Integrated treatment of copper industry wastes towards prevention of water resources contamination in Western Balkans

Ass. Prof. Panias Dimitrios and Ioanna Giannopoulou

National Technical University of Athens
9, Heroon Polytechniou str. 157 80 Zografos Campus
Athens, Greece

Abstract

The present paper aims at disseminating the knowledge obtained within the "INTREAT" research project that is financed by the European Commission within the FP6. The Project addresses the environmental pollution problems associated with solid and liquid wastes generated by the complex sulphide ore mining and metallurgical activities, in order to develop an innovative and cost effective integrated management scheme aiming at waste minimization, prevention of surface-, groundwater contamination and safeguarding the ecosystem of the affected areas. Two areas located in different Western Balkan countries were selected as case studies for the project: the area of Bor mines in Serbia and the area of Buchim mines in FYROM.

The case study of Bor area in Serbia is presented in this paper. Actually, the extent of the regional water resources contamination caused by copper industrial activities in the area of Bor, Serbia, is identified. Moreover, the waste treatment technologies investigated in the "INTREAT" project are summarized and evaluated according to their applicability and effectiveness for the prevention and minimization of the environmental pollution.

1 Introduction

The area of Western Balkans is rich in metallic and non-metallic mineral deposits. Among the most important of them are the complex sulphide ore deposits, which are used for the production of base and precious metals. The exploitation of these deposits, along with the production of the related metals, comprises a dynamic industrial sector for the Western Balkan countries that are included among the first fifteen worldwide producers of copper ores and copper metal. For years, the exploitation of complex sulphide ores in the area of Western Balkans, as well as the minerals processing and the metals production that follow, generated enormous quantities of wastes that caused and are still causing severe environmental pollution problems mainly related to the contamination of soils, surface- and ground- water. Due to the political and military crisis in the area of Western Balkans, little or no action has been taken during the last decade for the protection of the environment resulting in increase of the environmental damages in the area. Besides, the generally slower pace of economic reforms in this area than in the central Europe has created an uneven development of mining and metallurgical industries that, in combination with the lack of economic and technical means, caused a dramatic increase in the contamination of the local environment.

However, the majority of complex sulphide ore deposits occurred in the Western Balkans area remains undeveloped, establishing an important mineral wealth with extremely high added value. The exploitation of these deposits can promote political stability, economic development and social cohesion in the area of Western Balkans. In order to secure their continued operation, mining and metallurgical industries are called upon to address the demands of sustainable development and demonstrate continuous environmental improvements over long term. Thus, it is a matter of great importance for these industrial sectors to look for solutions and adopt the appropriate waste management and treatment technologies as to achieve prevention or reduction of the environmental pollution.

In this respect, the research project "Integrated treatment of industrial wastes towards prevention of regional water resources" (NTREAT) studies the interaction of copper industrial activities and the environment, in order to develop an integrated management scheme of preventative and remedial technologies for the environmental pollution, especially of soil and natural water resources, generated from the copper mining and metallurgical industry. Two areas located in different Western Balkan countries were selected as case studies for the project: the area of Bor mines in Serbia and the area of Buchim mines in FYROM.

The case study of Bor area in Serbia is presented in this paper. This area is strongly related with copper mining and metallurgical activities, which cause a huge environmental pollution. During the implementation of the project, different waste treatment technologies for the solid wastes and the wastewaters generated from the copper industrial activities were developed. So far, the evaluation of these technologies indicates the feasibility of an integrated management of the copper industry wastes for the elimination of the environmental pollution in the area, especially of the natural water resources contamination.

2 The case study of Bor area in Serbia

Bor city is located in the northeastern part of Serbia, near the borders of Bulgaria and Romania. The population of the city is about 40.000 people, while almost another 25.000 people live in the broad geographical area of Bor. Copper mining and metallurgy were and still continue to be the main economic activities in the area, considering that about 15.000 people are working in such industrial activities.

Copper mining and metallurgical industry in the area of Bor has a long history starting in the beginning of the 20th century. One of the larger copper industries in Western Balkans, the "Copper Mining and Smelting Complex Bor" company (RTB-BOR), is currently operating in the area of Bor. It concerns for an integrated industrial company in the field of copper production that comprises mining of complex sulphide ores, minerals processing, pyrometallurgical treatment of copper concentrates and finally, electro-refining of copper anodes.

