University of Belgrade
Technical Faculty in Bor

Ecological Truth and Environmental Research

EDITOR
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University of Belgrade EcoTER Technical Faculty in Bor
Ecological Truth & Environmental Research

MONOGRAPH

ECOLOGICAL TRUTH AND ENVIRONMENTAL RESEARCH

Dedicated to the memory of Professor Zoran S. Marković

Edited by:
Snežana M. Šerbula

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Dear Readers,

This monograph is dedicated to our late Professor Zoran S. Marković from the Technical faculty in Bor, who organized the Conference for many years. The conference was of a national character initially, until 2010, when the late Professor Markovic helped promote it into a conference of international scope. Since then it has become an multidisciplinary international conference, which has the official approval of the Ministry of Education, Science and Technological Development.

Since 2010, Professor Marković had organized the conferences with reputable professors, researchers and industrial engineers from around the world. As the longtime President of the Scientific and Organizing Committee, the late prof. Zoran S. Marković contributed immensely to the success of the Ecological Truth Conference. Therefore, this monograph is dedicated to the memory of him.

Professor Zoran S. Marković will always be remembered as an exceptional teacher, a scientist, a colleague and a dear friend. The authors of the current collection of six chapters are friends and colleagues who cooperated with Zoran.

We are grateful to all the authors, reviewers and readers for the time devoted to this special issue.

May 2018,

Editor: Snežana Šerbula, PhD, Full Professor

IN MEMORIAM
Prof. Dr Zoran S. Marković
(1949 - 2017)

Prof. dr Zoran S. Marković, a full professor at the Technical Faculty in Bor, the University of Belgrade, was born on 28th September 1949 in Mađere, Ražanj. He started working at the Technical Faculty in Bor in 1985, at the Department of Mineral Processing, where he worked until his sudden death on 9th July 2017. His scientific interest included various research areas, such as flotation, the physics and chemistry of mineral surfaces, raw materials testing and environmental protection.

Professor Marković was a member and the president of the scientific and organizing committees of several international conferences: International October Conference on Mining and Metallurgy, the Symposium on Mineral Processing and ECO-Truth. He was the president of the organizing committee of the first national Symposium on Recycling Technologies and Sustainable Development with international participation and the tenth international symposium. He was a tireless and committed teacher who had a remarkable relationship with his students. He was always there to help and give advice, and he was much appreciated and respected by his students and colleagues alike. Prof. dr Zoran S. Marković will always be remembered as an exceptional teacher, a scientist, a colleague and a dear friend.

Chapter 1

ECOLOGICAL STATUS OF THE TIMOK RIVER AND ITS MAIN TRIBUTARIES FLOWING THROUGH THE COPPER MINING AND SMELTING AREA

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ABSTRACT

Assessment of the Krivelj River and the Bor River quality, on their flow in the vicinity of the open pit mines, overburden dumps, flotation tailing ponds and industrial facilities in 2010 was presented. Special attention was focused on the Timok River after the inflow of the Bor River, and also on the Timok River mouth into the Danube River. Classification and ecological status of the analysed river water samples considering the measured parameters were defined according to the Serbian Regulations. Drainage waste waters from the overburden dumps of the Copper Mine Cerovo brought the highest Cu, Zn and Cd concentrations in the Krivelj River watercourse. Ecological status of the Krivelj River, especially after the inflow of all the waste waters in regard to the pH values, Cu, Zn and Fe contents was bad (Class V), and in the case of Ni and Cd contents the river water belonged to Class III/IV. The Krivelj River with such bad ecological status flows into the Bor River. Clear mining and metallurgical seal on the local water courses was reflected in bad ecological status (Class V) of the Bor River prior to the inflow into the Timok River, considering the pH values, as well as Cu, Fe, Mn and As concentrations, in almost all the sampling months. On the international level, relatively good ecological status of the river water at the Timok River mouth into the Danube River was most important, since the Timok River is a boundary river with Bulgaria and flows into the Danube River. The sampled water was of Class I, II or III considering the pH values, Class I or II according to Cu contents, Class I in regard to the As and Zn contents and Class II considering the Fe contents. The

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obtained results indicated that all the pollution loads predominantly stayed near the sources of pollution, so we could talk about local pollution character originating from the mining and metallurgical waste waters.

Keywords: The Timok River, Ecological Status, Mining, Metallurgy, Copper, Iron, Arsenic, Nickel, Cadmium

1. INTRODUCTION

Rivers and transitional waters were reported to have worse ecological status and more pressures and impacts than water bodies of lakes and coastal waters [1]. Hazardous substances are emitted to water bodies both directly and indirectly through a range of diffuse and point sources of pollution [2]. Surface water bodies in Europe are usually polluted by diffuse sources causing nutrient enrichment, and hydro–morphological pressures causing altered habitats [1]. More than 40% of the river and coastal water bodies are affected by diffuse sources, whilst 20–25% of them are also subject to 'point source' pollution (pollution from a large single source, generally related to human settlements). Notably, chemical status of 40% of Europe's surface waters have remained unknown, out of which one third includes lakes and more than a half comprises transitional waters [3].

Mining has a significant influence on the chemical and ecological quality of water resources in Europe, particularly in respect to the discharge of heavy metals. Abandoned mines represent a big threat since, in the absence of continued pumping, groundwater levels rise and, ultimately, discharge contaminants within the mine workings. Mining has affected the water quality in a number of locations across Europe [2,4–7]. It was reported that around 70% of industrial wastes in the developing nations were disposed untreated into surface waters, thereby contaminating the existing water supplies [8].

Heavy metals and metalloids are a significant contributor to poor status of rivers and lakes [3]. The concentration and distribution of heavy metals and metalloids in surface waters are a consequence of the geochemical situation and the pollution source, but seriously affected by mining leachate and chemical wastewater discharge [9,10]. Wastewaters from non-ferrous metal ore mining and smelting, electroplating and other industrial production processes, are an important pollution source of heavy metals [8,9,11–13]. Many researches indicated that mining and the smelting activities caused great destruction to the water environment [9,14,15]. After entering a water body, heavy metals are carried over the sea so that the river mouth and regions along the seashore become the ultimate point for these metals being transported into the environment [10].

Heavy metal pollution is characterised by high toxicity, abundance, and persistence, and its migration brings about a broader range of hazards [9,16]. The toxicity of trace metals has long been examined, considering that they cannot be removed from aquatic ecosystems by self–purification, thereby potentially threatening human health and ecosystems via the food chain. They can be transported downstream hundreds of kilometres along hydrologic gradients within a relatively short time. Moreover, metals and metalloids are released in both dissolved and particulate forms [12,17–21]. When released in particulate form or adsorbed onto particles, they settle and are deposited in the bottom river sediments under favourable hydraulic conditions. Therefore, sediments, which act as both carriers and sinks for contaminants, play a major role in determining the pollution pattern of aquatic systems, reflecting the history of pollution and providing a record of catchment inputs into aquatic ecosystems [12].

The Danube River Basin has been affected by anthropogenic activities as well. The Danube River Basin (Figure 1) is Europe's second largest river basin, with a total area of 801,463 km². More than 80 million people from 19 countries share the Danube catchment area, making it the world's most international river basin. The Danube connects with 27 large and over 300 small tributaries on its way from the Black Forest to the Black Sea. There are also a large number of lakes in the Danube Basin. Human activity has affected the Danube and its network of tributaries negatively in manifold ways. Industry, agriculture and tourism are all economically important and depend on the Danube as a resource, yet at the same time they also threaten the Danube as a biodiversity hotspot. The list of industrial pollutants generated by the countries through which the Danube flows south and east is long: fertilisers, farm pesticides and manure, as well as discharge from smelters, paper mills, chemical plants and tanneries [22]. Therefore, significant efforts were made in order to measure the level of pollution of the Danube River, as well as to find the most appropriate, optimal possibilities for the improvement of its actual state [23–30].

Figure 1 The Danube River basin [31]

The influence of the tributaries is very important for the Danube basin in general. In the lower part of the Danube basin, in Serbia, beyond the Iron Gates, the Lower Danube flows across a wide plain. Its main tributary in Eastern Serbia is the Timok River (Figure 2), which represents the biggest river in this part of the country, but also the boundary river, flowing the last 15 km along the Serbian and Bulgarian border. The Timok River is formed by conjunction of two rivers, having similar names–the Beli Timok River and the Crni Timok River, near the city of Zaječar. Its length from the conjunction point to the Danube River is approximately 88 km [32]. Mainly flowing through the plain landscape, it belongs to slow flowing rivers. The river mouth is only 28 m above the sea level, making it the lowest altitude in Serbia.

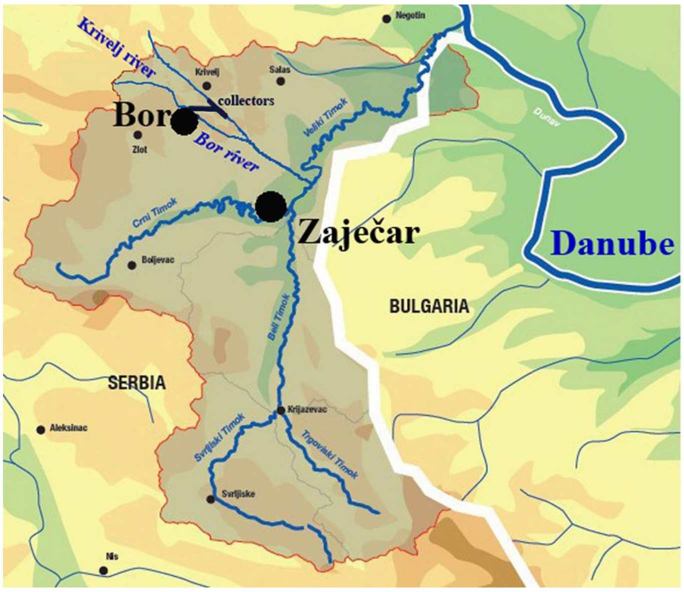


Figure 2 The Timok River, position and basin [7]

The Timok River has a very branchy system consisting of many short rivers and creeks which flow through or by villages, and also through an industrial area with numerous coal or metal mines, still active or abandoned, greatly affecting the water quality [33]. Especially strongly polluting influence was related to the waste waters which were generated by the Mining and Smelting Combine Bor due to the century-long mining and metallurgical activities. Waste waters were released either directly from the facilities, or indirectly in the form of the mining waters and acid drainage waters from the overburden dumps and flotation tailing ponds [11,13,34,35]. Directly, the most endangered were the Krivelj River and the Bor River, which belong to the Timok River Basin.

Historical copper mining and smelting in this area leave the permanent mark on the air, soil, water and biota environment [36–42]. Knowing that, the aim of this case study was assessment of the quality of the Krivelj River and the Bor River as the main tributaries of the Timok River, in the year 2010. It was also, analysed how these watercourses influenced the Timok River water quality, downstream of their inflow.

2. CLASSIFICATION OF THE SURFACE WATER QUALITY ON THE NATIONAL LEVEL

The Timok River quality was often examined in order to determine its polluting effect on the Danube River, especially considering pollution by metals and metalloids [32,33,43–45]. On the national level, the quality of surface waters on the territory of the city of Zaječar and the town of Bor and the surroundings is tested by accredited laboratories (such as the Office for Public Health "Timok" – Zaječar). The regulations of the Republic of Serbia set out the legal framework for the protection of surface waters using Classifications according to the level of contamination and use. The Limit values (LV) of several parameters of water according to the Regulations given in the "Official Gazette of the Republic of Serbia", No. 50/2012 [46] and 5/68 [47] are given in Table 1.

