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THE ENVIRONMENTAL IMPACT OF THE COPPER INDUSTRY IN THE FANI RIVER VALLEY (REPSI "HOT SPOT") MIRDITA, ALBANIA

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Abstract

For more than 40 years, full cycle Copper industry has exercised its activity in central Mirdita, as one of the priorities for the economic development of this zone. Copper deposits have been discovered in many parts of the territory of central Mirdita, whereas the main activity of the mining and processing industry is located in the Fan iriver valley. The interruption of industrial activity after the years '90, could not stop the negative environmental impact. The presence of dumps in Fani river banks (as in Repsi, Rresheni and Rubiku) and numerous mining works (addits) in Spaçi and Kodër Spaçi slopes, from which many acid waters drain, including also the natural leaching of surface outcrops of mineralized zones, make up a serious danger to the biodiversity of this area. Several recommendations to reduce the environmental impact of the tailings and copper ores in the dumps in Fani river valley are given in this paper.

Key words: *ore processing, environmental pollution, acid leaching.*

Περίληψη

Για διάστημα μεγαλύτερο των 40 ετών, η δραστηριότητα της βιομηχανίας χαλκού αποτέλεσε μία από τις βασικές προτεραιότητες για την οικονομική ανάπτυξη στην κεντρική περιοχή της Mirdita. Αποθέματα χαλκού έχουν βρεθεί σε πολλά σημεία της κεντρικής Mirdita, ενώ η βασική μεταλλευτική δραστηριότητα λαμβάνει χώρα στην κοιλάδα Fan iriver. Η διακοπή της βιομηχανικής δραστηριότητας μετά τη δεκαετία του '90, δεν κατέστη δυνατό να σταματήσει την αρνητική περιβαλλοντική επίδραση στην περιοχή. Η παρουσία χώρων απόρριψης στις όχθες του ποταμού Fani (όπως και στους Repsi, Rresheni και Rubiku) και πολυάριθμων μεταλλευτικών εργασιών στα πρανή Spaçi και Kodër Spaçi, που έχουν ως αποτέλεσμα την απορροή όξινων υδάτων αποτελούν σοβαρό κίνδυνο για τη βιοποικιλότητα της περιοχής. Στην εργασία αυτή δίδονται συστάσεις για τον περιορισμό του περιβαλλοντικού αντίκτυπου από τη μεταλλευτική δραστηριότητα στην κοιλάδα του ποταμού Fani.

Λέξεις κλειδιά: *επεξεργασία μεταλλεύματος, περιβαλλοντική ρύπανση, όξινη διύλιση.*

1. Introduction

For more than 40 years, full cycle Copper industry has exercised its activity in central Mirdita, as one of the priorities for the economic development of this zone. Copper deposits have been discovered in many parts of the territory of central Mirdita, whereas the main activity of the mining and processing industry is located in the Fani valley.

The discovery of Spaçi Deposit in 1955, and later on the discovery of Maja e Madhe, Gurth Spaçi, Repsi and Laj Repsi deposits (all located in the Repsi zone), initiated the construction of an ore processing plant in Repsi, the intensive population of this area and the building of a small miners' town. In the course of further developments, another processing plant was built in Ura e Fanit, Rreshen and a smelting and refining plant was built in Rubiku closing the cycle of the copper industry.

Aiming to achieve high production levels resulted in ignoring the environmental problems. Many prospect-exploration works, mines, great amount of technological waste from processing plants and different reagents, acids, slags of smelters discharging into the water created "hills of waste" in the banks of Fani river. All this problems had a great influence on the ecosystem of this valley, destroying flora and fauna, and having a direct or indirect influence on people's health.

The interruption of industrial activity after '90, could not stop the negative environmental impact. The presence of dumps in Fani river banks (as in Repsi, Rresheni and Rubiku) and numerous mining works (addits) in Spaçi and Kodër Spaçi slopes, from which many acid waters drain, including also the natural leaching of surface outcrops of mineralized zones, make up a serious danger to the biodiversity of this area.