2.1 Extent of the environmental pollution

The open pit copper mines located in the area of Bor, as well as the regional rivers network, are shown in Figure 1. Currently, two open pit mines located in Krivelj and Cerovo (Fig. 1) and an underground mine located in Bor are in operation. The open pit mine located exactly at the border of the Bor city (Fig. 1) has currently been exhausted. For the whole duration of the company's activities, large volumes of solid wastes, mainly overburdens from the ores excavation in the open pit mines and flotation tailings from the minerals processing, have been accumulated and dumped in two non-properly designed and operated disposal sites. It is estimated that the first of these sites contains about $200x10^6$ m^3 of sulphidic waste, while the sulphidic waste volume of the second accounts for more than $300x10^6$ m^3 [1]. In both dumping sites, serious technical anomalies have been encountered, mainly attributed to deviations from technical specifications during waste dumping or failure to perform hydrotechnical or other maintenance works due the bad economic situation caused by the last decade's war. As a result, dissolved heavy metals or sulfates, or both, are released from the dumping sites into the environment, causing serious and long lasting contamination in soil, surface- and groundwater in the whole basin of the network of rivers connected to the river Danube.

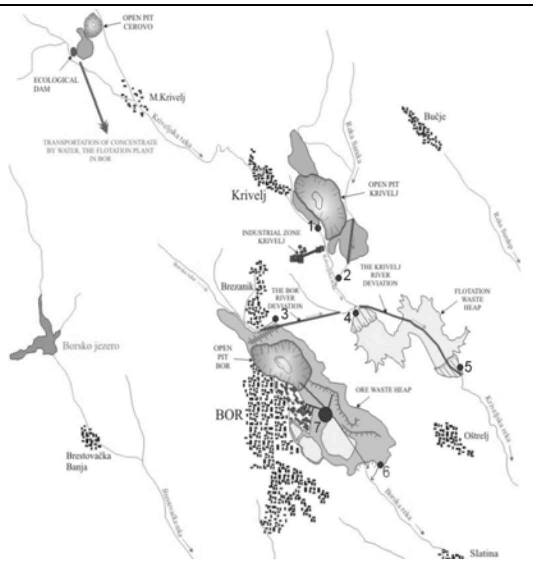

Figure 1: The open pit copper mines and the regional rivers network in the area of Bor

Furthermore, the operation of the metallurgical plant, that is located at the border of Bor city, creates serious environmental problems in the area. Wastewaters / effluents generated from the pyrometallurgical treatment of copper concentrates and the copper refining process are characterized by low pH, due to the high content of residual sulphuric acid and presented high concentration of heavy metals, such as Cu, Cd, Hg, Bi, Sb, Ni, Sn etc. and other hazardous substances. The majority of these heavily contaminated wastewaters are released untreated into the natural water streams and through the network of the regional rivers, contaminants end up to the river Danube.