The Limit value is a standard of the environmental quality expressed as a concentration of a polluting substance or groups of polluting substances or indicators of pollution in surface and groundwater as well as sediment, which must not be exceeded in order for the environment and human health to be protected [46]

Table 1 The Limit values of polluting substances in the surface waters

Parameter/Class	**Class I**	**Class II**	**Class III**	**Class IV**	**Class V**
***pH**	6.8–8.5	6.8–8.5	6.8–8.5	6.8–8.5	<6.5 or >8.5
***Arsenic (µg/L)**	<5 (or ^{a}nl)	10	50	100	>100
***Copper (µg/L)**	5 (^{b}T=10) 22 (^{b}T=50) 40 (^{b}T=100) 112 (^{b}T=300)	5 (^{b}T=10) 22 (^{b}T=50) 40 (^{b}T=100) 112 (^{b}T=300)	500	1000	>1000
***Zinc (µg/L)**	30 (^{b}T=50) 200 (^{b}T=50) 300 (^{b}T=100) 500 (^{b}T=500)	300 (^{b}T=10) 700 (^{b}T=50) 1000 (^{b}T=100) 2000 (^{b}T=500)	2000	5000	>5000
***Iron (µg/L)**	200	500	1000	2000	>2000
***Manganese (µg/L)**	50	100	300	1000	>1000
****Nickel (mg/L)**	0.05	0.05	0.1	0.1	^{c}/
****Cadmium (mg/L)**	0.005	0.005	0.01	0.01	^{c}/

*[46]; **[47]; ^{a}natural level; ^{b}water hardness (mg/L $CaCO_3$); ^{c}not defined

Surface waters which belong to the Class I are of excellent ecological status, and can be used for the following purposes: as drinking water with prior treatment by filtration and disinfection, bathing and recreation, irrigation, industrial use (process and cooling water). Surface waters which belong to the Class II correspond to a good ecological status, and can be used for the same purposes and under the same conditions as the surface waters belonging to Class I. Surface waters of Class III are of moderate ecological status, and can be used for the following purposes: as drinking water with prior treatment by coagulation, flocculation, filtration and disinfection, bathing and recreation, irrigation, industrial use (process and cooling waters). Surface waters of Class IV correspond to the poor ecological status, and can be used for the following purposes: as drinking water but after using a combination of previously mentioned treatments and advanced methods of treatment, irrigation, industrial use (process and cooling water). Surface waters of Class V are of bad ecological status, and can not be used for any purpose [46].

3. ECOLOGICAL STATUS OF THE KRIVELJ RIVER, THE BOR RIVER AND THE TIMOK RIVER IN THE VICINITY OF THE CEROVO, VELIKI KRIVELJ AND BOR COPPER MINE

Bor and the surroundings are well-known for copper deposits, which are among the largest in Europe. Mining production in Bor has existed for over 100 years. Within the Bor Copper Mines, two open pit mines operate (Cerovo and Veliki Krivelj), one for underground mining (the mine “Jama” in the town of Bor) (Figure 3) and two mineral processing plants (flotations in Veliki Krivelj and Bor). The Copper Smelter is located on the north eastern border of the town and processes sulphide copper concentrate with the accompanying elements Fe, Pb, As, Cd, Ni, Zn, Mn and precious metals. There are also Electrolytic Refinery, Copper Sulphate Plant and Sulphuric acid plant. In the vicinity of the open pit mines Cerovo and Veliki Krivelj as well as in the vicinity of the former open pit of the Copper Mine Bor, overburden dumps are located. There are four major flotation tailings which are loaded with the tailings from the two flotation facilities. One of them is in Krivelj, and the other one is situated in the town of Bor [38,40,48].

The Krivelj River flows through the Veliki Krivelj village, passes by the Copper Mine Veliki Krivelj and from the northeast side by the town of Bor. This river was formed by merging the Cerovo River and the Valja Mare River (Figure 3). The flotation tailing pond of the Copper Mine Veliki Krivelj is located in the part of the Krivelj River valley. The river is directed through a tunnel and the collector beneath the tailing pond [11].

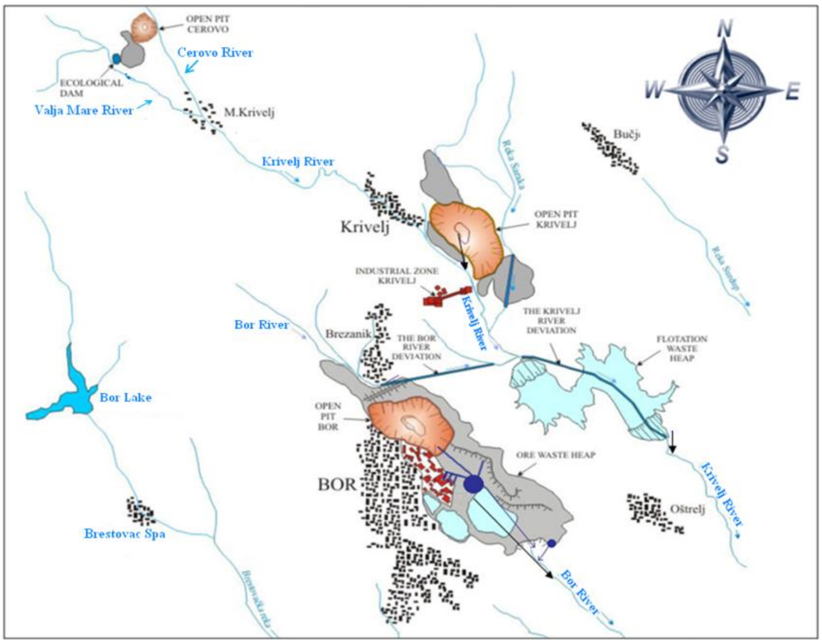


Figure 3 The flow of the Krivelj River and the Bor River relative to the position of the Cerovo, Veliki Krivelj and Bor Copper Mine [11]

The Bor River flowes almost parallel to the flow of the Krivelj River, in the same direction. As a result of the development of the Bor surface mine open pit, the Bor River has been interrupted, so it has two separate flows (Figure 3). Until it reaches the town of Bor, it flows through its natural riverbed, and then the Bor River deviates and flows into the Krivelj River. A part of the Bor River natural riverbed, in the length of several kilometres, does not exist, as open pit of the Bor Copper Mine and flotation tailing pond are located at that site. Downstream of the town of Bor, the Bor River again reappears, but this time containing the wastewaters from the metallurgical facilities, communal waste waters and waters of two streams, the Borski and the Savić streams. These streams are also conducted by collectors, underneath the town of Bor [11].

3.1. The Krivelj River quality

The water of the Krivelj River was sampled during 2010, at the end of March, June, September and December. The analyses of the samples were done by the Office of Public Health "Timok" Zaječar [49] and optionally by the Institute for Quality of Working and Living Environment "1. May" Niš [50].

The sampling points of the water samples from the Cerovo River, Valja Mare River and the Krivelj River are presented in Figure 4. The sampling was conducted at the following locations:

- The Cerovo River before it reaches the open pit of the Cerovo Copper Mine (sampling point 1),
- The water catchment of the overburden dumps of the Cerovo Copper Mine (sampling point 2) and a sampling point 2A,
- The Cerovo River after the open pit of the Cerovo Copper Mine (sampling point 3),
- The Valja Mare River before (sampling point 4) and after (sampling point 6) the ecological dam,
- The Krivelj River after merging of the Valja Mare River and the Cerovo River (sampling point 7),
- Waste waters from the open pit of the Copper Mine Veliki Krivelj (sampling point 8),
- The Krivelj River after the inflow of waste waters from the open pit of the Copper Mine Veliki Krivelj (sampling point 9),
- Waste waters from the flotation facilities of the Copper Mine Veliki Krivelj (sampling point 10),
- The Saraka stream (sampling point 12),
- The Krivelj River after the inflow of the Saraka stream and prior to the inflow of the Bor River deviation (sampling point 13),
- The Krivelj River before entering the collector (sampling point 15),
- Dam 1A (sampling point 16),
- Dam 3A (sampling point 18),
- The Krivelj River after the inflow of all the waste waters (sampling point 19).

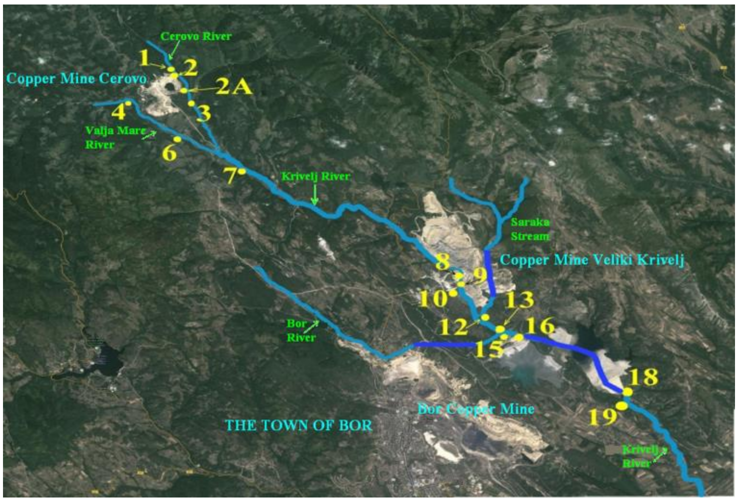


Figure 4 Map of the sampling points

The values of pH as well as concentrations of Cu, Zn, Fe, Ni and Cd of the sampled water from the study area are given in Figures from 5 to 10. Bars are missing in the cases when concentrations of the measured parameters were below the limit of determination, or the measurements were not conducted. Classification of the sampled water from the analysed watercourses considering values of pH, as well as the Cu, Zn and Fe concentrations were done according to the „Off. Gazette of the RS", No. 50/2012 [46], and considering Ni and Cd concentrations according to the „Off. Gazette of the RS", No. 5/68 [47].

The values of pH in Figure 5 indicate that none of the samples of water falls in Class V compared to the LV >8.5.

