the literature [27-29].

3.2 Quality of the Treated Effluent

3.1.1 pH

The quality of the effluent should meet the state regulations for the discharge of water bodies, in relation to the effluent of the UASB reactors, it is recommended post-treatment for a better efficiency of this system [1, 10]. Fig. 3 shows the variation of pH in relation to the months at the UASB stations in the city, where there is a trend towards the neutrality range with the highest average pH at the station Tenente Coelho, corroborating with other studies in the literature [30, 31]. The state standard establishes a pH range of 5.0 to 9.0 (Table 1), with all the stations under study complying with the legislation regarding this parameter (Fig. 3). The pH is an extremely important environmental condition in anaerobic processes, with an optimum pH range between 6.6 and 7.6; ideally between 7.0 and 7.2 [2]. The control process of this parameter must be made strictly, as it is affected by organic acids and the carbon dioxide de-equilibrium reactions [2]. The pH condition influences the development of the process, if the pH falls sharply, it means that the acids formed are not being neutralized by the absence of alkalinity in the medium, or not converted to methane gas, this process is known as reactor souring, leading to the collapse of the process [2]. In this case, the reactor after the souring process will only work again after the addition of external alkalinity [13].

3.1.2 *E. coli*

The state legislation establishes (Table 1) a maximum limit of *E. coli* in eviction after treatment of up to five thousand CFU (number of CFU) per 100 mL. Fig. 4 shows the results analyzed in the three stations with UASB technology in Juazeiro do Norte in relation to this parameter. According to Fig. 3, Tenente Coelho and Mutirão WWTPs, during the

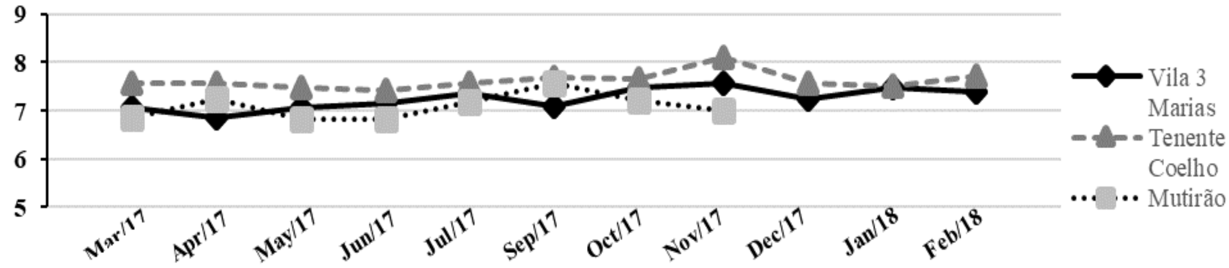

Fig. 3 pH in function of the months in UASB reactors of Juazeiro do Norte.

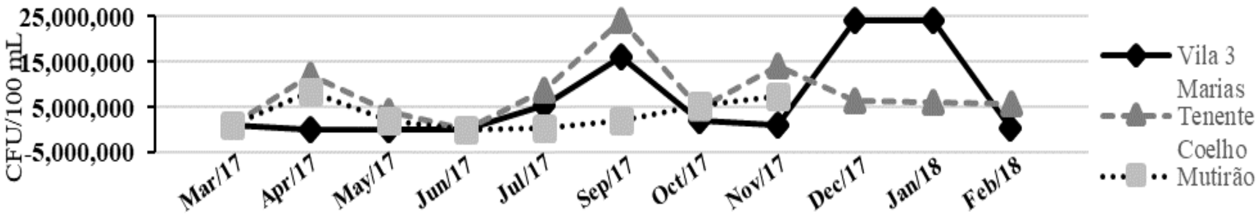

Fig. 4 *E. coli* in function of the months in UASB reactors of Juazeiro do Norte.

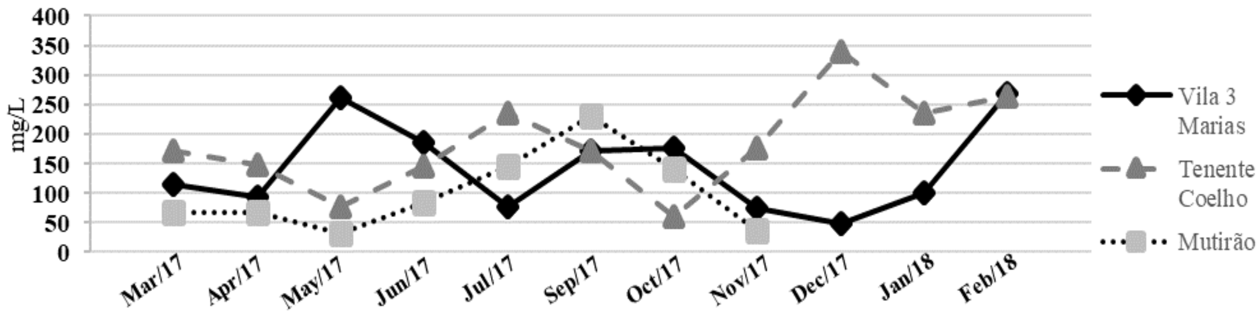

Fig. 5 TSS in function of the months in UASB reactors of Juazeiro do Norte.

whole analyzed period, did not present satisfactory results of *E. coli* equal to or below the maximum value allowed in the state standard.

The Vila 3 Marias WWTP (UASB + Chlorination) obtained a satisfactory result in the reduction of pathogens according to the legislation, only in the months of April (100 CFU/100 mL) and June (1 CFU/100 mL), the *E. coli* values in the treated effluent being still quite high when compared with some authors [32, 33]. Anaerobic reactors are not designed for the purpose of removal of microorganisms, this being a consequence of the retention of solids [14].

3.1.3 TSS

Fig. 5 shows the monthly concentrations of TSS at UASB WWTPs in Juazeiro do Norte.

In relation to the state legislation for the discharge of sewage treated in the environment (Table 2), according to Fig. 5, the Tenente Coelho WWTP (March, April, May, June, October and November) and Mutirão (April, July, November, December and February) obtained in five months values of compliance with resolution COEMA No. 02/2017 for the parameter TSS, against only two months (May and October) of the Tenente Coelho WWTP.

3.3 Statistics of WWTPs

Table 3 features measures of central tendency (average) and variation (minimum, maximum and standard deviation) of the UASB technology in Juazeiro do Norte operated by CAGECE.

Table 3 Parameters analyzed.