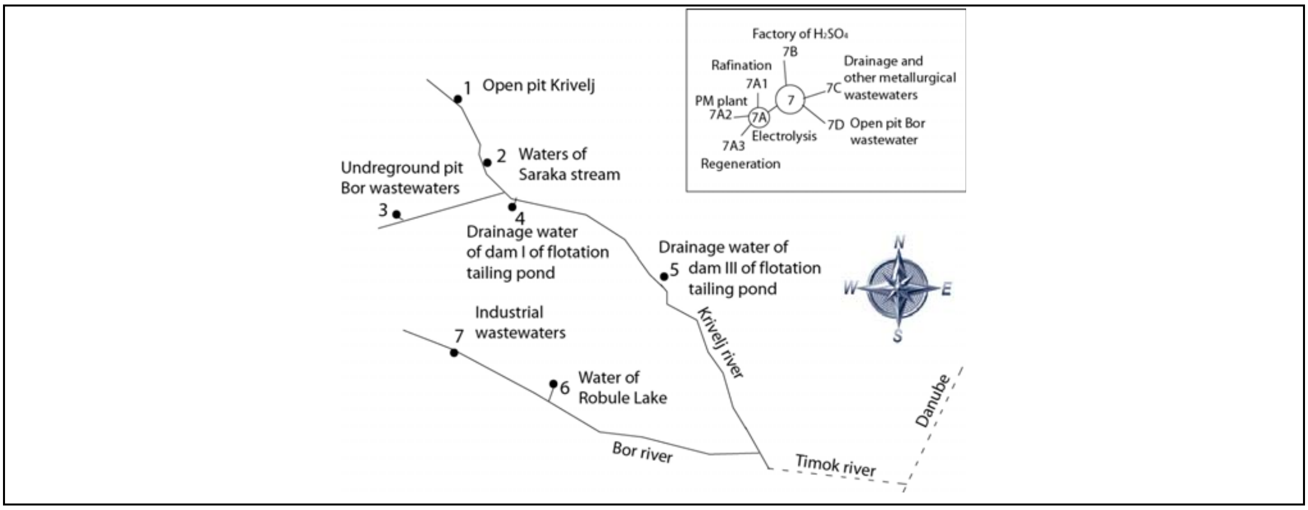

Figure 2: Wastewaters sources and their contribution to the water resources contamination in the area of Bor.

Diagram in Figure 2 presents the interaction between the mining and metallurgical activities in the area of Bor and the natural water resources. Seven different wastewater sources are presented in this diagram, corresponded to the locations of the industrial activities referred in Fig. 1. Wastewaters enter directly without treatment to the natural water streams of rivers Krivelj and Bor and through them to the river Timok and finally, to the river Danube creating very serious environmental problems. Almost 1.285 ton of iron, 502 ton of copper, 1.5 ton of nickel, 0.5 ton of arsenic, 52 ton of zinc, 2 ton of lead, 300 Kg of cadmium and 61 ton of manganese [2] are annually discharged in the above described network of regional and international rivers.

2.2 Preventative and remedial technologies for the solid wastes treatment

Solid wastes produced from copper industrial activities are mainly related to ores mining and minerals processing activities. These wastes represent the main sources of acid mine drainage (AMD) generation. AMD is generated by the natural oxidation of sulfide minerals when exposed to the combined action of water, oxygen and indigenous oxidizing bacteria. The acidic waters generated pollute waterbodies (groundwater, lakes, rivers, sea) and soils with the deposition of high loads of sulfates, proton acidity and heavy metals that may finally end through the food chain to animals and humans through ingestion, inhalation and dermal contact. Thus, AMD control techniques must be applied in order to prevent and eliminate environmental pollution. In the case study of Bor, treatment of solid wastes includes chemical leaching for the removal of valuable metals, stabilization of the contaminants, and bioremediation for the rehabilitation of the waste dumps. Moreover, the treatment of natural leachates and the prevention of underground water contamination were studied according to the metal precipitation and permeable reactive barriers technologies, respectively.

Chemical leaching of solid wastes was investigated under atmospheric, high pressure and ultrasound conditions, at different temperatures and in the presence, or not, of oxidative agents (H_2O_2, $FeCl_3$ and $Fe_2(SO_4)_3$, etc.) [2-3]. Laboratory scale experiments were performed with a large number of tailings from the old flotation plant near to the exhausted open pit mine of Bor (Fig. 1) and from the flotation plant “Veliki Krivelj”, near to the open pit mine in Krivelj (Fig. 1). In any case of chemical leaching, the achieved metals efficiencies were low, up to 60%, indicating that this technology is not efficient for the solid wastes treatment [4]. However, during oxidative leaching the sulphur content in solid wastes was decreased, as metals were captured in sulphidic form. In particular, during the oxidative leaching of tailings originated from the Veliki Krivelj flotation plant the content of sulphur was decreased from 13.6 to 1.23 wt. % [3].