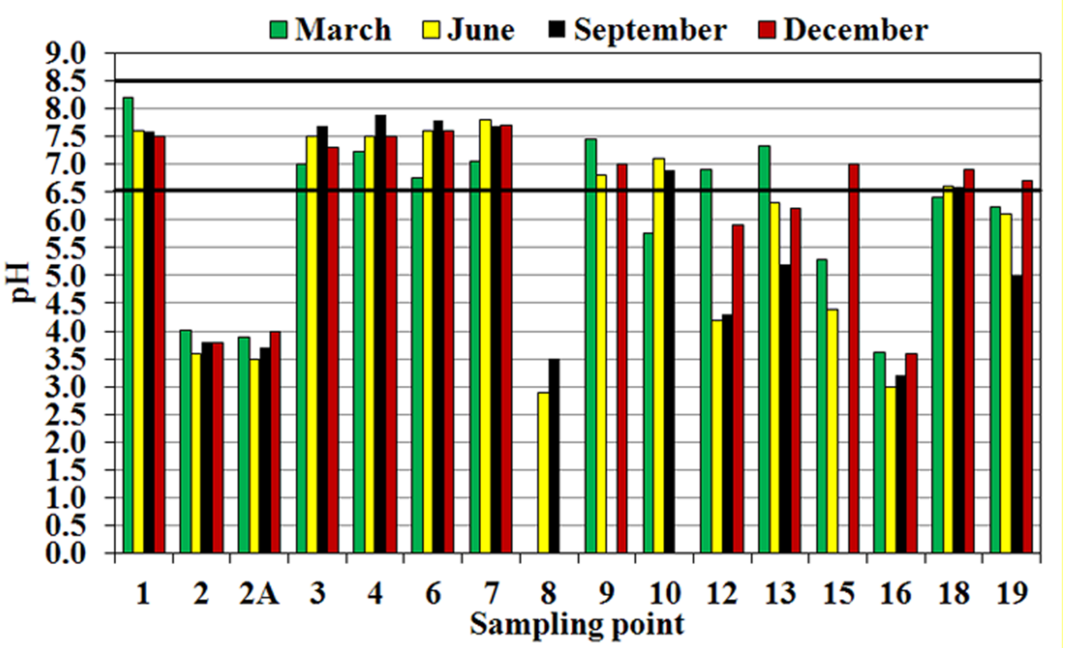


Figure 5 The pH values of the samples of the examined watercourses depending on the sampling points during the year of 2010. Black horizontal lines represent the LV for Class V

However, water samples from the sampling points 2, 2A, 8, 12, 13, 15, 16 and 19 had pH values <6.5 for at least two or three months of sampling, categorising these watercourses as Class V, which is of poor ecological status. Such condition of the Krivelj River, especially after the inflow of all the waste waters at the sampling point 19, represent a great danger to the environment downstream of the river flow, and also to the other tributaries. The lowest pH values were obtained for the samples from the sampling points 2, 2A, 8 and 16. Such results indicated that drainage waste waters generated from the overburden dumps of the Copper Mine Cerovo, the open pit of the Copper Mine Veliki Krivelj, and from dam 1A, were the most acidic. It could be said that waters from the sampling points 1, 3, 4, 6 and 7 were between Class I and III, which corresponded to ecological status from excellent to moderate, depending on the other water parameters which influenced the water quality.

From Figure 6a) it can be seen that the highest Cu concentrations were in the samples from the sampling points 2 and 2A, which represents water catchment of the overburden dumps of the Copper Mine Cerovo.

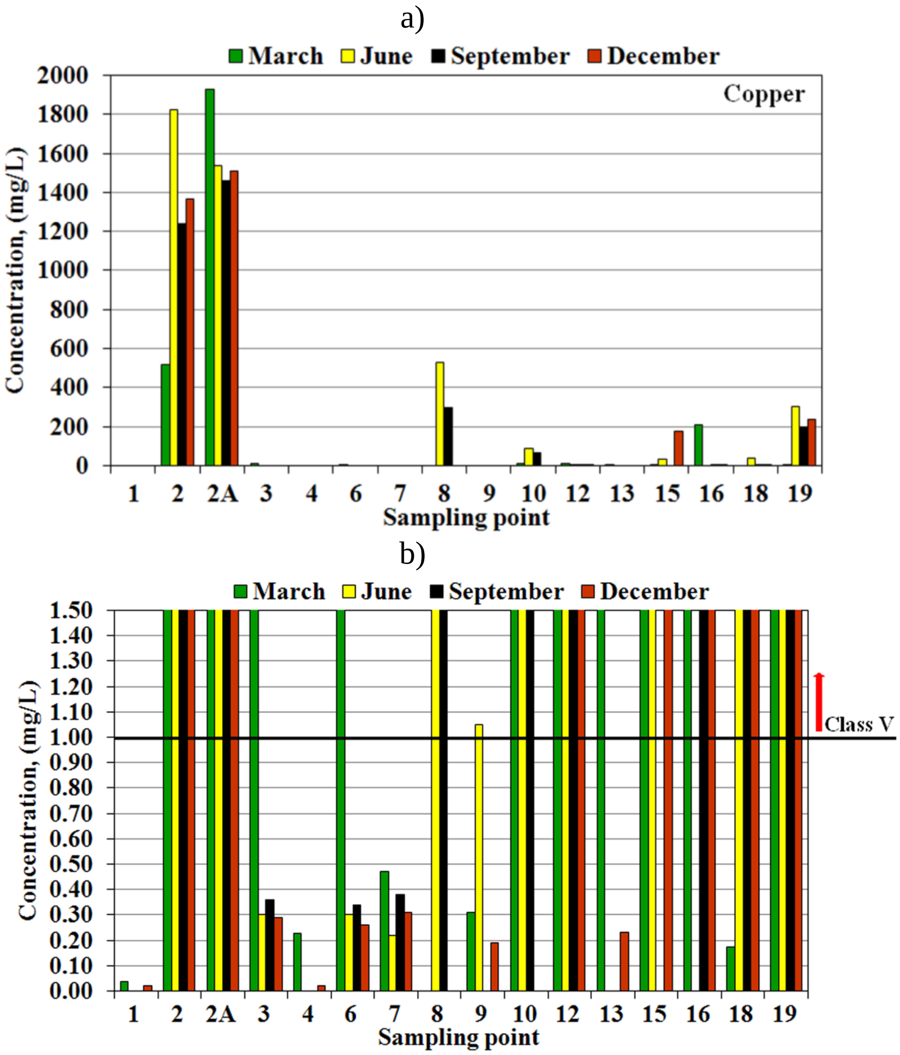
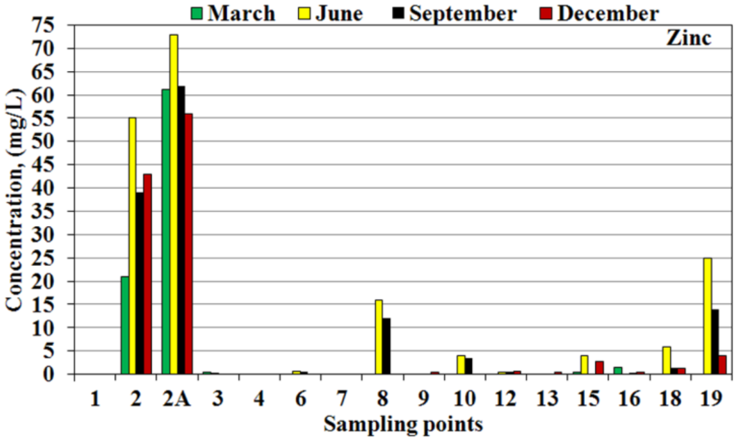


Figure 6 Copper concentrations in the samples of the examined watercourses depending on the sampling points during the year 2010: a) distribution; b) concentrations relative to the LV for Class V (black horizontal line)

There was no regularity in the ratio of concentrations considering the month of sampling. According to the results presented in Figure 6b), water from the sampling points 2, 2A, 8, 10, 12, 15, 16 and 19 could be classified in Class V, in all the months of examination. Class V of the Krivelj River water after the inflow of all the waste waters (sampling point 19) according to the Cu concentrations corresponded to poor ecological status, and could not be used for any purpose. The obtained high Cu concentrations were of great importance because of further flow of this river, which means merging with the Bor River and the inflow in the Timok River. It should be noted that samples of water from the sampling points 1, 4 and 7 could be classified in Class I and/or Class II which corresponds to excellent and/or good ecological status. Sampling points 1 and 4 belong to watercourses of the Cerovo River and the Valja Mare River, respectively, prior to the inflow of waste waters from the opet pit of the Cerovo Copper Mine and ecological dam. According to the obtained Cu concentrations, obvious influence of the waste waters generated from the copper mining operations, and disposal of gangue and flotation tailings, it could be seen.

As in the case of Cu, the highest Zn concentrations in the analysed samples during all four months were in the water from the sampling points 2 and 2A (Class V), which were under the influence of the waste waters from the overburden dumps of the Copper Mine Cerovo (Figure 7a,b).

a)



b)

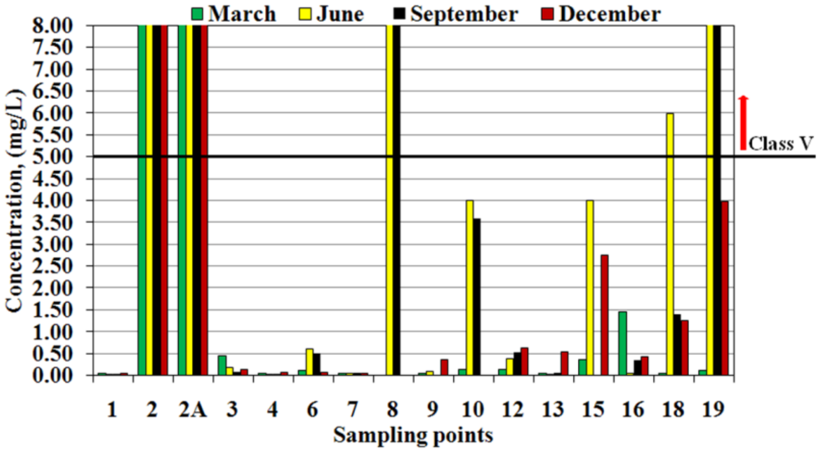


Figure 7 Zinc concentrations in the samples of the examined watercourses depending on the sampling points during the year 2010: a) distribution; b) concentrations relative to the LV for Class V (black horizontal line)

Water from the sampling points 18 and 19 also belongs to Class V, but not during all the months of sampling. This condition could be the result of the increased atmospheric precipitation and the effect of dilution during spring (March) and winter (December) months. Water from the other sampling points could be Classified in Class I and II, because their Zn concentrations were below the LV of 2000 μg/L. According to the obtained results, it could be said that the highest Zn contents were generated from the Copper Mine Cerovo.

Extremely high and the highest Fe concentrations were measured in the samples of water from the sampling point 19 at the end of June, September and December (Figure 8a). The Krivelj River with such a poor ecological status (Class V) merges with the Bor River, and that watercourse flows further into the Timok River. From Figure 8b) it can be seen that water from the sampling points 2, 2A, 16, 18 could also be classified as Class V, during three or four months of sampling.

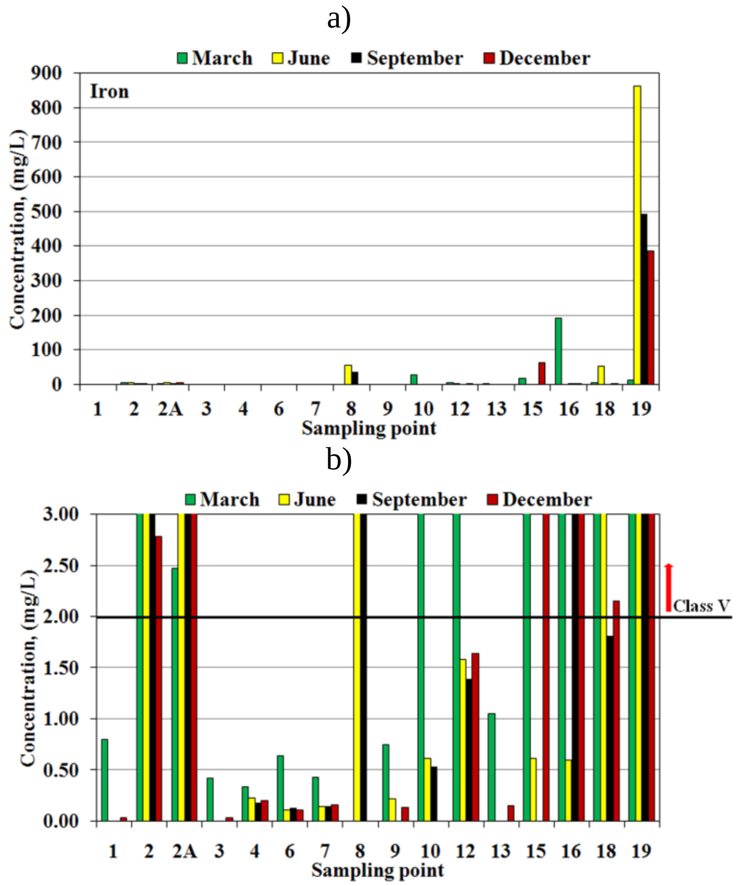


Figure 8 Iron concentrations in the samples of the examined watercourses depending on the sampling points during the year 2010: a) distribution; b) concentrations relative to the LV for Class V (black horizontal line)

The results obtained from the sampling points 1, 4 and 6 (Class I for three months), give the obvious indication of the quality of river water without the industrial influence. The Fe concentrations in the samples from the sampling points 3 and 7 also belonged to Class I for three months of sampling. The sampling point 7 represented the watercourse after merging of the Valja Mare River (Class I) and the Cerovo River whose one part of the watercourse was classified in Class V. Water from the sampling point 7 might have excellent water quality because of the effect of dilution of the polluted with the less polluted water, or because of the possible precipitation of the iron ions on the riverbed, under the actual conditions.