WWTP	Variable	COD (mg/L)	TSS (mg/L)	pH	*E. coli* (CFU/100 mL)
Vila 3 Marias	Average	254.93	114.00	7.37	6.61E+06
	Standard Deviation	57.51	75.26	0.25	9.79E+06
	Maximum	361.39	268.00	7.66	2.40E+07
	Minimum	177.27	47.50	6.84	1.00E+00
Tenente Coelho	Average	518.43	172.00	7.57	7.87E+06
	Standard Deviation	124.74	81.49	0.18	6.79E+06
	Maximum	773.49	340.00	8.09	2.40E+07
	Minimum	308.32	60.00	7.43	1.00E+00
Mutirão	Average	297.63	75.35	7.09	1.80E+06
	Standard Deviation	187.57	67.72	0.26	3.25E+06
	Maximum	721.78	230.00	7.57	8.20E+06
	Minimum	200.54	30.50	6.82	1.00E+00

Table 3 shows that among the three WWTPs studied with respect to the parameter TSS, the Mutirão WWTP obtained the lowest mean concentration (75.35 mg/L) of TSS, when compared with the Vila Três Marias (114 mg/L) and Tenente Coelho (172 mg/L) WWTPs. The highest average of the Tenente Coelho station (UASB + SAF) can be attributed to aeration problems [34], since it is the only station that has an aeration system among the others, besides that this station in none of the months reached the expected quality of the effluent as for the parameter TSS ≤ 30 mg/L [4].

Also, in Table 3, it can be inferred that the WWTP that obtained the highest COD averages was the Tenente Coelho WWTP, results that can be attributed to factors such as operational problems, bad station design, as well as problems of effluent distribution and hydraulic overload of the system.

4. Conclusions

The conclusions found in the study reveal that the treatment of domestic effluents through UASB reactor systems requires a later phase of treatment, since this technology without an adequate post-treatment had values well above those that are allowed in the state resolution for launching effluent in water bodies.

The performance of the UASB + SAF system stated that due to possible operational problems, they provided unsatisfactory average results for all parameters analyzed in this study (except pH) and did not comply with the environmental legislation of the State of Ceará, regarding the discharge of domestic sewage in water bodies.

As a result of the low levels of compliance with the legislation, it is concluded that there is a need for the concessionaire to take emergency measures in order to ensure the proper and safe treatment of domestic effluents as well as disposal within established standards.

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The First Occurrence of Red Tide Caused by *Karenia* sp. in the Atlantic Moroccan Coast (Oualidia Lagoon)

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Abstract: An intense bloom of *Karenia* sp. was reported in the Oualidia lagoon, part of Atlantic Moroccan coast. The highest concentrations are 1.04×10^7 cells/L, and have been noted at the park station 7. High nutrient concentrations have been observed, and PO_4 was the highest value (av. 396.18 µg/L) recorded at Parc 7. This massive proliferation caused a red tide which extended over 25 km from the Atlantic coast. This event was accompanied by stranding of macroalgae.

Key words: Bloom, dinoflagellate, red tide, *Karenia* sp..

1. Introduction

Occurrence of HABs (Harmful Algal Blooms), commonly known as "red tides", has increased and expanded in spatial extent worldwide in the recent decades in coastal waters [1, 2]. Indeed by several authors, the HAB problem was growing worse as a result of pollution [3] or other factors such as expanded aquaculture operations, superior competitive nutrient uptake, cyst formation or ballast water transfer of species [1]. In fact, the reasons for their substantial intensification can be associated with a set of physical, chemical and biological factors including climate changes and anthropogenic impacts [4].

So far, several phytoplankton blooms were frequently reported from the west coast of Atlantic Moroccan coast, among them, red tides are frequently occurring on blooms of *Lingulodinium poyedrum* (dinoflagellate) [5] and *Peridinium quinquecorne* [6].

In August 2014, a bloom of the dinoflagellate *Karenia* sp. was observed in the lagoon of Oualidia and caused a red tide. The objective of this study is to describe the environmental conditions that accompanied this bloom.

Area Studied

Oualidia lagoon (32°40′42″ N-32°47′07″ N and 8°52′30″ W-9°02′50″ W) is located on the Atlantic Ocean (Fig. 1). This lagoon is 7 km long, on average 0.4 to 0.5 km wide, and its total area is estimated at 3 km^2 [7]. In Ref. [8], the lagoon of Oualidia is characterized by three areas [9]:

—A main pass of about 150 m wide, permanent and active all year, and a secondary pass 50 m wide, only active during tides freshwater; these two passes ensure the lagoon a continuous communication with the Atlantic Ocean;

—A main channel, the maximum depth of which is not more than 5-6 m, secondary channels (deep maximum 1 to 1.5 m), intertidal zones and schorres overgrown with halophyte vegetation;

—An artificial dike separating the marsh lagoon salt.

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Fig. 1 The geographical location of the Oualidia lagoon and sampling sites.

2. Materials and Methods

For this study, the sample was according to three sampling stations: Passe, Parc 7 and Parc1 (Fig. 1) during 2014. They were chosen along the lagoon, from the pass to the bottom to better represent the spatial distribution of phytoplankton populations in the water column. The frequency of sampling was bimonthly for analysis of phytoplankton, and seasonally for physico-chemical parameters. The sampling of the summer season coincided with the appearance of the red tide. That is why we will focus only on this period.

Water samples were performed at high tide surface (photic zone) using a zodiac, and are collected by a 1 L bottle, then they are fixed directly with Lugol 5 mL/L.

2.1 Identification of Dinoflagellate Species

Samples for different dosages and measures were taken during the red tide period, from small, large bottles previously washed with distilled water. The samples are kept cool and obscurity. Samples for phytoplankton analysis are homogenized, poured into sedimentation tanks (25 mL) and placed on a flat surface without vibration in the dark at an ambient temperature for 6 to 8 hours.

After sedimentation, the identification and enumeration of species are using a type of inverted microscope (Nikon) according to the sedimentation method Utermöhl [10] after acid iodine fixation.

2.2 Physico-Chemical Analysis

For physico-chemical measurements, pH, salinity, temperature are measured directly *in situ*, using respectively, pH meter type WTW 597, salinometer type WTW LF 197, also using a thermometer.

The contents of nitrites, nitrates and orthophosphates were collected once, and determined, by chemical dosage according to the method of seawater analysis, reported in Ref. [11].

3. Results and Discussion

- Hydrographic Conditions

During the red tide period, the atmosphere over the region was sunny with weak winds (< 3 ms1). Water temperature varied between 17 and 18 °C at all sampling points during the time of collection and salinity of 35 from the pass to 33 to the bottom of the lagoon. pH did not show much variation, with averages of 8.01 and 7.9 (± 0.06) respectively. Concentration of PO_4 was the highest value (av. 396.18 µg/L) recorded at Parc 7, as compared to NH_4^+ (av. 48.65 µg/L), NO_3^- (av. 208.38 µg/L) and NO_2^- (av. 15.29 µg/L).

- Bloom Assemblage

Throughout the observation, the phytoplankton density varied from 2.4×10^5 cells·L^{-1} to 1.04×10^7 cells·L^{-1}, with a maximum density recorded on the first day of bloom at the Parc 7 station. Among these, dinoflagellate was numerically abundant group (72.2-99.2%) followed by diatoms (0.8-27.8%) and finally the Euglenophyceae (0.8-27.8%).

A total of 23 taxa of phytoplankton were identified in the bloom period (Table 1), four were diatoms, and

Table 1 Phytoplankton composition and abundances.