2. Fani valley in the geoenvironmental aspect and the Repsi Hot spot

Small Fani river valley, represents one of the most important ecosystems of central Mirdita. The valley has a beautiful landscape and flora, and fertile soils, which together with the river, have been very good permanent natural resources for the population of the zone.

The ecosystem of this valley has been considerably damaged during the communist regime, when into the Fani river waters were poured all technological wastes of Copper industry, which had a considerable negative impact in the biodiversity of the zone, transforming it from a natural environment, in an industrial environment, where anthropogenic activity played the main role.

Of course, one of this ecosystem elements is the Repsi industrial zone. Industrial activity began in 1970, when was built the Copper processing plant for the ore minerals of Spaçi, Maja e Madhe, Laj – Repsi, Gurthi, Thirra, Kaçinari deposits.

In this Plant have been processed in total 4.43 million ton of Copper ore. From the calculations emerge that at these dumps should have been deposited about 3.98 million ton of technological waste. By the factual measurements carried out at these dumps (Bazhella 2004), it results to have been deposited about 3.2 million ton of teehnological waste, the rest of 780.000 tons, is poured into the river, especially during winter time with heavy rainy days. These "wastes" have a granulometry under 0.074 mm, thus being a very fine material which increases the active surface. For what regards the environmental pollution Repsi is considered to be a "hot spot".

The presence of considerable amounts of pyrite minerals in all Repsi dumps, natural leaching of mineralized outcrops (which occupy about 0.7 km^2 in the Spaci area), prospect-exploration addits with their piled up "wastes" which drain during all seasons, are reflected in the pronounced acid character of flowing waters in the Fani valley. The content of SO_4^{-2} ranges from 300 to 1340 mg/l (Goskolli *et al.* 2003), whereas pH ranges between 2.5 - 5.15.

Numerous prospect-exploration works and mining works (as trenches, mining shafts, drills and addits) carried out in the above mentioned deposits have been a direct and harsh intervention in the environment which has led to a natural disequilibrium, creating a new system (the technological environment). Piled up ore wastes, mined from the underground works and deposited at the addit entrances (more than 12 only in the Spaci hills) have been a pollution source, considerably increasing the acidity of waters in Sefta e Spacit and Fani i Vogel rivers. This industrial panorama had its climax in the '70s, destroying almost totally the flora and fauna of the Fani valley. This situation brought almost full extinction of fish in these waters, whereas in the fertile soils appeared undeveloped plants. Use of lime to neutralize the acidity of the arable lands, never reached their rehabilitation.

Presently, the copper industry has stoped its activity, but its consequences still continue to pollute the environment, since no intervention is ever done to control the sources of pollutiou.

Mineralogical composition of copper ores processed at the Repsi plant

The copper ores processed at the Repsi enrichment plant are represented by disseminations, veins, and massive concentrations of pyrite, chalcopyrite, sphalerite, which are the main ore forming minerals, associated by magnetite, hematite, muschetovite, marcasite, bornite, galena, arsenopyrite, fahlores (tennantite and tetrahedrite), gold, gold-electrum, salt sulfates such as enargite, hessite, geochrouite, tetradymite etc, and rarely associated by malachite, azurite, covellite, chalcosite, arsenopyrite, smithsonite, cerussite etc. Main ore elements are: Cu, Zn, Au, S, whereas Pb, Ag, As, Cd, Sb, In occur to smaller amounts.

3. Ore processing in Repsi Plant

Repsi Plant began operation in 1971, at a processing capacity of 120 ton per year. Average recuperation reached 85 %. The Plant is located about 30 km from Rresheni town at a sloping terrain. The Plant has processed ores from Spaci, Kacinari, Thirra, Tuci, Maja e Madhe and Repsi deposits. Spaci deposit ores, processed by the Plant, contained about 1 % Cu and 4 % S.