Unlike chemical leaching that results in the removal of contaminants from solid wastes through chemical treatment, stabilization seeks to immobilize contaminants within their ″host″ medium (i.e. the soil, sand etc.). Stabilization is one of the most effective methods for contaminated soils, achieving the significant reduction of hazardous substances mobility through both, physical and chemical means. Soil samples from Dam 3_A (Fig.1), located at the end of Veliki Krivelj flotation tailings dumping area, were chosen as representative of heavy metal contamination. For stabilization of heavy metals and toxic elements into these soil samples fly ash, lime, cement, limestone and used foundry sand (UFS) were used, separately or in mixtures, as stabilizing agents [3]. The obtained results indicated that the use of mixture of UFS and lime, as well as of fly ash and lime, in different ratios could lead to effective stabilization of heavy metals into the soil of Dam 3_A. Actually, copper, zinc, iron and lead were efficiently stabilized and their concentrations into the drainage water were low enough to permit its safe discharged into natural water streams, according to the national environmental legislation [5]. Evaluation of results provided the conditions and the methodology under which, field tests in the area of DAM 3_A has to be implemented. The first four weeks results of field tests are satisfactory for the stabilization of hazardous substances in the contaminated soil.

Rehabilitation of the exhausted dumping areas was investigated in laboratory scale experiments examining the suitability of certain species of plants, along with the design of composite covers made of different materials. Evaluation of the experimental results indicated the most suitable plants and the optimum composite covers that had to be used in field tests for the rehabilitation of exhausted disposal areas. The rehabilitation field tests were build in succession of stabilizing field tests, on crest of Dam 3_A, close to edge of dam crest. Experimental fields were settled in 4 rows with 3 fields in each row. The first six fields were formed with addition of lime (3t/ha) and NPK fertilizer (400kg/ha), while the rest six were formed on the area without additions. Rye and oat were sowed alternatively in these fields. The first four weeks results indicated that better results were obtained where additives were used, with the plants being higher, having an intensively green colour and a stronger root system. Finally, oat gave better results than rye in both cases, with and without additives. In any case, rehabilitation of waste dumps with the proposed plants is possible [6-7].

For the treatment of natural lechates generated in the dumping fields, the metals precipitation method was investigated for the selective removal of the contained metals and sulphate. Based on a thermodynamic model developed for this reason [7], iron, copper and nickel were selectively precipitated in a tree stages process with NaOH or $Ca(OH)_2$, under the appropriate pH conditions. Evaluation of the obtained results indicated that the removal of the contained heavy metals is more effective in a two stages precipitation process with NaOH, where copper and iron are totally removed in the first stage and the rest metals in the second one [8-9]. Sulphate removal was more effective with Ca^{2+}, added as lime [9]. Precipitants resulted in this treatment process could be used into the copper concentrates pyrometallurgical processes, or in other processes, as secondary raw materials.

Treatment of the contaminated groundwater was investigated in laboratory and field tests, using the technology of permeable reactive barriers (PRBs). The Saraka stream wastewater (Fig.1) having an average volumetric flow of 3802 m^3/day was selected as representative sample of contaminated groundwater for the laboratory tests. As adsorption reagents zero valence iron (Fe^0), diatomite, anthracite, limestone, activated carbon, zeolite, chamotte powder, alumina, quartz, bentonite, fly ash, lime, organic and inorganic ion exchangers, as well as appropriate mixtures of these materials were used [9-12]. Although most of these materials gave satisfactory results for Cu, Fe, Mn, Zn and Ni reduction, they presented low permeability. Actually, evaluation of the experimental results indicated that Fe^0 and zeolite presented the higher absorption capacity Therefore, three semi-industrial scale permeable reactive barriers with Fe^0, zeolite and their mixtures as absorbent materials were built in Dam 3_A for groundwater treatment. The first results of the drainage water collected after PRBs shown generally low heavy metals content.

3.3 Wastewaters management and treatment technologies

Pyrometallurgical treatment of copper concentrates derived from complex sulfide mineral processing is strongly related to the generation of large volumes of wastewaters. In the case study of Bor industry, wastewaters generated from copper metallurgical activities are mainly originated from the operations of copper refining and electrolyte regeneration, as well as from the sulphuric acid and precious metals production plants (Fig. 2). For research reasons, these wastewaters streams are considered comprising a total wastewater stream, the industrial wastewaters stream. The average outflow of industrial wastewaters stream is estimated at 16 m^3/day [2] while, their high content in sulphuric acid involves extremely low pH values. Metals of particular interest in these wastewaters include Cu, Ni, Fe, As, Zn, Pb, Sn, and Bi in a concentration that can range from 3 to $6x10^3$ ppm [2]. Therefore, direct discharge of industrial wastewaters into the environment may cause serious environmental contamination problems and loss of valuable metals. In the cases of copper and nickel the annually loss of metals is estimated more than 34 ton and 3 ton, respectively.