	Abundance (cells·L^{-1})					
Species name	Passe	Parc 1	Parc 7	Passe	Parc 1	Parc 7
Diatoms						
Amphora sp.	0	80	0	0	0	0
Coscinodiscus sp.	0	0	0	0	0	0
Diploneis sp.	0	40	0	0	0	0
Grammatophora sp.	0	80	0	0	0	0
Guinardia stolterfothii	0	0	0	0	0	0
Gyrosigma sp.	0	0	0	0	40	0
Licmophora sp.	0	0	0	0	40	0
Navicula sp.	0	800	0	0	0	0
Nitzshia sp.	0	200	0	40	40	0
Paralia sulcata	0	0	0	320	0	0
Pseudonitzshia sp.	0	0	80	80	0	0
Thalassiosiera sp.	0	3,320	0	1,520	1,320	0
Dinoflagellates						
Alexandrium sp.	0	40	40	0	120	0
Ceratium	120	0	0	0	0	0
Ceratium fusus	200	120	0	0	0	0
Dinoflagellés sp.	0	0	0	0	0	0
Dinophysis sp.	0	0	0	0	0	0
Eutripsiella	0	0	0	120	0	0
Gonyaulax sp.	0	0	0	0	40	0
Gymnodinium sp.	80	0	0	0	0	0
Gyrodinium sp.	0	160	0	0	0	0
Lingulodinium polyedrum	40	0	80	0	0	0
Peridinium quiquecorne	0	0	0	0	160	0
Prorocentrum micans	0	640	0	0	0	0
Prorocentrum scutellum	6,960	0	0	0	40	0
Prorocentrum sp.	0	8,960	0	120	0	0
Protoperidinium sp.	0	80	0	40	0	0
Pyrophacus sp.	0	0	0	0	0	0
scripsiella sp.	160	2640	0	40	0	0
Oesteopsis sp.	0	0	40	0	0	0
Karenia sp.	1,044,000	245,880	0	0	0	120
EUGLENOPHYCEAE	18,080	2,140	7,450	1,980	4,910	3,912

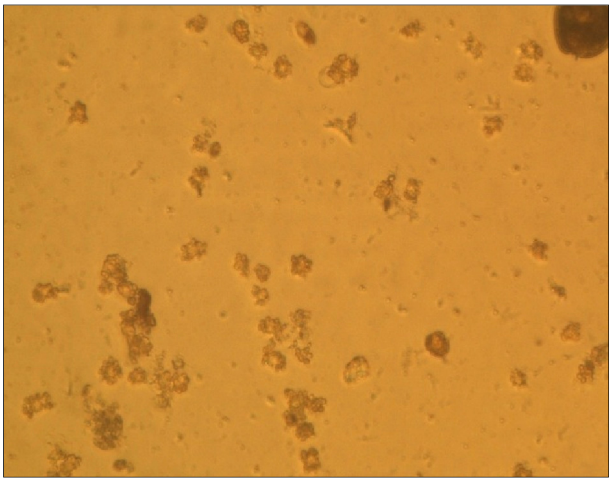

Fig. 2 Bloom of *Karenia* sp.

19 were dinoflagellate and Euglenophyceae. Among the diatoms, *Nitzshia* sp. (av. 46.6 cells·L^{-1}), *Navicula* sp. (av. 133.3 cells·L^{-1}) and *Thalassiosiera* sp. (av. 133.3 cells·L^{-1}) were observed. Whereas *Ceratium fusus* (53.3 cells·L^{-1}), *Peridinium quinquecorne* (av. 1.06 × 10^2 cells·L^{-1}), and *Prorocentrum scultellum* (1.16 × 10^3 cells·L^{-1}), *Prorocentrum* sp. (av. 1.5 × 10^3 cells·L^{-1}), *Scrippsiella* sp. (av. 4.73 × 10^2 cells·L^{-1}), and *Karenia* sp. (av. 2 × 10^5 cells·L^{-1}), were identified under dinoflagellate. Microscopic analysis revealed that the discoloration was caused by an unarmored dinoflagellate (Fig. 2), *Karenia* sp. [12]. It contributed up to 98%, which belongs to order Gymnodinials, family Gymnodiniaceae. Earlier, it was known as Gymnodinium and recently has been changed to the genus Karenia [13].

- *Karenia* sp. [12]

Karenia is genus containing at least 12 species of marine unarmored dinoflagellates [14]. Most produce toxins (during proliferation) and have been described as a result of investigations on massive fish kills causing an important economic losses or human health problems. That is why; this species has been the subject of several studies in order to predict the economic consequences.

Bloom of *Karenia* species dates back a long time, in Florida, the first blooms of *K. brevis* were reported in 1844 predating the rapid economic growth and development of the mid to late twentieth century by many decades [15]. Historical records demonstrate that these blooms have occurred almost annually in the years since the 1940s (FFWCC, 2001). According to Oda [16], in 1953, *Karenia mikimotoi* was responsible for an episode of mortality in oysters and fish in Japan.

In the Gulf of Mexico, animal mass mortality, and respiratory distress were caused by frequent blooms of *K. brevis* [17]. However, blooms of newly discovered species of *Karenia* have developed in many parts of the world. In Irish water, a protracted toxic bloom of *Karenia mikimotoi* occurred in summer 2005 along the northern half of the western Irish coastline. Major mortalities of benthic and pelagic marine organisms were observed and a complete decimation of marine faunal communities was reported and observed in several locations [18]. In the Southwest coast of India, an intense brownish discoloration was observed in the surface waters in 2009 [19]. Moreover, between 1997 and 2007, the dinoflagellate *Karenia selliformis* represents 68% of the blooms occurred in the gulf of Gabès in Tunisia [20].

Actually, prolonged dense blooms of *Karenia mikimotoi* in other regions of the world are frequently, but not always, associated with fish kills and the death of invertebrate species, although it is common in many other regions of the world (Texas, Gulf of Mexico, Arabian Sea, Australia, China, Ireland, England, France, Hong Kong, western India, Japan, New Zealand, North Sea, Norway and Scotland).

In Morocco, the first observation of a red tide due to the *Karenia mikimotoi* was in 2005 in TanTan, the southern of Morocco. This has caused significant mortality of fish [21].

In Oulaidia lagoon waters, the first occurrence of red tide is caused by *Karenia* sp.. It is possible that similar blooms have occurred, but have not been recognized. The massive proliferation of *Karenia* sp. was accompanied with macroalgae bleaching. Nevertheless, there were no fish kills visible from the area during the occurrence of present bloom. The same case was noted by Madhu, et al. [19], which could be explained by dilution of water to the adjacent coastal waters by tidal effect.