The most endangered watercourses in regard to the pollution with Ni were at the sampling points 2, 2A, 8, 10 and 19 (Figure 9). According to that, the highest Ni concentrations were emitted with the drainage waste waters from the overburden dumps of the Copper Mine Cerovo and waste waters of the flotation facilities of the Copper Mine Veliki Krivelj. The watercourse of the Krivelj River after the inflow of all the waste waters, was not most polluted with Ni, but still belonged to Class III/IV, which was not good for the environment, downstream.

The biggest emitter of waste waters rich in Cd was the Copper Mine Cerovo, according to the results in Figure 10a). Water from these sampling points (2, 2A) belonged to Classes III or IV during all of the four months of sampling. Water from almost all the rest of the sampling poins belonged to that Class but mostly during one month of sampling (Figure 10b).

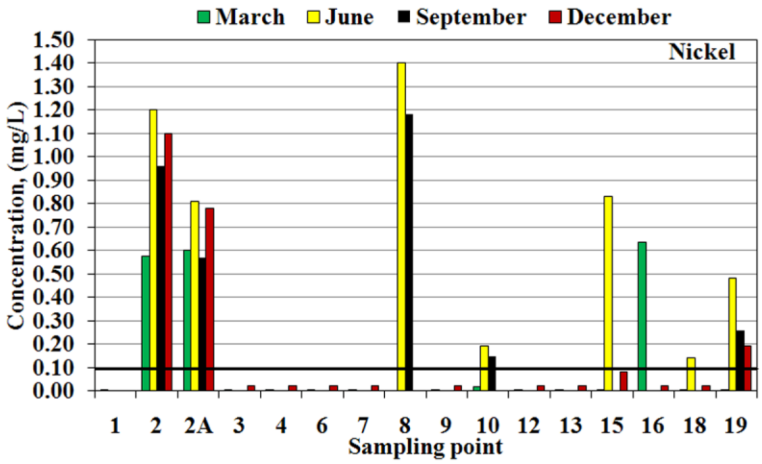


Figure 9 Nickel concentrations in the samples of the examined watercourses depending on the sampling points during the year 2010. Black horizontal line represents the LV for Class III/IV.

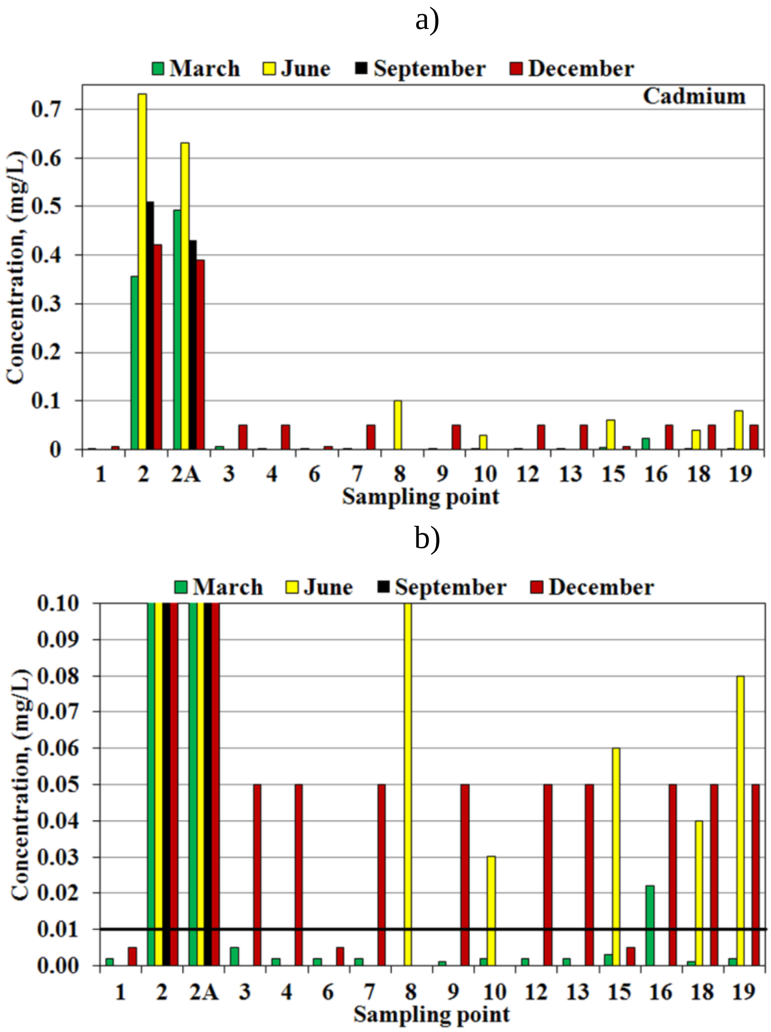


Figure 10 Cadmium concentrations in the samples of the examined watercourses depending on the sampling points during the year 2010: a) distribution; b) concentrations relative to the LV for the Class III or IV (black horizontal line)

3.2. The Bor River and the Timok River quality

In order to provide an insight in the water quality of the Timok River, a study supported by the Ministry of Agriculture, Forestry and Water Management, of the Republic of Serbia, was conducted during 2010 by the following institutions: University of Belgrade, Technical Faculty in Bor (University of Belgrade), Institute for Chemistry, Technology and Metallurgy, Belgrade, and the Office of Public Health, Zaječar [32]. A part of these investigations, concerning the contents of heavy metals and metalloids along the Bor River and the Timok River flow, from its formation near the city of Zaječar to the inflow into the Danube River, are given in the following results. Special attention was paid to determination of the magnitude of water pollution with metals and metalloids brought in by the Bor River, and their further distribution along the Timok River length.

The samples of watercourses were analysed by the Office of Public Health "Timok", Zaječar on different physical, chemical and biological parameters, according to the standard operating procedures for sampling of surface waters and sludge [49,51]. However, only the data on pH values, and several metals and metalloid~~s~~ contents will be considered in this study. Complete additional results of the analysis can be found in Nikolić *et al.* [32].

All samplings, measurements and tests were carried out three times in autumn 2010, i.e. once in September, once in October and again in November. The samples of water were taken from nine sampling points (Figure 11):

- The Crni Timok River before merging with the Beli Timok River, the city of Zaječar (sampling point 1);
- The Beli Timok River before merging with the Crni Timok River, the city of Zaječar (sampling point 2);
- The location after merging of the Crni and Beli Timok Rivers, the city of Zaječar (sampling point 3);
- The location at the Bor River before inflow in the Timok River, the village Vražogrnac (sampling point 4);
- The Timok River before the inflow of the Bor River, the village Vražogrnac (sampling point 5);
- The Timok River, the village Halovo (sampling point 6);
- The Timok River, the village Tamnič (sampling point 7),
- The Timok River, the village Mokranje (sampling point 8)
- The Timok River mouth into the Danube River, the village Srbovo (sampling point 9).

Illustrations of the locations of some of the sampling points are given in Figures from 12 to 14.

The pH values and the contents of metals and metalloids in the water samples from all the sampling points are presented in Table 2, for the investigated period from September to November of 2010.

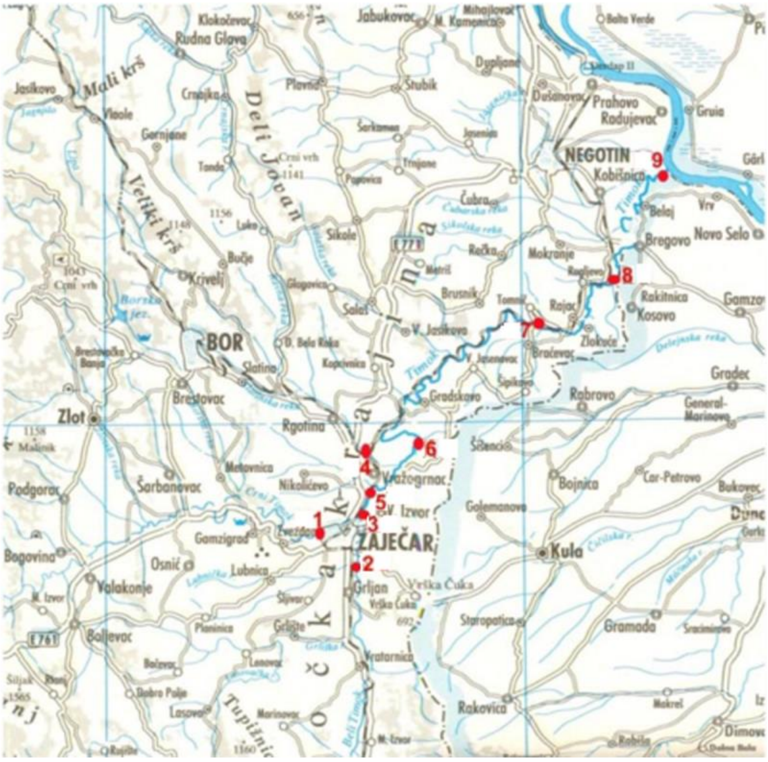


Figure 11 Sampling points along the Timok River

Figure 12 Illustration of the location of the sampling point 1

Figure 13 Illustration of the location of the sampling point 4

Figure 14 Illustration of the location of the sampling point 9

The samples of water from the sampling point 4 had the lowest pH value in September and October, which corresponded to the location of the Bor River prior to the inflow in the Timok River (Table 2). These pH values <6.5 indicated Class V of the sampled water at the sampling point 4. Water from the rest of the sampling points, including the sampling point 9 (the Timok River mouth into the Danube River) could be Classified into one of Classes from I to III, depending on the other measured parameters.

According to Cu concentrations at the sampling point 4, water of the Bor River prior to inflow in the Timok River during September, October and November could be classified in Class V. Water at the sampling point 6 also belonged to Class V, during September and October, although the Cu concentration was about nine time lower than at the sampling point 4 in September, and about 6 time lower than in October. This location sampling point 6 represented the first sampling point after the inflow of the Bor River into the Timok River. Downstream of the inflow of the Bor River into the Timok River (sampling points 7, 8 and 9), Cu concentrations decreased, thus improving the river water quality (Classes I, II), which probably was the influence of dilution and/or precipitation of Cu ions. The Cu contents obtained for the samples from the sampling points 1, 2, 3 and 5 were quite low and without high variations, within one month, probably because watercourses at these locations were without the impact of industrial activities.

Although the highest, Zn contents in the Bor River (sampling point 4) were not the indication for Class V of surface water. Water sampled from the sampling point 4 in all three months belonged to Classes II or III depending on the water hardness. In September and November, water from the sampling point 6 could be classified in Class I or II. Water from all the other sampling points except the sampling point 4 (all months) and 6 (in November), could be classified in Class I, according to the Zn contents. It is noticeable that there was no such extreme pollution of the Timok River considering the Zn contents in the water samples.