The mineral selective enrichment was the technological scheme. Initially, copper concentration with about 20 % Cu is separated by flotation in an environment of pH 11- 11.5. After, in an environment of pH 5–5.5 pyrite mineral is flotated and pyrite concretation obtained with S content of about 35 %.

For the deposition of the Repsi Plant waste, have been constructed 4 dumps (Fig. 1), where have been deposited 3.2 million ton of technological waste, the rest (0.78 million ton of waste) have been discharged into the Fani river.

The wasre material of the dumps has a granulometry under 0.074 mm. Being a very fine material, it is very dangerous to the environment.

4. Outcrops of sulfide mineralized zones

On the surface of Spaçi, Lamskoni, Mashtërkori and Laj Repsi deposits are exposed some intensively oxidised sulfide mineralized zones, represented by limonites (gossans). Primary minerals of copper and altered pyrites are rarely encountered on the surface. On the surface of Spaci deposit in the basalt pillow lavas occur intensive zones of chloritization and silicification 50-100 m up to 200 m thick that are followed along the strike for 1200-1500 m. The presence of pyrite favours at a large scale the acid leaching. Their location in a steep terrain favors also natural leaching and their draining to Fani and Sefta e Spacit rivers. (Figs 1, 2).

5. Chemistry of dump nr. 1, Repsi area

The chemical composition of Repsi dumps shows some important variations regarding the content of heavy metals and S (Table 1).

Taking into the consideration the heterogenity of dumps construction, and the way that waste is discharged into the dumps, these variations are mainly related to the nature of processed ore. Very fine granulometry (< 0.074 mm) makes difficult the identification of present minerals in the dump, meanwhile it facilitates the acid leaching.

Figure 1 - Acid waters flowing from dump 1

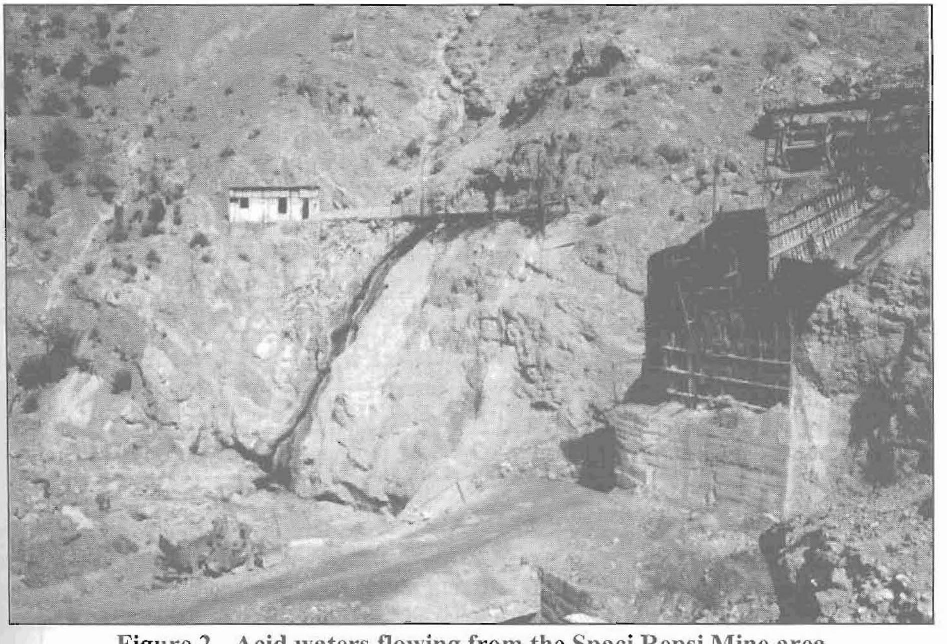

Figure 2 - Acid waters flowing from the Spaci Repsi Mine area

6. Acid leaching and its effects

The dumps of Repsi enrichment Plant for tens of years are exposed to atmospheric agents (Fig. 1). Although they are no more operative, these dumps still continue to be intensive polluting sources.