The close relationship between HAB's and nutrient growth has often been reported in coastal waters [22-24]. In this study, the bloom of *Karenia* sp. coincided with an increase of orthophosphate. This obtained result is an agreement with the study of Robin, et al. [25], where they explain that explosive growth of *Karenia mikimotoi* in the water of Southeast Arabian Sea is due to sudden increase in supply of nutrients, especially PO_4^{3-}. On the other hand, this latter conditioned negatively the presence of *Karenia stelliformis*, which prefers and proliferates in waters rich in nitrate [26].

Furthermore, the amount of Euglenophyceae during the bloom reflects a good exposure to sunlight [27], which could lead to the proliferation of *Karenia* sp. According to Barnes et al. [28], the precursor causes of large *Karenia mikimotoi* blooms are suggested to include enhanced growth by sunlight-driven phototaxis.

4. Conclusion

Even though many studies are available on red tides, the information on the incidence of *Karenia* sp. bloom in the Oualidia lagoon waters proves the theory of extension of HAB events. In this study, authors tried to highlight the different environmental conditions that could start the bloom of *Karenia* sp.. The results obtained show that orthophosphate and sunlight reflects the favorable conditions for the proliferation of *Karenia* sp.. However, it remains essential to study the cysts, in parallel, to be able to define the different phases of the life cycle of *Karenia* species, and then provide these blooms.

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Scale up in Public Economics

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Abstract: The purpose of the paper is to present a modified model of an internalizing external costs caused by the operation of a manufacturing unit in conjunction with the new reality created. The environment is characterized as a public good. Public goods are goods that provide benefits for society as a whole or part of it, usually regardless of whether the individual people are willing to pay to have these benefits. All entities, whether individuals or businesses or public agencies, have some financial resources with which they seek to achieve specific objectives (e.g. profit maximization). To achieve a specific objective, usually there are many alternatives and possibilities. To be effective, i.e. to utilize the existing resources in the best manner possible, should be selected that the solution maximizes the desired outcome or minimizes the required sacrifices.

Key words: Goods, benefit public, cost, environment, optimization.

1. Introduction

The procedure for the selection process is called optimization, optimization or maximization. In the business world, almost all the decisions may be considered as optimization problems. The optimization can be applied not only to maximize profit and minimize the cost of production, the use of the optimal size ad in the employment of the highest quantity of a productive factor.

When you come from markets not operate effectively, the price does not reflect the true social costs them. With the CBA (Cost-Benefit Analysis) all critical parameters problem attributed to a single base assessment, which facilitates decision making process. The basis of evaluation is to compare benefits and costs. If the benefits are larger, then the project (or activity) is socially desirable otherwise considered socially beneficial. “Weak” Treaty Pareto: a project or a policy measure is socially acceptable when improving the welfare of every member of society. ‘Strong’ condition Pareto: a project or a policy measure is socially acceptable when ensure improved welfare even one person without reducing the welfare of another [1].

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The Pareto principle is based on individual conception of welfare, whereby the people regarded as the best exponents of their own prosperity through their options. He has limited use, since there is almost no action to improve. As someone while continuing to deteriorate the position of others. Not discussed concepts such as social justice or income redistribution. The search for suitable instruments or for the best possible combination of the use of command and control and of economic instruments nowadays constitutes one of the most complex points of discussion on environmental economics. The environmental reassessment of economic procedures and the change in production and consumption of non-conservation friendly models, which constitute the fixed position of the European Union and the OECD, could be achieved by using suitable economic instruments. We are focalising the present study on environmental taxes, the most well-known and widespread category of economic instruments, by studying the advantages and disadvantages of their enforcement [2].

2. Methodology

According to the first theorem of economic prosperity, under certain conditions, a competitive economy guarantees a Pareto-optimal economic outcome. In other words, a competitive market leads to allocations of resources to the property that any position cannot improve not worsen the position of another. This allocation is done automatically through the price mechanism, e.g. where there is a demand the price goes up and when a bid price it falls.

With the adjustment of prices solves the problem of distribution of goods. The second fundamental theorem states that through the competition of firms that have objective the maximization of profits and consumers who view their maximize the benefits can be excellent (in Pareto) distribution of resources regardless the initial distribution [3].

Therefore it is necessary to have a central designer will decide who gets what in the economy. In fact, the free market is can lead to great disparities that can be removed by state intervention (e.g. taxation). According to the criterion of a Pareto distribution is effective when there is no other way allocation to improve one's position without diminishing someone else [4].

3. Implementation

The expression 'think globally, act locally' is frequently used as a slogan urging people to consider the health of the entire planet or a global system and to take action in their own localities. The same expression is also a Principle in Environmental Management suggesting decentralization as a basic method for sustainable development. Nevertheless, the decentralization degree D should not exceed an optimal value D_{opt} if maximum benefit $B_{max} = (B_1+B_2)_{max}$ is to be achieved, where the partial benefits $B_1(D)$ and $B_2(D)$ represent development of skills/capabilities and coordination achievement, respectively, as functions of D.

The former dependent variable, B, is an increasing function of D with a decreasing rate (i.e $dB/dD > 0$, $d^2B/dD^2 < 0$), because of the validity of the Law of diminishing (differential) returns (LDR). The latter dependent variable, B_2, is a decreasing function of D with a decreasing algebraic or an increasing absolute rate (i.e., $dB_2/dD > 0$, $d^2B_2/dD^2 < 0$ or $d\ |dB^2/dD| /dD > 0$), because of the validity of the LDR too. Evidently, D_{opt} is the abscissa of the equilibrium point in the tradeoff between B_1 and B_2, where $d(B_1+B_2)/dD^2 < 0$ is confirmed for the D-value found by solving the equation representing the first order necessary condition ; in economic terms, $MB_1 = MB_2$, where $MB_1 = dB_1/dD$ and $MB_2 = |dB^2/dD|$ are the marginal benefits respectively [5].

By introducing expert systems in order to use case/models/rules based reasoning, for further support of skills/capabilities development, the B_1-curve will move upwards to its new position B'_1 becoming also steeper, since the higher difference in B_1-values will appear in the region of higher D-values, where the decline of the original curve is more expressed; as a result, D_{opt} is shifting to D'_{opt}, where $D'_{opt} > D_{opt}$. Similarly by introducing a controlled vocabulary within an ontological scheme/network for further support of coordination, the B2-curve will move upwards to its new position B'2 becoming also more flat, since the higher difference in B2-values will appear in the region of higher D-values, where the needs for better coordination are more intensive; as a result, D_{opt} is shifting to D''_{opt}, where $D''_{opt} > D_{opt}$.

It is worthwhile noting that the vectors (D'_{opt}-D_{opt}) and (D''_{opt}- D_{opt}) have the same direction, denoting a very tendency for increasing decentralization in environmental decision making and subsequent implementation of respective decision. In a similar way, we can reach an identical conclusion by setting the Centralization Degree C, as the independent variable, in order to find C_{opt} in the Discussion section of the present work, where certain other factors are also examined [6].