Table 2 The pH values and concentrations (mg/L) of metals and metalloids in the water samples from the nine sampling points during the year 2010

Parameter	pH	Cu	Zn	Fe	Mn	As
Sampling point/Month	**September**					
1	7.38	0.004	0.005	0.052	0.012	0.002
2	7.68	0.004	0.050	0.110	0.016	0.003
3	7.55	0.004	0.050	0.042	0.038	0.003
4	5.65	12.270	1.786	53.800	4.930	0.101
5	7.60	0.005	0.050	0.095	0.052	0.004
6	7.28	1.351	0.223	3.585	1.030	0.110
7	7.80	0.135	0.059	0.289	0.388	0.002
8	7.80	0.070	0.049	0.224	0.175	0.002
9	7.61	0.047	0.049	0.239	0.086	0.003
Sampling point/Month	**October**					
1	7.80	0.006	0.049	0.121	0.013	0.003
2	8.11	0.004	0.049	0.209	0.020	0.002
3	8.03	0.004	0.049	0.068	0.025	0.002
4	6.16	8.640	1.561	46.040	4.652	0.168
5	8.01	0.008	0.049	0.135	0.037	0.003
6	7.83	1.324	0.230	6.996	0.846	0.029
7	7.81	0.094	0.049	0.200	0.402	0.001
8	7.84	0.074	0.049	0.243	0.316	0.001
9	7.72	0.053	0.049	0.202	0.150	0.001
Sampling point/Month	**November**					
1	7.73	0.004	0.049	0.050	0.012	0.001
2	7.91	0.012	0.049	0.102	0.013	0.001
3	7.88	0.004	0.049	0.098	0.020	0.001
4	7.57	6.536	1.015	30.24	4.064	0.040
5	7.88	0.004	0.049	0.114	0.230	0.001
6	7.93	0.457	0.049	1.817	0.276	0.006
7	7.90	0.136	0.049	0.624	0.416	0.003
8	7.96	0.004	0.049	0.051	0.018	0.002
9	7.92	0.141	0.049	0.596	0.402	0.002

Red cells indicated the pH values or the concentrations of the analyzed elements in the Class V of water.

Similar as in the case of Cu, water sampled from the sampling points 4 and 6 during September, October and November, except the sampling point 6 in November, belonged to Class V according to Fe concentrations. Downstream, at the sampling points 7, 8, and 9 the ecological status of the Timok River has improved to Class II during September and October, because Fe contents decreased. The most of the water samples from the rest of the sampling points belonged to Class I, which was the indication of the absence of the industrial influence on the analysed watercourses.

The Mn concentrations in the samples of the analysed watercourses indicated Class V of water sampled from the sampling point 4 during three months of sampling, and from the sampling point 6, only in September. The river water prior to the inflow of the Bor River (sampling points 1, 2 and 3) belonged to Class I. Downstream of the sampling point 6, the water quality varied, with no obvious regularity in regard to Class of the surface water.

According to As water contents, the samples from the sampling points 4 and 6 had the bad ecological status (Class V) during September, as well as from the sampling point 4 during October. The water samples from the rest of the sampling points belonged to Class I, except of sampling points 6 (during October) and 4 (during November). After the inflow of the Bor River into the Timok River, the quality of the sampled water was improved from Class V (sampling points 4 and 6) to Class I (sampling points 7, 8, and 9), which probably was the effect of the dilution or the precipitation of As ions along the riverbed.

4. CONCLUDING REMARKS

Presented assessment of the Krivelj River, the Bor River and the Timok River quality considering the pH values, and contents of several metals and metalloids, gave some important insights into the influence of anthropogenic activities on the local and the international scale of river water pollution. International scale of surface water pollution considered the pollution load which the Timok River brought by the inflow into the Danube River.

The potential pollution of the Bor River and the Krivelj River was expected from the acid mine drainage waters, leaching waters from the overburden dumps and flotation tailing ponds, as well as industrial waste waters generated from the Copper Mine Cerovo, Coper Mine Veliki Krivelj and Bor Copper Mine.

Water quality of the Krivelj River, especially after the inflow of all the waste waters considering the pH value, Cu, Zn and Fe contents belonged to Class V, which corresponded to bad ecological status. Water sampled at that location was classified in Class III/IV according to Ni and Cd contents. Such bad ecological status of the examined river water represented a great danger to the environment downstream of the river flow. Drainage waste waters generated from the overburden dumps of the Copper Mine Cerovo, the open pit of the Copper Mine Veliki Krivelj, and from dam 1A, were most acid. Drainage waters of the overburden dumps of the Copper Mine Cerovo were most polluted with Cu, Zn and Cd compared to the other examin~~at~~ed samples of river water. Unlike that, the highest Fe concentrations were measured in the water from the sampling point on the Krivelj River after inflow of all waste waters, probably because of the influence of the nearby flotation pond and the overburden dump. Watercourses of the Cerovo River and Valja Mare River, prior to the inflow of the waste waters from the open pit of the Copper Mine Cerovo and ecological dump usually were of good ecological status and the good example of unpolluted watercourses.

In the case of the Bor River and the Timok River, special attention was focused on the sampling points at the locations of the Bor River prior inflow in the Timok River, the Timok River after the inflow of the Bor River and the Timok River mouth into the Danube River.

Bad ecological status (Class V) of the Bor River prior to the inflow into the Timok River was indicated according to pH values, as well as Cu, Fe, Mn and As concentrations, in almost all sampling months. This situation was clear anthropogenic seal on the local water courses. There was no such extreme pollution of the Bor River according to Zn contents in the water samples. Quality of river water from the first sampling point after the inflow of the Bor River into the Timok River still stayed in Class V, but not in all sampling months.

The quality of the water at the Timok River mouth into the Danube river was the most important. The measured parameters in water samples from this sampling point indicated that ecological status was improved from Class V, to Class I, II or III considering the pH values, Classes I or II in regard to the Cu contents, Class I according to the As and Zn contents and Class II according to the Fe contents. No regularity was observed considering Mn concentrations in the river water. Ecological status of the Timok River mouth into the Danube River considering the examined parameters was good. Such improvement of the water course quality might be connected to the precipitation of the analysed metals and metalloids ions on the river bed bottom. This would mean that all pollution loads stayed near the sources of pollution, in which case we could talk about local pollution character of the waste waters.

These results from the year of 2010 were only a case study of the pollution of the rivers in the vicinity of the Mining and Smelting Combine Bor. It is possible that the quality of the Krivelj River and the Bor River was improved after the year 2015, due to newly reconstructed sulphuric acid plant, introduction of new smelting technology and reconstruction of an old existing wastewater treatment plant.

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Prof. dr Dragana Živković (1965-2016)

Professor Dr Dragana Živković, a prominent scientist, a distinguished professor, a dear colleague and above all a great person, passed away on 26th November 2016. She was a full professor, the Head of the Department for Metallurgical Engineering, the chairperson for Extractive Metallurgy, the vice dean of Scientific Research and the Dean of the Technical Faculty in Bor, University of Belgrade. She was also a full member of the Academy of Engineering Sciences of Serbia, Editor-in-Chief of Journal of Mining and Metallurgy, Section B: Metallurgy, the founder and the president of the Committee for Thermodynamics and Phase Diagrams of Serbia.

Prof. Dr Dragana Živković was born on 13 September 1965 in a respectable family from Zaječar, to Todor and Gordana Živković. She completed her elementary and secondary education in her hometown Zaječar. She graduated in 1989, finished her MA in 1993 and PhD studies in 1995 at the Technical Faculty in Bor, University of Belgrade, at the Department for Extractive Metallurgy. In the course of her studies she was recognized as a great potential which, after her graduation, enabled her to get a job at the same university. For the twenty-seven years she worked at the Technical Faculty in Bor, she was elected to the position of the teaching assistant (1989), the assistant (1993), the assistant professor (1996), the associate professor (2000) and the full professor in the field of extractive metallurgy and metallurgical engineering in 2005 and the full professor in the field of industrial management in 2006.

She gave an immeasurable contribution to the development of science and education in the fields of thermodynamics, metallurgical engineering and materials science. Dragana was so exceptional a person who left a deep trace, unique in its nature, not only in Serbia and the Balkans, but also in the world.

She was a visiting professor at the Central South University, Changsha (China), as well as a guest lecturer at doctoral studies at the Naravoslovno-tehniškoj fakulteti Univerze, Ljubljana (Slovenia).She was elected as the Deputy Director of Research Centre for Innovative Materials Design and Application, as well as the permanent partner of the Science Centre for Materials Design and Preparation, Central South University, Changsha (China). As a world renowned scientist she presented the results of her numerous studies at lectures at several foreign universities (Osaka, Genoa, Miskolc, Changsha, London, Krakow, Brno, Aachen, Porto, Ljubljana, Zenica, etc.), along with the continuous professional development through short study stays at universities in Japan, Italy, Hungary, China, Sweden, Germany, Slovenia, and others.

The biggest part of her life was dedicated to scientific research. Her extensive scientific opus included various research areas: thermodynamics of multicomponent metal systems, advanced metallic materials, kinetics of metallurgical processes, environmental protection, archaeometallurgy, as well as innovation management and knowledge. She published more than 350 papers, of which more than 180 papers in international journals with more than 400 citations and 500 presentations at international and national conferences. She wrote 3 university textbooks, 2 exercise books and 3 monographs with co-authors, edited a great number of proceedings of national and international conferences and realized 5 technical development solutions. She participated in more than 20 national research projects and projects for the economy.,She also participated in 15 international projects: COST535 - THALLU (2002-2006).; COST531– LFS (2002-2006); COST MP0602 -HISOLD (2007-2011).; COST MP0903 (2011-2014); PHARE CBC RO (2008- 2009); PHARE CBC RO (2008-2009); DAAD Project (2009-2014); TEMPUS-MCHEM: (2010-2013); TEMPUS-DEREL: (2010-2013); Erasmus mundus - Basileus (2010).; EU HETIP (2010-2014).; IISP (2012-2013); WORLD Development programme, University of Zagreb (2011-2015); Erasmus+, (2014.); and JST SATREPS (2014-2019) and she realised significant international cooperation with many research centers in the world and the region. She was also the head of 4 bilateral projects. She was the head of the three projects in MoESTD as well as the person in charge of the "Caravan of science Timočki Scientific Tornado - TNT13".

She was also active in the cultural life of Zaječar and Bor as a member of the chamber choir "Labyrinth" which was a winner of a significant number of prizes and awards at national and international choir competitions, as well as a member of a music ensemble "VIS doctors", the Slovensko pevsko društvo "Josip Vošnjak", the artistic weaving workshop „Snovatica" in Zaječar, and of the Academic cultural club of the Technical Faculty in Bor.

As a colleague and associate, prof. Dr Dragana Živković, with her inexhaustible energy, cheerful spirit and enthusiasm, was the driving force and the main motivator not only for the Department of Metallurgy but for the whole Technical Faculty as well. An erudite, an altruist and a philanthropist, she was a professor, a scientist and above all a good person. For anyone who had been stumbling on the thorny road to science, she always had a word of encouragement and a word of wisdom.

Technical Faculty in Bor is proud of and grateful to prof. Dr Dragana Živković who by her work of many years contributed to its development and reputation. And for us, her colleagues, associates and students who had the honour and the privilege to know and to work with her, she will always remain a part of indelible memories.