Table 1 - Chemical analyses of the dump nr.1 of Repsi

Sample number	pH	Elements in %					
		Cu	Zn	Pb	As	S	Fe
3	4.8	0.17	0.04	0.25	1.75	7.20	11.15
4	2.9	0.18	0.03	0.05	0.23	6.06	10.16
5	3.7	0.04	0.02	0.10	0.16	1.18	14.64
6	4.5	0.27	0.04	0.31	0.12	28.85	13.44
7	4.7	0.78	0.04	0.21	0.29	12.94	24.14
8	4.2	0.20	0.06	0.46	0.21	44.25	34.65
9	4.6	0.41	0.03	0.31	0.28	11.40	20.10
10	4.4	0.10	0.02	0.051	0.10	4.98	18.39
Reps 1*		0.25	0.08	0.065	-	15.70	20.95
Reps 2*		0.11	0.025	<0.05	-	7.50	9.18
Reps 3*		0.14	0.04	<0.05	-	8.12	9.37

Analyses carried out by ITNPM (2003)

Among numerous minerals, only two of them, pyrite (FeS_2) and pyrhotite ($Fe_{1-x}S$) are the most responsible minerals for acidification of drainage waters. But in some places, a considerable influence in reducing pH have other iron sulfides such as marcasite (FeS_2 -rhomboid) or arsenopyrite (FeAsS), especially in cases when they are the main components of iron or associate pyrite and pyrhotite.

Typical processes, developed in a sulfide environment affected by oxidation are:

- Alteration of iron sulfides and formation of acid solutions
- Solution of other sulfides by non-neutralized acids

An important role in the degradation of environment, often more than the low pH of water, is done by the elements dissolved in water. Such is for example arsenic, obtained by dissolving of arsenopyrite or other arsenic bearing sulfides, which can be transported by drainage waters even when pH of these solutions is high. Among the elements considered as possible toxic polluters originated by mining waste, can be distinguished: Zn, Pb, Cu, Ni, Cd, Hg, Mo and As. Other elements such as Cr, Co and Se, can be polluters in various zones too.

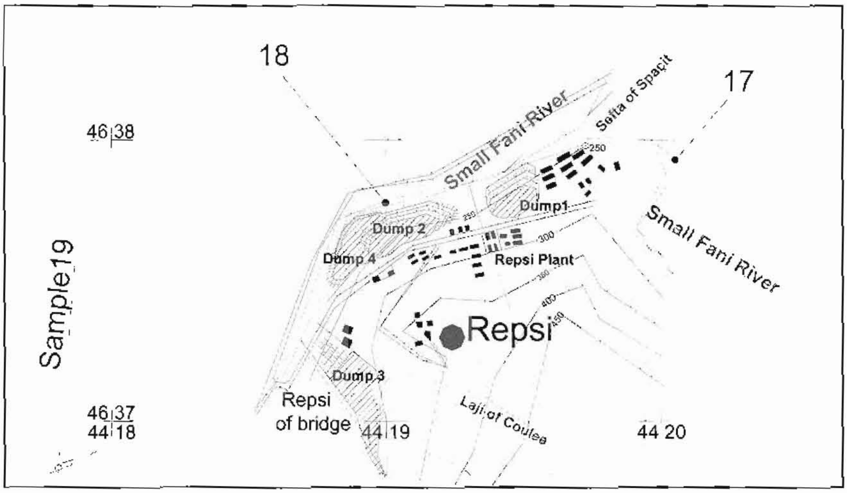

Figure 3 - The scheme of dumps location

Acid leaching and its effects

The data of Enrichment Plant and processed ore composition, confirmed also by chemical analyses and field observations, show that primary factor for generation of acidity in Repsi dumps is pyrite oxidation, which makes up over 90 % of dump's sulfides. This oxidation takes place under direct influence of bacteria, from which the best known are *Thiobacillus Thiooxidans* (oxidation of S^0 + S^{2-} and formation of sulfate iones), and *Thiobacillus ferrooxidans* (oxidation of Fe^{2+} in Fe^{3+}).