4. Suggestion

When there is a clearly defined system of property rights, the market mechanism will lead to an efficient allocation of resources. In environmental policy, the polluter (whether company or individual, or the State) pays applicable in several countries the world. This is automatically an incentive to reduce pollution at least at the level where the marginal cost of reducing pollution equals the marginal cost of damage causing this pollution. Also, many countries apply the system of subsidies for the pollution control. This suggests that property rights are particularly importance in the formation of environmental policy.

Who should have rights property the polluter or the victim worked the R. Coase (1960). In theory places great emphasize the importance of ownership of natural resources and to negotiate between those who pollute and those who suffer from pollution. One of the conclusions of R. Coase was that under certain conditions the creation of property rights can be lead the parties are on opposite sides have interest to negotiate among themselves to find an agreed solution on the level pollution would be considered socially acceptable [7].

The adoption sustainable development as a central policy choice, but as a principle of both international and European and domestic legal systems (especially after the revision of Article 24 of the Greek Constitution) creates new standards for the role, nature and function of environmental policy tools.

In particular, the passage of regulatory approach to environmental protection, which was based mainly on the use tools of direct intervention on the strategic and integrated approach, which requires an overall strategy for sustainable development. Main aim towards sustainable development is the environmental redefinition of economic processes a fixed position of the European Union and OECD agreed at the World Johannesburg [8].

Environmental redefinition of economic processes and changing unsustainable patterns of production and consumption agreed at Johannesburg, cannot achieved with tools to intervene directly, but rather the use of economic tools. The same should be accepted and to solve the environmental problems the second generation, such as climate change, biodiversity loss and soil erosion, as taking effective measures in this direction requires the use of other tools except those of direct intervention. The key feature of economic instruments is that the type of conduct which guides the operators of production processes associated with a particular economic advantage.

The logic function consists in particular to internalize partially or completely, of “externalities” (externalities), i.e. the impact on the environment, which is secondary effects of production processes and consumption and which are not calculated as a cost to those who cause it. This is also an established position in economic theory. It should also be noted that all financial instruments not show the same degree of compatibility with the market mechanisms (e.g. permits emissions have the greatest degree of compatibility with respect to subsidies, which a minimum) [9].

These tools provide economic incentives for environmental change behaviour either through direct changes in the levels of prices and costs through fees products, duties on carbon or on raw materials, or through indirect changes in prices or the cost through financial and fiscal instruments such as direct subsidies, loans, or end through creating new markets for environmental goods, such as tradable licenses etc [10].

The production and consumption of goods and services has resulted create adverse impacts on the environment. Starting thus with the principle “I live, so befoul” and realizing that one cannot speak for the elimination of pollution, the problem lies in “how much pollution.” In other words, in what will be the “optimum” level of environmental pollution or environmental protection from pollution, based on various economic, technological, social, psychological and other parameters that apply to a society in a given period [11-13].

5. Conclusion

Externalities or external economies (externalities) occur when a person acts or a business affect other people or companies when a company imposes a cost on others, but does not compensate, or end, when a company brings benefits in other businesses but does not receive remuneration for providing this benefit. We can distinguish two types of externalities, public e.g. air pollution, the water that affects the welfare of many people and private e.g. a person casts trash in the yard of neighbour. (This movement affects the welfare of the neighbour and any other).

The cases where the activity of an individual or business impose costs others refer to as negative externalities or external costs. When induced positive externality in the production of a commodity, the social costs production is less than the private cost. The optimal quantity of good Q optimum is greater than the equilibrium quantity Q market. Notice that in both either cases us external charges, or has external economies, the price mechanism does not give enough information to the recipient of decisions. In one case, the values do not represent the actual cost and the other is not represent a real benefit. We say market failure.

According to Pigou, in his 'The economics of Welfare', taxation is a effective tool for addressing the external charge. In the case foreign economy is given subsidy represents the real benefits of business. Unlike the Coase in his 'The problem of social cost, 1960' as a way of supporting addressing externalities awarding property rights over natural resources. He argues that if the contaminant obtains a right of victims of pollution, then pollution will pay the first to stop or reduce the polluting activity. Unlike the pollutants to be able to benefit from the natural resource should compensate the victims, which have acquired the right to operate.

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The Stava Valley Tailings Dams Disaster: A Reference Point for the Prevention of Severe Mine Incidents

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Abstract: On July 19, 1985, at Stava near Tesero (Italian Alps), two reservoirs collapsed, causing the death of 268 people and the destruction of many buildings. The two adjacent basins were constructed for the decantation and storage of fine-grained waste material, which was pumped from a nearby fluorite mine. The consequence of the failure was a vast flowslide that found its way downstream along the Stava valley destroying many houses in the village of Stava, eventually reaching Tesero, where more property was wrecked or severely damaged. The Stava valley disaster was one of the most tragic of its kind. This paper aims to give a contribution on the technical aspects related to the causes of this catastrophic event. It also describes alternative technical solutions for the proper management of mining waste disposal and environmental protection proposed by the Stava 1985 Foundation for disseminating knowledge and awareness on how to make these geotechnical structures safer and more profitable and avoid other similar disasters that still keep occurring every year around the world.

Key words: Stava disaster, tailings dam failure, safety measures and incident prevention.

1. Foreword

Mining activities require the use of ore washing plants for separating concentrated mineral ore from the waste rock that will not be used. This is generally attained by means of froth flotation, a process relying upon the capability of finely ground minerals to aggregate with water or reject it.

The processed waste—or tailings—is a liquid mixture of sand, silt and water that is discharged into a purpose-built reservoir, named a tailings dam. A tailings dam can grow progressively to a considerable height (up to over 60 m). Therefore, proper construction and management are of paramount importance in order to guarantee long-term stability [1]. Unfortunately, to date there has been no economic interest in the construction of tailings dams, since very little revenue results from waste material. Therefore, many mining companies tend to spend as little as possible on these geotechnical structures, to the detriment of their stability.

The catastrophic failure in the Stava valley and other similar disasters here reported can teach us an important lesson concerning the safety of tailings dams and new techniques for recovering extra useful minerals from tailings.

2. Introduction

The Stava disaster of July 19, 1985 (Italian Alps) was caused by the collapse of two tailings dams, which stored fine-grained waste (tailings), originated by the beneficiation of fluorite produced at the Prestavèl mine in the upper Stava valley near the village of Tesero (Fig. 1).

This disaster caused the death of 268 men, women and children, destroying also many houses, hotels,

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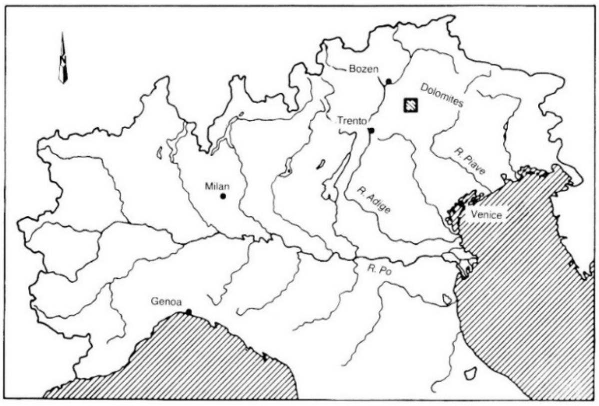

Fig. 1 Location of Stava valley, northern Italy (shaded square indicates disaster area).

bridges, industrial and commercial activities as well as vast environmental devastation.