Biography was taken from J. Min. Metall. Sect. B-Metall. 53 (2) B (2017) 83 – 84, with permission of Editor-In-Chief of this Journal.

Chapter 2

MANAGEMENT AND BENEFICIATION OF RESIDUAL MATERIALS: AN OVERVIEW

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ABSTRACT

This paper proposes a general reflection on the management of human activities solid and liquid residues, including their beneficiation and elimination. A special emphasize is given to toxicity considerations. Although it concerns also non-mineral materials (organic polymers, papers, glasses, wood compounds), the management of residual materials often involves separation and extraction techniques and treatments derived from mineral processing or extractive metallurgy. In fact, the management of residual materials is also strongly impacted by cultural aspects, thus depending on communities and local conditions. Many residual materials can be reused or recycled in diverse applications with economic realism, which not only utilizes their intrinsic value but also saves the cost of their management. Some applications are related to industrial materials, energy saving, secondary metallurgies; others are unexpected and constitute innovative industrial routes. Thanks to the academic knowledge, in a near future, some progresses can be expected concerning the new design of reversible confinement matrix involving nano-composite additives and specific formulae that could insure the long-term stability of deposits for hazardous substances that cannot be beneficiated at present time.

Keywords: Residual materials, Wastes, Beneficiation, Toxicity

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1. INTRODUCTION

Any transformation of matter, chemical, biological or physical substance generates co-products with properties that are very far from those targeted by the transformation process. For example, the production of electric power through coal combustion produces fumes and bottom ashes, the electrolytic refinement of cooper produces anodic mud; machining metal parts produces scraps and whatever the material, produces off cuts and used media, for example contaminated cutting lubricants or solids originating from the non-recycled fraction of casting moulds. Mine cavities, non-converted heat, noise and radiations are also co-products. Material co-products are named “effluents”.

Under given conditions some co-products can immediately be beneficiated in diverse uses, they are then evacuated toward the corresponding utilizations and do not accumulate; others have no immediate use and must be eliminated or stocked at least temporarily, though they can contain some valuable matters, other are pure nuisances, they are named residual co-products. It must be noticed that the advantage of beneficiating co-products can result in their value as much as the saving of expenses generated by their simple possession, disposition, management or elimination.

The transformed matters are involved in assemblies assuming a given function. These assemblies or parts of assemblies satisfy their function for a given time, beyond which their efficiency decreases due to wear, ageing, or simply technical and regulation obsolescence, these assemblies are then replaced. Two families of materials are then produced, wearing products and decayed materials. Most of the times, wearing products are disseminated just after their production, due to the general impossibility of collecting them, except in very special conditions like permanent friction devices or filters from dust removers. To the contrary, decayed materials such as engines, structural elements or used nuclear devices can be collected, dismantled, processed and their components sorted. The components of decayed materials and residual co-products belong to the general class said “residual materials”.

Residual materials can be totally, in part, or not at all made of valuable components. If relevant, their separation defines a so-called secondary resource and their non-valuable fraction is a waste. When the beneficiation of a secondary resource generates, after a separation step, some residue that cannot be used, this residue is named secondary waste, this is the case of bottom ashes produced by second melting of metals or recovered metal alloys. When all the valuable matters have been extracted from a residual material or when this material does not contain any valuable matter in the local conditions the resulting product is named ultimate waste. Actually, most of the regulation rules are based on this definition.

In fact, the culture concept of “waste” is more complex; in Europe, it is connoted by the idea of excrement and death [1]. More generally, the name of “waste” is attributed to any transformed matter which owner seeks to dispose of. Some economists choose to name “waste“ any substance that, in an exchange, moves in the same direction as its exchange value.

Attempts to generalize and synthesize these questions have been done [2,3].

2. BACKGROUND OF ENVIRONMENTAL ENGINEERING

2.1. Introduction

Most of the management routes for the matters for which we are concerned here are based on the background of separation techniques from mineral processing. Mineral engineering has three traditions. One tradition concerns solid/solid, solid/liquid and solid/gas separations, including preliminary modification of interfacial properties by adsorption of surfactants. A second tradition deals with elements or small molecules extraction, including liquid/liquid extraction and differential precipitation, vaporization or condensation. The last tradition is related to supervision and control of the reactivity. These three traditions allow treating diverse situations of management of residual materials, taking into account the level of action and of the conditions of the problems to be solved.

Environmental engineering can also deal with separation, immobilization or passivation of phases according to the concepts of mineral engineering and use the same techniques. To the contrary, building confinement barriers or more generally isolation matrix belong to civil engineering or public buildings and different work sectors techniques.

2.2. Levels of action

The strategies to manage residual materials and wastes imply four levels of action that cannot be considered separately.

1) Limit the quantities.

2) Improve recycling and beneficiation.

3) Optimize collecting, stocking and passivation of unavoidable or ultimate residual materials.

4) Be in conditions of remediating damages in case of accident.

These strategies are summarized by the “seven **R**” rule.

*“**R**educe, **R**ecycle, **R**euse, **R**ecover, **R**eclaim, **R**eject and **R**emediate”.*

On each of these levels, a reflection must be added on:

1) Education,

2) Regulations,

3) Control of public opinion.

3. TYPOLOGY OF SITUATIONS

The relationship to residual materials can be divided into two major types of situations.

1) The residual material contains at least one substance for witch the beneficiation is possible according to a known and economically realistic process. Then it can be considered as a secondary resource and its beneficiation will generate a secondary residual material.

2) The residual material can be considered as a pure nuisance due to:

- its volume (non-reactive mining wastes),
- troubles it generates:
    - bad smell,
    - non-aesthetic aspect,
    - proliferation of insects, rodents, birds,
- the dangers resulting from its characteristics:
    - chemical,
        - toxics,
        - reactive matters,
        - rests of catalysts and antiageing formula,
    - physical,
        - fine particles,
        - radioactive wastes,
    - or biological
        - fermentable wastes,
        - hospital wastes,
- the prohibitive cost of their management:
    - collect,
    - neutralization-stabilization,
    - stocking,
- its impact on major natural mechanisms.

3.1. Cases where the residual material can be considered as a secondary resource

Valuable matters or elements can be separated by conventional methods from mineral processing or extractive metallurgy.

Collected metals: this field is the most traditional one (off cuts, machining effluents, material collected from decayed devices, residual materials containing elemental species); the problems are then the same as in secondary metallurgy, however a de-pollution step may be necessary (diversely spoiled metals; poisoned catalysts, paints, varnish, anti-corrosion treated metals, mixtures of complex alloys, toxic doping agents). After that, the collected metals are sent toward the usual industry of secondary metallurgy.

The main advantage of secondary metallurgies is, of course, to recover the values of metals, but it is not the only one. In fact, concerning the family of non-ferrous metals, the “deposit” of recovered metals is a secondary resource with a better grade than that of ores. This recovery products metals with a lesser energetic expense and less polluting than the primary metallurgy. For example, the recovery of copper from electric applications produces a very pure metal (99.9% Cu), though a copper ore issued from porphyry copper has a grade of 0.7% Cu, and the one from poly-sulphide ore has an average grade close to 5% Cu, and that in both the case, the vector is a sulphide. The emission of hazardous compounds deals with bearing sulphides, sulphates, arsenates, mercury and other metals from associated minerals [4,5].

One similar observation concerns metallic lead, sulphates and lead oxides from batteries, that is solved by reducing melt, but generates a problem of residues management due to remaining doping agents based on tin and antimony, and remains of halogenated plastics.

Unusual sources: Some special effluents constitute non-traditional ores. For example due to its organophilic character, uranium fixes on peat lignite and coal, as a consequence, the ashes of thermal power plants burning these kinds of fuels contain residual uranium and its non-volatile lineage. If the ashes contain uranium, this one can be recovered by a hydro-metallurgical process and thereafter the ashes initially too highly radioactive can be used as raw component in clinker plants. Within the same idea, decayed electronic assemblies represent an acceptable ore of precious metals (Au, Ag, etc.).

Transition metals and refractory metals can be extracted and separated using the conventional and alternative methods of extractive metallurgy (chlorination, carbo-chlorination, oxy-chlorination, nitrification, sulphurisation, oxidation, reduction, etc.) [6–24]. In a first step, they were carried on for recovering metals from decayed assemblies (catalysts) or residues (bottom ashes) with high metallic contents. Today, they are also used, as de-polluting techniques or as preparation methods. It is possible to model with reactions thermodynamics and kinetics to foresee the physical conditions of separation of element-bearing species, in complex media.

A special mention must be done for mine heaps and metallurgical rejects. Some of the corresponding deposits are now very old and, taking into account the academic and technical progress, they can be work again; this is the case of copper or gold old mining heaps [4,25]. In addition, some minerals were without any interest years ago but are sought after now, for example some gangue minerals such as the white micas from porphyry cooper or kaolin rejects, or niobium and tantalum from tin metallurgy [10,12,26]. The regulation rules progressively changed also, based on public health and environment protection, such as for arsenic, mercury, cadmium, etc., or reagents like glycol ethers and cyanides [27]. Another point is that some compounds, sometimes containing hazardous element, that were considered as wastes, can enter in large diffusion materials as building ceramics, also immobilizing the hazardous elements [28,29]. A last point is that the initial mine operator disappeared.

One part of electrical assemblies, mainly household devices, joins the category of residues issued from vehicle shredding and is ground. Ferrous metals are recovered by magnetic separation and can be recycled in electrical steel plants [30] (what generates a problem linked to surface coatings: Zn, Ti, chromates, etc,). The non-ferrous metals can be recovered using Eddy currents separators. The residual fraction (27.7%) contains 8.5% of plastics, 4% of rubber, 3.5% of glass, 1.2% of textiles, 0.5% of papers, wood, gravels, sand, fluids, metals, etc. This residue is considered as a non-inert material the stabilization of which is expensive. The stake of 100% recyclable automobile for year 2000 in Europe was not reached [31], neither was the goal of total recycling household electric devices because the most fractions generated are not recyclable for example halogenated plastics.

The residual material or a by-product is of the same nature as a commonly used substance.

Examples:

Residual calcium sulphates are common by-products for many industries, the largest volumes are produced by phosphates industry and fume desulphurization. Many of them are very pure substances, available as powders that could provide the industries of plaster and clinker. However, they need sometimes an adaptation of process (α plasters) [32–34].

Residual calcium chlorides from de-chlorination processes can be used for clearing the snow off the roads. In some traditions, they are used for extracting potash from potassic lavas.

Building demolition effluents can be used, at least in part, as aggregates. In addition to the economic and technical gains, this application aids to solve the following questions:

- the lack of silicated aggregates,
- the elimination of un-aesthetic landfills,
- the environmental problems due to gravel pits works,
- the alteration of surface water flows,
- the recovery and recycling of concrete steel reinforcement materials.

However, new practices are necessary on the working sites, as for example selective sorting of wood, plastics and plaster. This domain concerns special "niches" such as the integral recycling of electricity transportation pole (0.3 million of annual units in France).

Diverse bottom ashes are used as raw materials in cement industry and as aggregates in civil engineering. The main limitation to use them in civil engineering results of the reactivity of calcium silicates, sometime combined with the mobility of aluminium and other metals contained, generating expansive crystallizations (e.g. Ettringite).

A residual matter can become a new material if a specific channel is open and if the corresponding product may have constant properties.