Generation of acidity under direct effect of sulfideaters bacteries *Thiobacillus Thiooxidans* is shown below (Torma 1988) :

$$2FeS_2 + 7O_2 + 2H_2O \xrightarrow{bacteria} 2FeSO_4 + 2H_2SO_4 \qquad (4.1)$$

Palencia *et. al.* (1991), suggests another reaction which ends, except for sulfates, with oxidation of Fe^{2+} in Fe^{3+}, that is developed under direct effect of bacteries *Thiobacillus ferrooxidans* :

$$4FeS_2 + 15O_2 + 2H_2O \xrightarrow{bacteria} 2Fe_2(SO_4)_3 + 2H_2SO_4 \qquad (4.2)$$

Pyrite continues to be attacked by $Fe3^+$ iones, forming native S.:

$$FeS_2 + Fe_2(SO_4)_3 \rightarrow 3FeSO_4 + 2S^0 \qquad (4.3)$$

Which reacts with ferro sulfate to produce ferro sulfate and sulphuric acid:

$$2S^0 + 6Fe_2(SO_4)_3 + 8H_2O \rightarrow 12FeSO_4 + 8H_2SO_4 \qquad (4.4)$$

Such reactions that form high acidity (i.e. $16H^+$ for one molecule FeS_2 in reaction 4.3 + 4.4) are responsible for very low values of pH (Table 1), generating the acid alteration of the dump. Based on topographic data of the study entitled : "Monitoring the dumps and wastes" by E. Goskolli *et.al.* (2003) for Repsi dump 1 (Fig. 3), amounts of wastes deposited results to be 551 460 ton.

Acid leaching : Sulfide oxidation →produce $SO_4^{\ 2-}$ → acid environment is formed. Knowing that, main generators of acidity are sulfides (especially pyrite), acid potential can be easily calculated:

$$2\ FeS_2 + 15/2\ O_2 + 7\ H_2O \rightarrow 2\ Fe(OH)_3 + 4H_2SO_4$$

According to the formulae **kg acid/ton = 30.06 * (% S)** can be calculated that the water flow leaching the material of the dump will contain:

Table 2 – Acid potential of dump 1

S (%)	acid P (kg/t)	material (Ton)	acid (Ton)
14.72	442.483	551 460	244 011.8

This is the acid potential of whole Repsi dump 1, if it should be totally oxidized. Some amounts of this acid can be neutralized by wall rocks, depending on their composition. Neutralising capacity measured at an averaged sample of Repsi dump 1, resulted 3.3 kg H_2SO_4/T. Then, the real acid potential (RAP) based on above mentioned measurement is:

RAP = acid Potential (kg/t) – 3.3 kg/t = 442.483 – 3.3 kg/ton acid (coefficient of rock neutralising capacity) =439.183kg/t.

So that, from the dump 1, can be released by acid leaching the amount of metals as follow:

Table 3 – Amount of metals that can be leached from dump 1

Dump	Volume	Volumetric weight	Amount of metal (ton).					
			Cu	Zn	Pb	As	S	Fe
Dump 1	303000	1.82	1466.8	220.6	1103	2162	81175	1026 82

7. Transportation of heavy metals and of sulfate ions from Fani waters

Refering to water analyses of monitoring stations 17, 18 and 19 in Fani i vogel waters (SWECO International 1999), in vicinity of Repsi dumps (Fig. 1), element compositions are as follows:

Table 4 – Element content from samples of the monitoring stations

Stations where samples have been taken.	pH	Elements						
		μg/l Cu	μg/l Zn	μg/l As	μg/l Pb	μg/l Cd	mg/l S	Mg/l Fe
17	6.9	4.0	6.0	< 1	< 0.50	< 0.1	3.3	0.11
18	6.4	130	140	< 1	< 0.50	< 0.1	11	0.67
19	5.5	100	101	1.1	0.71	0.19	25.7	7.79

According to water analyses of discharges in Repsi dump 1, carried out by (Goskolli *et.al.* 2005), pH and sulfate ion are as follow:

Table 5 - pH and sulfate ion at repsi dump 1

Number of measurements.	Sampling place.	pH	SO_4 in mg/l
1	Damba nr. 1 Reps	3.12	800
2	Damba nr. 1 Reps	3.30	670
3	Damba nr. 1 Reps	4.23	380

Monitoring results of flowing waters in Fani i vogel river basin carried out in 1998, January, April and Septembre 1999 (SWECO International 1999), are given in table 6.