Following this tragic event, criminal trials were carried out which eventually led to the conviction of ten defendants, guilty of criminal negligence and multiple manslaughter. Before the final verdict, scientific investigations were performed on the failed structures [2, 3].

The "Stava 1985 Foundation"—a registered charity established in 2002—has been spreading information worldwide on the Prestavèl mining activities and the reasons and responsibilities for the Stava valley catastrophe[1]. In addition, particular importance has been given to information about the technical, economic, political and managerial choices, which allowed the construction of tailings dams in an area which was shown, after failure occurred, to be the least suitable from the geomorphological, geotechnical and hydro-geological viewpoint. In addition, there were also planning and construction errors in the two reservoirs, leading to instability and eventually disastrous failure [4, 5].

This paper aims to contribute to the knowledge of the technical causes of this disaster, the mine and beneficiation processes. It also describes the efforts of the Stava 1985 Foundation for the safety of mining activities, mining waste disposal facilities and environmental protection, in order to disseminate knowledge and awareness about the Stava valley catastrophe and other similar disasters that have occurred around the world since then.

3. Mine Description

The mining operations in the Prestavèl fluorite mine, in the upper Stava valley, were carried out in a sub-vertical seam, included in a red porphyry rock mass and metamorphic porphyroid [4].

Access to the seam was given by means of four tunnels, excavated on the slope of the mountain at different levels. The tunnels were on either side of the mining areas in which the working panels were developed. The mineral was exploited in horizontal slices, backfilling the foot of the excavation with the waste material produced during excavation. The raw mineral was dumped into vertical shafts and arrived at the bottom hauling level by gravity. From there, it was transported to the washery by means of a ropeway, where a beneficiation process extracted the fluorite, concentrating the mineral at the acid grade of 97% and eliminating the rock waste by sending it to purpose-built basins (Fig. 2).

In the late period of the life of Prestavèl mine, the ore beneficiation process was based on froth flotation. In earlier times, the concentration was carried out by means of different techniques in order to obtain a grade of about 80% of fluorite, suitable for smelting plant uses.

The capability of useful minerals to aggregate with water or reject it during flotation can be enhanced by using suitable chemicals or natural conditioners. Because fluorite is conditioned to be hydrophobic, it tends to link to air bubbles and float. On the contrary, the tailings sink to the bottom of the vessels and are conveyed to a settlement basin together with the washing water. Once in the pond, the slurry is

[1] The duty of the Stava 1985 Foundation (www.stava1985.it) is to keep alive the historical memory of the Stava valley disaster in order to make sure that 268 innocent people did not die in vain. Its main goal is to strengthen the culture of prevention, correct territorial management and safety since shortcomings and negligence were the cause of this and many other man-induced, foreseeable and avoidable disasters.

Fig. 2 View of the Stava lower basin in 1969.

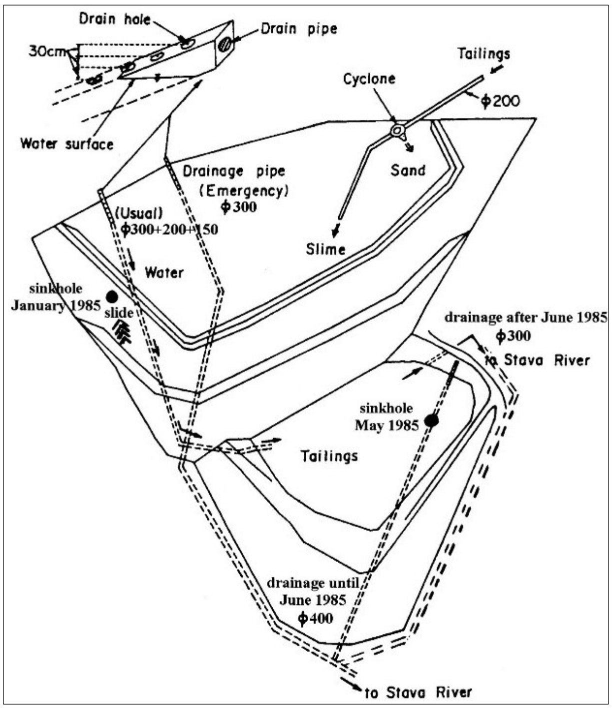

Fig. 3 Location of the drainage pipes through the Stava dams [2].

processed using a hydrocyclone that separates the coarse material (mainly sand) from the finer material (mainly silt). The sand is discharged immediately at the inner edge of the tailings dam, in order to build up the so-called delta or beach and to increase the thickness of the dam itself. The silt, in the form of liquid mud, is pumped in the central part of the basin, where it settles. Vertical shafts are positioned at the center of the pond. The bottoms of the shafts are connected to a drainage pipe that runs through the basin and drains away the water in excess (Fig. 3). The Prestavèl plant had a capacity of 200 t of raw mineral per day.

4. Construction of the Stava Tailings Dams and Causes of the Collapse

In 1961, new mining facilities were constructed adopting the froth flotation system and high-grade fluorite, suitable for use in the chemical industry. At the same time, the first tailings dam was constructed for storing and decanting the waste thus produced (Fig. 2). The downstream slope of this dam was raised with an angle of about 32° to an ultimate height of 25 m. In 1969, in order to deal with increased mining production, it was necessary to construct a second tailings dam just upstream of the first one. The dam of this second basin was raised without any provision either for anchoring it to the ground or for drainage. As the dam grew higher, the base of its embankment grew wider until it eventually rested partially on the silt of the lower basin (Fig. 4). Drainage pipes were placed inside the basins, which discharged the water outside by passing through the dams.

In those days, there was no proper urban planning in the Stava valley and permission was easily granted for the construction of tailings dams at the top of a valley of considerable scenic beauty, highly appealing to tourists. Two incompatible activities were sharing the same territory: on the one hand, the traditional mountain buildings and hotels in a charming Alpine

Fig. 4 The two Stava tailings dams and the Prestavèl mine facilities (October 1981).

valley and on the other, an industrial activity with heavy environmental impact. Technically, this means that together with tourist development also exposure to potentially hazardous events increased, but this was totally ignored by the people in charge of the basins' construction.

The causes of the persisting instability of the tailings dams, which eventually led to their failure, were as follows: (i) the ground on which they had been built was marshy and poorly drained and, as such, unstable and unsuitable to support heavy geotechnical constructions and did not allow the consolidation of tailings; (ii) the dams had been built on a very steep slope, with an average inclination of 25%; (iii) the dam of the upper basin had been raised with an excessive slope (over 80%), was lying in part on the unconsolidated silt of the lower basin and did not allow water drainage or the consolidation of tailings; (iv) the overflow and drainage pipes had been wrongly positioned inside the basins.