Examples:

- Solid effluents of water de-sulphatation by calcium aluminates as pigmentary mineral fillers based on ettringite:

$$3CaSO_4+Ca_2Al_2O_5+H_2O+6Ca(OH)_2+26H_2O+5CO_2 \rightarrow Ca_6Al_2(SO_4)_3(OH)_{12}\cdot 26H_2O+5CaCO_3$$

- Ferrous sulphates, issued of the synthesis of titanium oxides from ilmenite route can be used as raw materials for the synthesis of super-oxidants based on potassium ferrates [35,36].
- Silica dusts from silicon metallurgy as reactive fillers in concretes reduce the porosity and convert the excess of portlandite into secondary calcium silicate hydrates (CSH).
- PVC concentrates as source of chlorine in metal chlorination process [30,35].

The best-established tradition concerns the recycling of organic polymers [36].

The technology of composite polymeric materials generates complex assemblies that cannot be recycled in their original applications, except in some rare cases of selective collections. In addition, a large majority of plastics/minerals composites materials are practically impossible to separate in acceptable economic conditions.

Paradoxically, re-using large volumes of organic polymers (e.g. in civil engineering) often results in spreading wastes in the environment. This practice that goes to the opposite of the protection of environment, raises problems of long-term evolution, mainly concerning the uncertain behaviour of minor components as catalysts residues, anti-ageing formula, and process additives as vulcanisation accelerators.

Clinker kilns of cement industry can accept vulcanized rubbers up to 12% of the fuel, this limit has two reasons: alkaline sulphates are volatile and their accumulation by re-circulation lead to concretions that can forbid the reuse of dusts; in addition, calcium sulphate is used as setting regulator and must be carefully dosed.

The use of decayed tires concerns a series of traditional applications in road technology [37].

Ground rubber and rubber powders can be incorporated in bitumen.

$$\text{Bitumen} + \text{aromatic oil} \xrightarrow{200^\circ\text{C}} \text{partial de} - \text{vulcanization of rubber}$$

The lightest fractions enter the reticulated network of the polymer. This process, has been practiced since 1960, it is also to the origin of incorporation in shingles, sport grounds, concrete resisting to frosting when poured.

Sorted plastics: plastics can be separated each from others by hand sorting, cycloning, after differential grinding; by differential rebounds with possible preliminary thermal treatment to temperatures close to the glass transition of one of the components; by selective dissolution [38]; by flotation [39–41] or sink float technic separation [42].

Recovered poly-ethylene (RPE).

RPE + polyethylene wax (PE) ⟶ binder for road gravels

The final cost of the gravel is then doubled but the mechanical properties are significantly improved in spite of a cooling shrinkage [43].

The RPE ozonation [44,45] improves the properties and the product can then be used in the rolling layer, “COMPOTEM®” process.

Peroxide vulcanized Ethyl-Vinyl-Acetate (EVA) can be used, after de-vulcanisation (re-functionalising) as a white binder for gravel in rolling layer.

Cut off of Polypropylene, Polycarbonate and Acrylonitrile Butadiene Styrene (ABS) can be re-formed (in-plant sorting and collecting) in alveolar boards, used in grass rolling and parking zones. The “ECOGREEN™” process re-forms recovered canvas cover out of Low Density Poly Ethylene (LDPE).

Poly Vinyl Chloride (PVC) is not compatible enough with bitumen to be incorporated in road binders but is compatible with coal tar, however its operating conditions in road technology is very complicated [46].

RPE + 20% PVC + coal tar + gravel ⟶ rolling surface

Other more complex formula incorporate Poly-Methyl-Meta-Acrylate (PMMA).

Phenolic, epoxy, polyesters, resins can be used as binders for sand to produce diverse garden containers (pots, jars, garden boxes, etc.).

Mixed plastics: Lamellar wastes can be used for reinforcing of berms, grounds and slopes: “PLASTERRE®” process. Bales of flexible plastics are used to lighten civil engineering structures.

Re-formed bales (fusion), small bales and ingots are used in civil engineering or for energy recovery (incineration), problems can arise from reactions between plastics and fermentation of other organic residues (food residues).

Recycling under the form of buckets, feeding dishes, stakes, pipes, and fence elements can also be mentioned.

Fibrous materials: They can be used for concrete, plaster, soil tiles, roof tiles, slates substitutes, coating materials especially thrown (e.g. “SIKA TOP 122 F™”) or in geo-textiles and marking nets.

The PVC Problem: PVC enriched fractions are available from diverse sources (particularly from flotation where its polar property facilitates the separation, and floating when filled with dense minerals), however it is difficult to find a channel to use them; their incineration itself is problematic due to the formation of HCl.

The cement industry can accept high-grade PVC fractions as source of chlorine and to recover energy.

1) In “low-alkali” clinkers. The principle is based on the vaporization of alkaline element chlorides (if necessary by adding $CaCl_2$) and pump them off the gas phase.

2) In alinite (Ca_3SiO_5, $CaCl_2$) clinkers.

- The de-carbonation temperature is very low (540°C).
- The clinker formation occurs at 1 100°C instead of 1 500°C.
- There is no formation of vitreous phase.
- The mechanical properties seem very interesting.

PVC enriched residual fractions can also be beneficiated as source of chlorine. One goal has been reached which is the hydrothermal decontamination of jarosites, using various organic wastes, namely recovered PVC (VERTEC process). Subsequently, the jarosite can be used as oxidant of organic matters and decomposes it into more simple minerals which can be separately beneficiated. The proposed treatment allows extracting 97% of non-ferrous metals, limiting the chlorination of iron oxides to less than 3% [35].

Though the beneficiation of residual plastics is very diversified, the amount really recycled or reused is low (close to 10% in developed countries) the rest is burnt as fuel or co-fuel or buried in landfills.

3.2. Case where residual matter is a pure nuisance (ultimate waste)

3.2.1. Case where residual matters are physically or chemically inert

They raise only problems of volume. They can be stocked outside, as materials for *in situ* backfilling, or scattered, if they do not present any high eco-toxicological risk.

3.2.2. Case where residual matters are physically active

The fineness can be a nuisance since in aqueous media, a too high abundance of suspended fine particles changes the illumination conditions and, as a consequence, can break down the food chains, generates severe perturbations of eco-systems, that can ruin some local businesses (lake fisheries in Cambodia), or some agricultural activities (rice production in Vietnam).

For example, this issue is a penalty for the industry of dielectrics based on delaminated micas produced by wet processing, since the resulting fine particles dispersed in water are considered as reactive products and must be separated and confined. Only a small quantity can be reused as lamellar de-compacting agent in horticultural soils [47].

The wastes from uranium ores are generally chemically inert except for the wastes from *in situ* or heap leaching.

3.2.3. Case where residual matters are chemically active

Waste materials may contain poisons such as heavy metals, arsenic, antimony, mercury, etc. More simply, sulphides (e.g. sulphide based luminophores to the origin of sulphuric acid, itself mobilization agent); they can also contain residual separation or extraction reagents (surfactants, extraction reagents, cyanides, etc.), they must be stocked in controlled conditions.

Different neutralization traditions of wastes exist, some of them are process imitating the natural mechanisms (so-called “geo-mimetic“); others are derived of adsorption mechanisms carried on separation process. Finally, others are mainly oriented toward a limitation of biological effects and try to separate the microorganisms from the “batteries” from which they use to collect their energy.

3.3. The unavoidable wastes

Many branches of industries produce ultimate or unavailable residues that must be destroyed, stabilized and/or stocked in controlled conditions. One can mention:

- The chemical wastes as un-desired by products of synthesis, surface treatment effluents, used media as lubricants, solvents, insulating materials, dielectrics or washing effluents.
- The combustion residues, gas, ashes, muds from fume cleaning, bottom ashes.
- Clarification effluents from beverage industries, water treatment, vegetal oil treatment, milk industries, tanneries, etc.
- By-products from decontamination operations: elements from recycled alloys decontamination, ion exchange resins, salts from desulphurization or de-chlorination or from pollutant extraction, etc.
- Wastes from electro-nuclear industries.

If the toxicity results from molecular properties and not from element properties of components it can be neutralized by destroying the corresponding molecules, either through a well-controlled incineration either through a soft chemical process (oxidation with ferrates, ozone, permanganate or hydrogen peroxide, etc.).

If the toxicity results from elemental properties, such as heavy metals, soluble salts, organics or long life radiogenic materials, the wastes must be stabilized/solidified. It must be noticed that in developed countries, the sites remaining available, with a total storage safety of deposit, became very rare. In the future, the possible destruction of undesired or namely dangerous radionuclides in fast-breeder-like devices will probably become possible.

4. THE QUESTIONS OF TOXICITY, ECO-TOXICITY, DANGER, RISK

Toxicology is the science of poisons and poisoning. The concepts of poison or of toxic diversely relate and depend on numerous factors. According to Paracelse's paradigm the first factor is the dose, "*Sola dosis fecit venenum*", "Only the dose makes the poison" this proposition is at least incomplete and sometimes wrong, since other factors as the differences between individuals or species, administering way (ingestion, inhalation, injections, contact) as well as the habits and local customs strongly nuance it. However, it remains that the basic tool for evaluating the toxicity is the relation between dose and effect. Particularly, the determinations of the NOAEL value (No Observed Adverse Effect Level), of the Acceptable Daily Intake (ADI) for humans and of the Maximum Acceptable Concentration (MAC) define the basis of most of the regulation rules. In fact, most of the time, these operative rules do not directly refer to the real effects, but to their translation into laws and regulations, which offers the entry of lobbying groups in environmental management.

In addition, the doses are quantified in diverse ways. For example, as amount of toxic material generating an effect per unit of corporal weight, or as the exposure concentration leading to an effect and given as weight of toxic per unit of ingested mass (for example for water or foods) or in weight of toxic per unit of inhaled volume (e.g. for gas).

Finally, the concept of dose itself must be really defined concerning the speciation of concerned toxic or supposed toxic elements, since it cannot be dissociated from the chemical form in which it occurs. For example, the arsenate ion AsO_4^{3-} is very toxic, in the other hand, arseno-betaine is not toxic for humans. There would not be any relevance to consider for both these compounds a dosage that would be the element content per unit of weight of ingesting organism. The same question arises for the low toxicity of metallic forms of tin or mercury compared to the toxicities of their organic compounds.

Though in some cases, the dose is very difficult to evaluate, for example, for the intoxications by contact, the toxicity concept is qualitatively and quantitatively based on its own methods, and defines measurement algorithms through specific parameters.

Toxicology varies seen under different angles, and therefore many toxicologies exist.

- The experimental toxicology evaluates the behaviour of an agent in an organism, depending on physiologic mechanisms, solubilisation, distribution, transformation and elimination (toxico-kinetic) and its consequences (toxico-dynamics).
- The clinical toxicology concerns the effects of intentional intoxications (suicides and crimes), or accidental ones.
- The medicine toxicology mainly studies the secondary effects of drugs, including the long-term (e.g. trans-generational) aspects.

- The food toxicology deals with the contamination of food with pathogenic compounds or elements incorrectly also named residues, from their dissemination media to their effects on living organisms (pesticides, plant-care products, veterinary products, disseminated metals, preservatives, colouring agents, etc.).

- The eco-toxicology studies the behaviour of substances on natural media and their effect on the environment.

Another classification is superimposed to this one, based on the distinction between acute and chronic toxicity that is often expressed by very dissimilar effects, inevitably postponed in duration and for largely lower doses for chronic cases than for acute ones. It follows that the measurements cannot be based on the same methods for both cases. For example, the chronic toxicity of arsenic has never been noticed for a very long time because its effects appear for durations largely longer than the longevity of rodents used for experimentation; to determine these chronic effects using epidemiological methods was necessary.