Table 6 - Monitoring results of flowing waters in Fani i vogel river basin

Number of samples.	Flow (m^3/s)			
	April 98	January 99	April 99	September 99
17	14	7.5	8.0	1.4
18	20	15	17	1.7
19	25	8.2	17	2.2

Refering to above mentioned measurements, annual average discharge results to be:

Table 7 - Annual average discharge

Station number.	Annual average flow (m^3/s)	Annual average flow (m^3/vit)
17	7.7	242827200.00
18	13.4	422582400.00
19	13.1	413121600.00

Based on the data of tables 4 and 7, transportation of heavy metals in Fani i vogel river during one year is:

Table 8 – Annual ttransportation of heavy metals in Fani i Vogel River

Station 17	Cu	Zn	As	Pb	Cd	S	Fe
kg/m^3	$4*10^{-6}$	$6*10^{-6}$	$< 10*10^{-6}$	$< 5*10^{-6}$	$< 1*10^{-6}$	0.0033	$110*10^{-6}$
ton/year	0.97	1.457	< 0.24	< 0.12	< 0.024	801.3	26.7
Station 18							
kg/m^3	$130*10^{-6}$	$140*10^{-6}$	$< 10*10^{-6}$	$< 5*10^{-6}$	$< 1*10^{-6}$	0.011	$670*10^{-6}$
ton/year	55	59	< 0.42	< 0.21	< 0.042	4648.4	283
Station 19							
kg/m^3	$100*10^{-6}$	$101*10^{-6}$	$1.1*10^{-6}$	$0.71*10^{-6}$	$0.19*10^{-6}$	0.0257	$7790*10^{-6}$
ton/year	41.3	41.7	0.45	0.3	0.078	10617	3218

8. Measures for the reduction of pollution

Pollution from the copper ore processing industry is caused by sulfide oxidation through oxygen (O_2) of surface waters and the air. As mentioned above, during the process of oxidation are formed soluble products which pollute soils, as well as the surface and underground waters.

Waters can be polluted by heavy elements released during acid leaching. Soils are polluted by polluted waters, air and sediments transformed in soils, whereas air is polluted by dusts which can be evidenced by measuring pH of water and rain.

Based on this study, several recommendation can be defined for intervention in order to minimise pollution in waters, sediments and soils. These interventions can be carried out to reduce as much as possible sulfide oxidation, isolation of products that cause acid leaching, and neutralisation of toxic elements.

To minimise oxidation and leaching of dumps by surface waters, these measures should be taken:

1. Covering with membrane of all depositions in Repsi dumps, and placing a clay sheet over the membrane to create a full isolation.
2. Cleaning the side trenches of dumps and drainage channels in order to keep away flowing waters from the dumps.
3. Ploughing and planting of dump slopes to keep into control the erosion.

For isolation of acid leaching products is necessary :

1. To isolate the products in the dumps. This can be done by reducing to a minimum the acid leaching applying the above mentioned measures.
2. To isolate flowing waters of the dumps that contain toxic elements through reservoirs which will impede their discharge into the river.

To neutralise toxic elements, these ways can be advised:

1. To construct limestone walls around the dumps and reservoirs of flowing waters, in order to reduce the acidity and precipitation of Cu in the form of insoluble carbonates (malachite, azurite).
2. To drain the flowing waters by using a chlorite filter. These minerals neutralise H_2SO_4 by reacting with it.
3. To drain flowing waters by using zeolite filters. Absorbing and cation exchange capacity of zeolites is wellknown (Kirov *et al.* 1997). The purpose of their use is absorption of Pb,

Zn, Cd, Cu etc. As results also by the study of zeolites of stellerite and stilbite types of Munella (Sinojmeri and Beqiraj 2002, Beqiraj 2004), they have good absorbing capacities of these cations. Their use is more effective because these minerals have permanent effect.