Furthermore, in the last three years before disaster the hydrocyclone was no longer moved periodically along the embankment of the upper dam but was located in a fixed position at the corner near the washery. In order to create the sand delta, the coarse tailings were distributed using front-end loaders and trucks, causing heavy vibrations that compromised the correct settlement of the material. In the meantime, the drainage pipe at the bottom of the upper dam was obstructed and could not discharge water to the downstream pond. During the entire life of the two tailings dams, maintenance was poor, there was no control at all over drainage and the general management of the tailings dams was definitely inadequate.

In the end, unnoticed and persisting high-pond conditions weakened the foundations of the upper dam with a progressive increase of pore water pressure, leading eventually to its collapse and causing also the failure of the lower dam. Consequently, 180,000 m^3 of liquefied mud and water spilled out of the failed dams

Fig. 5 The failed dams and the devastation of the Stava valley (July 1985).

plus nearly 50,000 m^3 of material resulting from soil erosion, destruction of buildings and uprooting of trees. The entire Stava valley was completely devastated (Fig. 5).

5. Several Cases of Tailings Dam Failures around the World

The continuous occurrence of incidents affecting reservoirs confined by earth dams and, in particular, tailings dams[2] all over the world reproposes the risk of these geotechnical structures for the environment and human settlements. This is not a new problem, and it regularly arouses the interest of the media and the scientific-technical world after every catastrophic failure of earth dams. This was the case for several disasters similar to that of the Stava valley, such as Merriespruit in South Africa[3] (Fig. 6), Aznalcóllar in Spain[4], Baia Mare in Romania[5], Kolontár in

[2] 110 incidents have been recorded from 1960 to date, of which 69 occurred after the Stava valley disaster of 1985. Three tailings dam failures took place just in 2018 with loss of human lives and serious damage to the environment [6].

[3] This incident took place on February 22, 1994 when, following heavy rains, 1,500,000 m^3 of polluted mud overflowed the embankment of a tailings dam. Seventeen persons lost their lives, 80 more were injured and many houses were destroyed in the suburb of Merriespruit, Virginia, Free State.

[4] 4,600,000 m^3 of water and toxic mud, resulting from the working of phosphates, spilled out of a tailings dam on April 25, 1998. Pollution severely affected thousands of hectares of farming land.

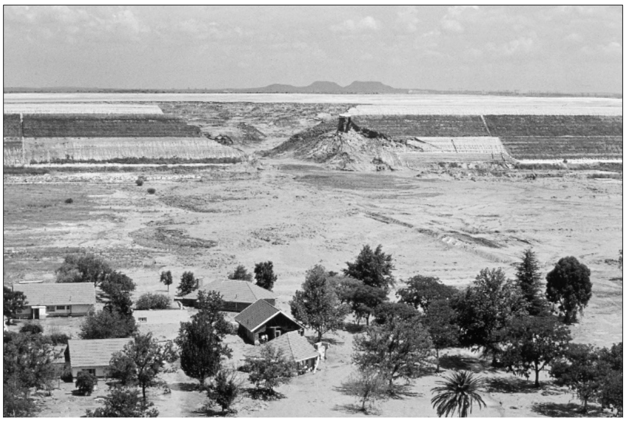

Fig. 6 The devastation of the mudflow following the Merriespruit tailings dam failure, South Africa (February 1994).

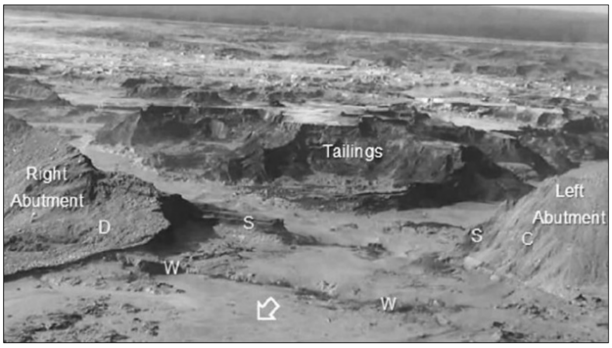

Fig. 7 View looking upstream through the breach at Mount Polley tailings storage facility (arrow shows direction of the outflow) [8].

Hungary [6], Mount Polley in Canada [7] and Bento Rodrigues in Brazil[8].

[5] 100,000 m^3 of cyanide-rich fluids, resulting from the working of gold, spilled out of a tailings dam on January 30, 2000. The Somes Creek, tributary of the Tisza River, was heavily polluted, thousands of fish were destroyed and drinking water supplying over two million inhabitants was contaminated.

[6] 1,500,000 m^3 of toxic mud, resulting from the working of bauxite, spilled out of a tailings dam on October 4, 2010. Nine persons lost their lives and 120 were injured. The consequent heavy pollution required the demolition of numerous houses, which were rebuilt elsewhere, the removal and transport of the contaminated ground to a landfill and its substitution with some 30 cm of fresh soil along the path of the flowslide, which was 40 km long with a front of 300 m.

[7] The flowslide, which spilled out of the tailings dam on August 4, 2014, was made up of 7,300,000 m^3 of tailings and over 17,000,000 m^3 of water.

[8] Over 30,000,000 m^3 of mud flowed out of a basin on November 11, 2015 following the failure of two tailings dams. An entire village was destroyed, 17 persons were killed and 75 injured. Several watercourses were polluted over a total length of 660 km, 15 km^2 of land was contaminated and water supply serving 250,000 inhabitants was interrupted.

A few considerations should be made about the Mount Polley tailings dam disaster since this was the largest documented spill of mine tailings into the environment [6] (Fig. 7).

The Mount Polley Mine is an open pit and underground copper-gold mine, processing an average of 22,450 t per day of ore. The mine is located 8 km southwest of Likely, BC (Canada), approximately 400 km northeast of Vancouver. On August 4, 2014, a failure occurred in the perimeter of the tailings storage facility. The embankment breach released tailings, water and construction materials which affected several bodies of water [7].

According to the results obtained by the Independent Expert Engineering Investigation and Review Panel [8], the breach was induced by the failure of a glacio-lacustrine layer located about 8 m below the embankment's foundation. The Panel concluded in its report that "the dominant contribution to the failure resides in the design. The design did not take into the account the complexity of the sub-glacial and pre-glacial geological environment associated with the perimeter embankment foundation". The breach was interpreted by the Panel to have been caused by shear failure of weak dam foundation materials (i.e. a glacio-lacustrine layer). The Panel identified this weak rock layer in the breach area and stated that past subsurface investigations were not focused on identifying potential complexity of the embankment foundation soil.

The morphology of the Hazeltine Creek, downstream of the Mount Polley tailings storage facility, was intensively altered by the sudden release of tailings due to considerable erosional processes along the creek banks [9].

The environmental clean-up operations were swift: within one year of the event a significant volume of the spilled tailings were removed from the major receiving watercourse and an extensive river restoration scheme was under construction [8].