Treatment of the industrial wastewaters is focusing both, the recovery of valuable metals and the safe discharge into the environment. The high copper concentration in these wastewaters renders economically attractive its removal. For this reason, electrolysis and cementation treatment technologies were studied for the selective recovery of copper from the industrial wastewaters, in combination with the metal precipitation process for the removal of the rest heavy metals contained in the wastewaters. In addition, heavy metals complexation and membranes separation technologies were investigated for the wastewaters treatment. Finally, the wastewaters purification before their safe discharge into the environment was studied by electrodyalisis [7,14].

The electrolytic treatment of the industrial wastewaters was investigated in laboratory scale experiments using synthetic solutions. In these experiments the effect of different electrolysis parameters, such as the cathode potential, current density, etc., on the selective recovery of the contained metals was investigated. Moreover, the current and energy efficiencies were calculated in order to be defined the optimum conditions for the performance of in-situ tests with real industrial wastewaters. So far, experimental results indicated that except for copper, the selective recovery of the contained metals is not favored [7]. In particular, copper is electrolytically recovered at a percentage almost 100% with co-deposition of As, Sb, and Bi, while the recovery of the rest metals is not feasible under the investigated conditions. The effluent resulted after the electrorecovery of copper is proposing to be treated according to the metal precipitation method in order the final discharged wastewaters to be environmentally accepted. Recovered copper can be recycled in the copper production process, while precipitate may be used in nickel production, because of its high nickel content. Figure 3 illustrates the combined process for an integrated treatment of the industrial wastewaters, including also the final stage of wastewaters purification [7].

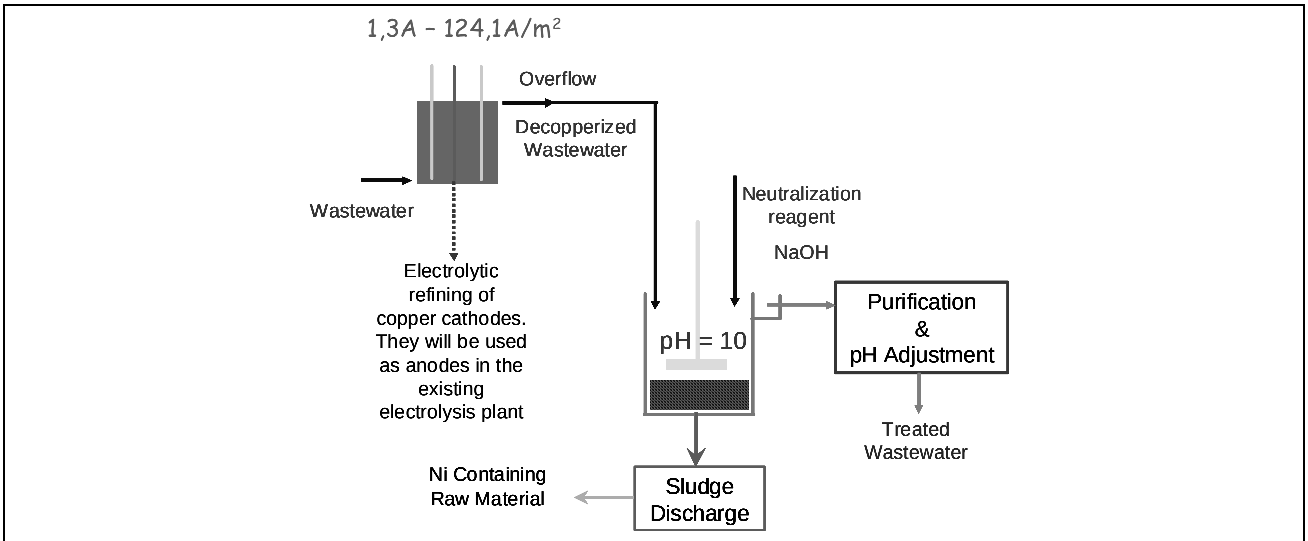

Figure 3: Combined process comprises copper electrorecovery, heavy metals precipitation and wastewaters purification for the integrated treatment of the industrial wastewaters.