9. Conclusions and recommandations

Repsi dumps with a volume of 1 758 242 m^3 or 3.2 milion ton of technological waste, make up the hottest spot of the region regarding the environmental pollution problem.

Average composition of toxic elements in Repsi dump 1 is *0.266 %* Cu, *0.04 %* Zn, *0.2 %* Pb, *18.6 %* Fe, *0.4 %* As, *14.7 %* S.

This element composition is due to the presence of pyrite, chalcopyrite, galena, spbalerite and arsenopyrite in the dumps.

Distribution of toxic elements in the dumps is not the same. It is closely related to the nature of the processed mineral in different periods of time and with the place where they are deposited.

Pyrite results to be the main responsible mineral for the creation of acid leaching.

For dump 1, real acid potential is estimated to be about 440 kg/ton, which means that this dump can release in total about 240000 ton sulphuric acid (H_2SO_4).

As a consequence of acid leaching, from Repsi dump 1 can be released about *1 467 ton* Cu, *220 ton* Zn, *1 100 ton* Pb, *102 700 ton* Fe, *2 160 ton* As and *81 175 ton* S. These figures show the extraordinary toxic potential of Repsi dumps.

Fani river transports each year to the Repsi dumps *1 ton* Cu, *1.5 ton* Zn, *27 ton* Fe and *800 ton* S, collected from the mining works and mineralized zones exposed in its uppermost parts.

Further down of Repsi dumps, the material transported annually by Fani river reaches about *41 ton* Cu, *42 ton* Zn, *0.3 ton* Pb, *0.08 ton* Cd, *3 200 ton* Fe, *0.5 ton* As and *10 600 ton* S. Such an increase of the material transported by Fani river after passing the zone of the dumps, shows the influence of the dumps in water pollution.

Covering with membrane the dump depositions will reduce their oxidation and minimise leaching.

Cleaning of dumps side trenches and drainage channels, will reduce acid leaching.

Constructing separate reservoirs for the dumps water flows and forming limestone encircling walls, would impede a part of the toxic elements to be discharged to Fani river.

Filtering of reservoirs flow waters by natural chlorites and zeolites would reduce the toxic elements in the Fani river waters.

Foresting the dump slopes to keep into the control the erosion will stop direct discharge of soils in the river, and will limit considerably the re-exposure of dump fresh materials to oxidation. A positive effect in this case will be the creation of a green belt around the dump.

10. References

Bazhella, Gj., 2004. *Mining inheritance in Mirdita.*

Beqiraj, E., Touray, J.C., Muller, F., and Sinojmeri, A., 2004. Mineralogical characterization of Munella zeolites,*Albanian oil,* Nr. 2, 29–34.

Fani River Enviromental Rehabilitation Programme (Projekt shqiptaro-suedez) grup autoresh., 1999. ITNPM Archives, Tirane.

Goskolli, E., 2003. Monitoring dumps of Enrichment Plants and massive piled up wastes of Mines in our country and Preparation of a legal board about dumps, *ITNPM Archives*, Tiranë.

Palencia, I.R., Wan, W., and Miller, J.D., 1991. The electronical behaviour of a semiconducting natural pyrite in the presence of bacteria, *Metall. Trans.*, B22, 765–774.

Sinojmeri, A., and Beqiraj, E., 2002. Munella zeolites and their features, *Symposium II-Documents and their us* , Tiranë. 6p.

Tashko, A., 2003. *Biochemistry and Environment.* (prepared lectures for postuniversity students)

Torma, A.E., 1988. Leaching of metals, *Biotechnology*, 6B, 367–390. VCH. Verlagsgesellschaft, Weinheim, Germany.