The Mount Polley spill highlighted the high global environmental risk of these incidents, due to the growing number of mining operations and greater waste produced, and due to the high vulnerability of this type of environment to extreme hydro-meteorological events [10]. In addition, the introduction and deposition of contaminants poses a serious risk to the resident and anadromous fish stocks supporting Native American fisheries [11].

The Mount Polley failure, along with the November 5, 2015 Bento Rodrigues dam disaster in Brazil, has done great harm to the credibility of the mining industry as a whole.

6. Towards Safer Management of Tailings Dams

As previously stated, the Stava 1985 Foundation is pursuing the aim of making public institutions and industrial operators aware of the importance of adopting new approaches and technologies to prevent future disasters. An important target for the Stava 1985 Foundation is to promote initiatives directed to public opinion and technical stakeholders regarding the use of the BAT (Best Available Technologies) for the management of mineral processed waste, having as a primary objective the safety of the population and the conservation of the environment [12].

Recent available technologies allow strategic targets to be attained by reducing pollution and maintaining at the same time high safety standards. Among the methods of dealing with mining waste, forced filtration seems to be very promising, although it is not yet widely used due to its high cost. This process allows the quick separation of the two phases of tailings by means of filter presses, belt filters, disk filters or drum filters. Thus, water is completely recovered and recycled while the hauling of the resulting mud—that has a residual humidity of 15% to 30%—is carried out with standard front-end loader machines and trucks. The advantages of this method are in avoiding hazardous disposal structures, the occupation of large areas of soil, better control of the contaminants and possibility of the stockpiling of dried mud (called filter cake) for recycling or reprocessing [13].

Tailings could be converted by giving them a new life as basic material for civil engineering use, based on the principles of circular economy. This measure would also cut down the need for mineral waste disposal sites and the risk of their collapse. Finally, environmental pollution could be curtailed by reprocessing the tailings in order to recover useful elements.

Apart from new techniques concerning the accumulation and management of processed mine waste, the so-called landfill mining of tailings storage facilities has assumed a role of paramount importance for setting up the safety of tailings dams. Thanks to this practice, economically significant amounts of useful minerals or metals can be recovered from tailings impoundments, thus changing the role of tailings from waste to resource.

In South Africa, important developments have been made regarding the economic convenience of mine mineral waste recovered from no longer active tailings dams. Moreover, at Motlosana (formerly named Klerksdorp) in the North West Province, some tailings dams containing hundreds of millions of cubic meters of mineral waste, resulting from digging out gold[9], are being recovered. In the city's outskirts, a large tailings dam was completely dismantled for safety reasons, considering its proximity to a residential area. Three other tailings dams are now being re-exploited for economic use as landfill mines. According to this practice, the already consolidated tailings are mixed with a large amount of water and turned into an ore-pulp, which is pumped again into the mine plant where some 0.5 grams of gold are recovered out of 1,000,000 kg of tailings. The ore-pulp containing the tailings of the second processing is then conveyed to a vast decentralized storage reservoir. This large

[9] In order to have an idea of the size of gold mines, it is enough to consider that out of a ton of raw mineral only 4 to 5 grams of gold can be recovered.

impoundment already contains several hundred millions of cubic meters of tailings. Finally, the water utilized for the second processing is recuperated and used once more in the working cycle.

The managers of Harmony Gold Mining Company Ltd. entrusted the construction and maintenance of their tailings dams to other specialized companies or consultants in soil mechanics. In addition, they regularly draw up insurance contracts for their tailings dams. This guarantees, on the one hand, certainty and a short liquidation time in case that damage occurs[10] and, on the other hand, proper checks resulting from economic interest.

Both these choices are not due to the respect of mandatory norms but are taken freely as a result of a management philosophy inspired by a strong conscience of the social and environmental accountability of the company. This responsible attitude aims to prevent incidents and consequent negative repercussions on the environment and the residing population. Therefore, in South Africa the use of water for enriching the mineral[11] and the correct management of tailings dams are of paramount importance in order to implement concrete measures for risk mitigation.

Besides applying proper technical management to their tailings dams, South African mining companies do not neglect the fact that possible incidents may always occur. Therefore, they stipulate adequate insurance contracts also for their tailings dams. This responsible free choice bears witness to the awareness that tailings are an element of mining production and should not be considered as useless costly waste. On the contrary, the management techniques previously described make these materials profitable on the market. Similarly, the South Africa experience shows the importance of involving insurance companies in the management of tailings dams, since their recurrent checks, which respond to the company's own economic interest, would be more effective and thorough compared with those carried out by public boards that most of the time intervene only on a bureaucratic level.

It might seem normal that the construction and management of tailings dams is entrusted to qualified technicians. Nevertheless, this was not the rule when the Stava valley disaster occurred. Indeed, only in 2006 did the European Union implement a Directive concerning the management of mineral waste from mining activities (no. 2006/21/CE). This directive declares that "in order to guarantee that reservoirs for storing tailings are properly constructed and subjected to correct maintenance, the member States should intervene adequately to ensure that the planning, location and management of these structures are the responsibility of technically qualified persons".

If the European Parliament and Council considered the implementation of such a rule mandatory from 2006, it obviously means that before this date tailings dams were not necessarily managed in an appropriate way, as demonstrated by too many incidents.

7. Conclusions

There is also a negative legacy left by mining activity. Not only are tailings dams no longer active and abandoned to their destiny[12], often with a load of polluting material, but there is also risk of soil subsidence, resulting from the collapse of tunnels and empty underground spaces, and contamination of

[10] In the case of the Merriespruit incident of 1994, where the tailings dam had been insured, the insurance company liquidated compensation for damages to all the people affected by the disaster within three weeks. In addition, the mining society itself carried out the restoration works [14, 15].

[11] In South Africa, the water used for enriching minerals is usually recovered from the tailings dams and depurated in order to reuse it in the working cycle. At Stava, the processed water and the tailings were conveyed to the reservoirs where, after the settlement of the solid fraction, water was discharged directly into a stream without being depurated.

[12] In Italy, the basins for the storage of tailings make up hundred millions of cubic meters. The provisional inventory published on the ISPRA website [17] lists 650 storage structures, including those that are no longer in activity. They all have "considerable negative repercussions on the environment or can constitute, in the short or long term, a serious threat to human health and the environment".

watercourses and groundwater.

Nevertheless, one should be aware that by means of proper management it is possible to mitigate the negative consequences of mines and their structures no longer in use on the environment and human settlements [16]. These positive goals, which necessarily require higher production costs, can be achieved if the decisions of the mine administrators do not exclusively aim to maximize profits by minimizing costs to the detriment of safety. On the contrary, there should be full awareness of one's own accountability and a widespread culture inspired by civil responsibility and enterprise, always bearing in mind that the cost of prevention is always immensely lower than the cost of damages[13].

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[13] In the case of the Stava valley disaster, the total cost for rescue, environmental restoration, reconstruction and liquidation of damages was one thousand times higher than the investment that would have been necessary and sufficient in order to avoid the failure of the tailings dams.

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