Copper cementation was investigated as an alternative treatment technology for the industrial wastewaters, because of its simplicity and low cost. Moreover, copper industry in Bor offers a cementation plant that used to be in operation for years. The application of this wastewaters treatment alternative was investigated in laboratory scale tests using different iron forms as cementation agent. The effect of different process parameters, such as excess of cementation agent, agitation rate, wastewaters pH, etc. was investigated in order to be defined the optimum conditions for the efficient application of this method [2,7]. Results of these experiments shown that cementation is a viable and cost effective treatment technology for the recovery of copper from the industrial wastewaters. Recovered copper can be reused in the pyrometallurgical process for copper production. For the effluents generated after the wastewaters treatment according to this technology, the application of the metals precipitation method, as in the case of the electrolytic treatment, is proposed. The combined process for an integrated treatment of the industrial wastewaters [7], including also the final stage of wastewaters purification, is illustrated in Figure 4.

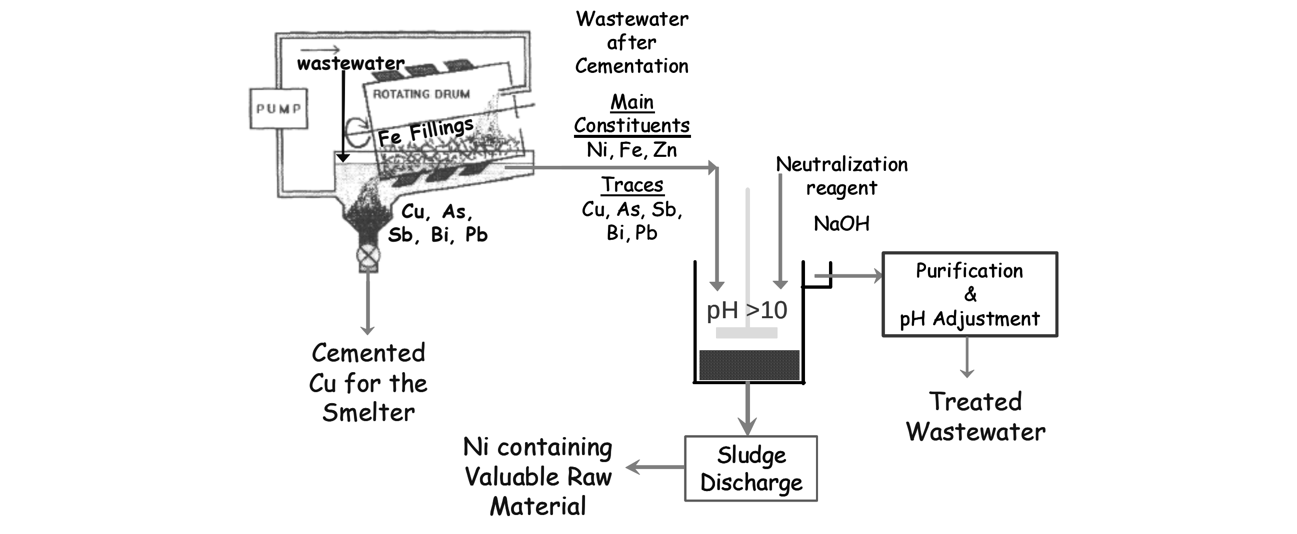

Figure 4: Combined process comprises copper cementation, heavy metals precipitation and wastewaters purification for the integrated treatment of the industrial wastewaters.

Heavy metals complexation / membranes separation technology for the treatment of the industrial wastewaters was studied in laboratory scale tests using different water soluble oligomers, such as polyvinyl alcohol, carboxyl-methyl-cellulose, polyvinylethylenimin and pectin, in combination with two types of commercially available membranes, the UF- 6PAN and the UF-10PAN. This treatment method targeted the removal of the divalent metal ion Cd, Co, Cu, Ni, Pb and Zn. Results from the performed experiments were evaluated and the optimum conditions for the heavy metals complexation were defined [7]. According to these conditions, an efficient retention, higher than 99%, was achieved for Cu, Fe, Mn and Pb [13].

Wastewaters purification was studied in laboratory experiments by electrodialysis. According to the obtained results, acid separation from the industrial wastewaters by electrodialysis is more effective at low acid concentrations, achieving high metals retention [7,14].

4 Conclusions

The integrated management of solid wastes and wastewaters generated in copper industry is studied in the frame of the "NTREAT" research project. The project deals with the investigation of viable and effective technologies for the wastes treatment, focusing at the prevention of environmental contamination and the recovery of valuable metals.

So far, evaluation of results obtained from laboratory scale experiments and field tests indicate that the development of an integrated system for the management of these wastes is feasible, even thought it is enough complicate and its applicability requires the compromise of certain parameters.

Mining and metallurgical industrial sectors in Western Balkans will strongly affect the area's political stability and social and economic prosperity in the near future. Therefore, it is first priority for them to successfully face the new challenges of sustainable development and be transformed to competitive and dynamic industrial sectors in the region.

5 Acknowledgements

The authors gratefully acknowledge the financial support of the European Commission under the Research Project "INTREAT" (INCO-CT-2003-509167), within the Sixth Framework Programme for Research and Technological Development (FP6).

6 References

[1] INTREAT (INCO-CT-2003-509167): Publishable Executive Summary. Available at www.labmet.ntua.gr/interat/.

[2] INTREAT (INCO-CT-2003-509167): 1st Year Periodic Activity Report. Available at www.labmet.ntua.gr/interat/.

[3] INTREAT (INCO-CT-2003-509167): Optimum operating conditions of each studied technology for the treatment of solid wastes - Deliverable D5. Available at www.labmet.ntua.gr/interat/.

[4] OBRADOVIC, LJ., STEVANOVIC, Z, TRUJIC (2006): Copper and gold recovery from Bor, Serbia, old flotation tailings dam, "AMIREG 2006" – Hania, Greece (proceedings), ISBN: 960-89228-1-X, pp. 759-761.

[5] INTREAT (INCO-CT-2003-509167): National and EU environmental legislation framework - Deliverable D1. Available at www.labmet.ntua.gr/interat/.

[6] INTREAT (INCO-CT-2003-509167): Optimum operating conditions of each studied cover for the rehabilitation of the waste dumps - Deliverable D6. Available at www.labmet.ntua.gr/interat/.

[7] INTREAT (INCO-CT-2003-509167): 2nd Year Periodic Activity Report. Available at www.labmet.ntua.gr/interat/.

[8] PAVLOVIC, J., STOPIC, S., FRIEDRICH, B., KAMBEROVIC, Z. (2006): Selective removal of heavy metals from metal-bearing wastewater in a cascade line reactor, Environ. Sci. Pollut. Res., pp. 1-5.

[9] INTREAT (INCO-CT-2003-509167): Optimum operating conditions of each studied technologies for the treatment of natural leachates and groundwater - Deliverable D7. Available at www.labmet.ntua.gr/interat/.

[10] BARTZAS, G., KOMNITSAS, K., PASPALIARIS, I. (2006): Laboratory evaluation of Fe0 barriers to treat acidic leachates, Minerals Engineering 19 (2006), pp.505-514.

[11] FAFOUTIS, I., KOMNITSAS, K. (2006): Manganese and copper removal from leachates using slag and red mud reactive barriers, “AMIREG 2006” – Hania, Greece (proceedings), ISBN: 960-89228-1-X, pp. 735-740.

[12] MARKOVIC, R., DRAGULOVIC, S, TRUJIC (2006): Heavy metal removal from eastewaters using low-cost materials, “AMIREG 2006” – Hania, Greece (proceedings), ISBN: 960-89228-1-X, pp. 755-758.

[13] NENOV, V., BONEV, B. (2006): Bonding agents for heavy metals complexation, “AMIREG 2006” – Hania, Greece (proceedings), ISBN: 960-89228-1-X, pp. 749-754.

[14] BONEV, B., NENOV, V. (2006): Copper recovery from acidic wastewater by ED, “Waste - Secondary Raw Materials III” – Kosice, Slovakia; Acte Metallurgica Slovaca – Special Issue, pp.39-44.