The acute toxicity is evaluated through a unique administering of a substance the effect of which could lead to death (lethal effect). Its evaluation is carried on administering diverse amounts of a given substance at cohorts of experimental organisms, for example mice, the mortality of which is measured 24 hours and 7 days after the administration (differed toxicity). Some quantitative parameters are deduced from this type of evaluation. Surprisingly, these parameters are almost never directly used to decide actions but are used to define norms and regulation rules to which the responsible persons refers. The main parameters are:

- the MLD, Minimum Lethal Dose equivalent to the 0% lethal dose or the maximal dose that does not provoke the death (LD_0),
- the MTD Maximum Tolerated Dose, maximal dose without effect,
- the LD_{50} dose provoking the death of one half of the cohort,
- the LD_{100} minimal dose provoking the death of the totality of the cohort.

Concerning the inhalation of toxics, the parameters refer at the concept of Lethal Concentration (LC); the LC_{50}, concentration provoking the death of one half of the cohort, this parameter is also used for water in the case of aquatic organisms.

Since the toxicity differs from one specie to the other, the determination of quantitative parameters must be carried out on various species, for example, on mice and on hamsters, though these species of rodents are very close. The DL_{50} of the mice for tetra-chloro di-benzo di-oxan (TCDD: dioxin) is of 1 mg/kg, the one for hamsters is 0.1 mg/kg. In addition, the toxicity would have to be evaluated with reference to other parameters as sex (for sexed organisms), isolation, weight, breed, age, biotope, population density and factors connected to stress.

The toxicity measurements are also sensitive to combined factors. The additive (or synergic) effects are well known (potentiation), however, indirect factors can play a role, as the water hardness that affects the solubility and the nature of dissociated forms, or the presence of surfactants that change the dispersion conditions. Finally this evaluation can depend on variations induced by the own characteristics of the experimenter himself (idiosyncrasy). Thus, the good practices need complex and precise protocols, at the origin of high analytical and experimental costs of relevant determinations.

The chronic toxicity is characterized by a progressive outbreak of symptoms resulting from a long-time exposure. For a given substance, the chronic toxicity symptoms may be very different from those of the acute one. For example, in the case of lead, the acute intoxication leads to digestion troubles, from where the name "painter's colic" derives which was a professional disease of painters when the paints contained lead carbonates; the chronic intoxication (saturnism) is characterized by non-reversible neurodegenerative effects.

Another difference is related to nominal doses, usually, the doses responsible for chronic diseases, are largely lower than those responsible for acute diseases. References can be made to the following examples:

Fluorine:	acute toxicity LD_{50} 1 to 1.5 g/kg of Corporal Weight (CW). chronic toxicity, bone pathologies from 5 to 10 mg/kg CW during one month.
Poly chloro benzene:	acute toxicity 1 g/kg CW. chronic toxicity, hepatic necrosis from 20mg/kg for one month.
Copper:	acute toxicity LD_{50} 200 to 300 mg/kg CW gastroenteritis. chronic toxicity 20 to 30 mg/kg CW during some weeks, hepatic necrosis or 2 ppm in drinking water for some years, anaemia and troubles of protein synthesis.

Finally, a third difference is related to the time before the apparition of symptoms, for example, in the case of arsenic, the immediate effect of acute intoxication is the apparition of haemorrhagic diarrhoeas (LD_{50} of sodium arsenite 4.5 mg/kg of rat *per os*), the first chronic effects for concentrations of 50 ppb in drinking water appear within a period of ten years: hyperkeratinisation, discolouration spots and skin cancer; after a time of twenty years, cancers of bladder, lung, liver, colon and kidney appear.

One of the peculiar angles of the chronic intoxication concerns the accumulation effects, some toxics are specifically stocked in specific organs or tissues, as fats, and their effects are revealed on the occasion of illness, stress, therapeutic loss of weight, or hibernation weakening fats (e.g. liberation of the lipophilic organo-chlorine molecules).

It remains that if some substances are toxics over a given dose, their absence under another and lower dose, provokes a deficiency and for some living species, the deficiency threshold can be very close to the toxicity limit; for example, this is the case for cooper in sheep food. A similar concept exists for drugs or molecules with medicinal properties, or medicinal effects, for these ones, an effect dose (ED_{50}) is defined, that of course must be lower than the LD_{50}. A safety index or therapeutic index $IT = Dl_{50}/DE_{50}$, an absolute safety index $ASI = DMT/DE_{100}$, and a therapeutic coefficient: TC = maximal acceptable daily intake/maximum acceptable dose: MADI/MAD are also defined.

One of the tools of chronic toxicology is epidemiology, its principle is to consider populations exposed to toxic risks and compare their pathologies with those of other distinct populations, only in principle, since the tested and reference populations are not subject to the same risks. Epidemiology works then according to an analogical thought process and needs a very rigorous interpretation of statistics. Finally, it proceeds by long and scrupulous field investigations indeed with setting up permanent observation of populations. This is pointing at if it cannot be associated to another supervision activity, financed by other sources (occupational medicine, NGO, defense or protection, statistic of specialized medicines, etc.), its cost largely exceeds the experimentation one.

Eco-toxicity is a quite ambiguous concept: some of its aspects reveal properties of non-hazardous matters aspects in the general sense of acute or chronic toxicities, but which can perturbate some natural mechanisms, among other those governing large scale phenomena, possibly, by activating phenomena involving themselves toxic materials or impacts on undesired living organisms, animal (rodents, birds, insects, etc.) or vegetal (invasive species, green algae, etc.). Another aspect of the ambiguousness is that concerned phenomena are sometimes under debate and under the influence of lobbyists groups.

The acid rains really result from the effect of combustion gas (SO_x, NO_x, etc.) on plants. However the resulting forests degradation is not a consequence of the direct impact of acids on the aerial system of plants, but is due to the effect of such rains on the forests soils. The acidification of acid soils leads to a destabilization of clay-humus complex, mainly to the desorption of small carboxylates fixed on soil alumino-silicates, what generates the production of Al^{3+} ions, toxic for the plants.

The thinning of the stratospheric ozone layer results from interferences between light halogens (F, Cl) and the mechanism of formation–destruction of O_3, ozone or tri-oxygen. In fact, this mechanism protects the biosphere from solar ultraviolet radiations. Cryo-fluids (freons, CFC and substitutes) and some gaseous dielectrics (SF_6) content these halogens; this is the reason why their use and the dismantlement of decayed cryo-equipments and dielectric containing devices is strictly regulated.

The greenhouse effect is a global warming resulting from the reflexion toward the earth of infrared radiations by the atmosphere, normally reflected by it in space. The parameter that measures the greenhouse effect is the Global Warming Potential GWP (Table 1).

Table 1 Values of GWP for different common substances

Substance	GWP at 100 years
NH_3	0
CO_2	1
Isobutane	20
Propane	20
CH_4	23
NO_2	296
CFC 11	4 600
HCFC 12	1 700
HFC 134a	1 300
SF_6	24 000

The SF_6 compound (sulphur hexafluoride) is used a gaseous dielectric (and also as plastic expander to form plastic foams), it is totally non-toxic, but its contribution to the greenhouse effect per mass unit is $24{\cdot}10^3$ greater than that of CO_2.

The pollutions by fine or coloured particles are sometimes hazardous what justified large-scale decisions for example concerning diesel engines. One other effect is to alter the luminance and the illumination spectrum in hydrologic systems, though these particles may have no intrinsic toxic properties.

A toxic matter can be hazardous by nature or its dose, but it can present no danger if it is inaccessible or cannot be disseminated. On the contrary, it becomes more and more hazardous when the exposure probability increases. The risk is a peculiar concept; it results from the conjunction of a danger with an exposure probability for an organism or a group of organisms.

An example: compared dangers of the different productions of electric power.

Table 2 gives the number of workers victims (left column) and public ones (right column) associated to different operation fields (building, exploitation, maintenance, re-treatment, etc.) of electric power. The data of this table concern a production of 1 GW/year of electricity.

Table 2 Number of victims associated to the production of 1 GW/year of electric power [48] (For each type of fuel, the left column concerns the number of workers victims and the right one, the number of civil victims)

	Coal		Petrol		Natural gas		Peat		Wood		Nuclear	
Mine silicosis	0.30	-	-	-	-	-	-	-	-	-	0.10	-
Mine accidents	1.10	-	0.90	-	-	0.40	1.0	-	1.2	-	0.04	-
Mine radiations	0.02	0.3	-	-	-	-	-	-	-	-	0.04	-
Transport	0.10	0.5	0.50	0.05	0.02	0.03	-	-	0.8	-	0.01	0.05
Treatment	0.06	-	0.50	-	0.05	-	-	-	-	-	0.06	-
Building	0.15	-	0.15	-	0.06	-	-	-	-	-	0.10	-
Maintenance	0.16	20.0	0.05	6.0	-	0.02	-	0.9	-	-	0.10	-
Product-rad.*	-	0.7	-	-	0.25	-	0.002	0.1	-	-	-	0.02
Retreat.-accid.*	-	-	-	-	-	-	-	-	-	-	0.01	-
Retreat.-rad.*	-	-	-	-	-	-	-	-	-	-	0.05	0.12
Elimin. rad.*	-	-	-	-	-	-	-	-	-	-	0.47	0.25
Total	**23.4**		**8.2**		**0.83**		**2.0**		**2.0**		**0.5+0.9 =1.4**	

*Product-rad. concerns the radiation victims when producing the fuel. Retrait-rad, retrait-accid. and elimin-rad. concern the victims of the used fuels re-treatment and elimination of wastes either due to radiations or to accidents.

5. THE SOLIDIFICATION/STABILIZATION PROCESS

5.1. General data

The solidification consists in encapsulating the waste in a solid matrix. The aptitude to be leached is lowered by reducing the specific surface, the porosity and the permeability, and by the use of additives that could trap the possible mobile compounds [5,49–53].

The immobilization in mineral binders, usually Portland cement, is the most common method to stabilize the ultimate residues. The main concern is to control the long-term behaviour. The confinement systems may imply some specific additives of pollutants present in the wastes; the mechanisms of trapping, the mobility of pollutants, the structure and texture of rendered inert materials must be studied.

Some additives as Double Lamellar Hydroxides (DLHs), hydrogeno-phosphates or diverse iron hydroxides have specific affinities for soluble salts or metals. Doping cement-based binding materials allow reducing the pollutant mobilization by 30 to 40%. Due to their low cost, their reactivity and their easy implementation, the phosphate additives are the most interesting. In concrete media, the monetite transforms into apatitic phases trapping the pollutants under cationic and anionic forms; aluminium phosphate contributes to the formation of crandallitic traps.

The final status of pollutants can vary. One part of pollutants is mechanically encapsulated in the cement matrix under the form of soluble salts (such as $PbSO_4$), another one precipitates as hydroxides due to the elevated pH, and another one is incorporated in mineral structures. Depending on the concrete type, the hydration of bi and tri-calcium silicates may be incomplete; under leaching, the residual calcium silicates are hydrated into calcium silicate hydrates (CSH), that incorporate metallic cations in the place of calcium. This late maturation traps the pollutants in structural positions and reduces the permeability of formed inert materials [51].

The leaching kinetics depend on numerous parameters. At young ages, the most soluble chemical species located in the contact zone with the solution are extracted according to a diffusion mechanism, but the corresponding model is not valid after a given time, since new phenomenon modify the chemical activities and the porosity is progressively blocked by precipitates that limit the leaching effects. Lastly, as mentioned before, the addition, of chosen salts to confinement systems also limits the development of interconnected porous network to the origin of permeability.

Today, the first landfill deposits of stabilized wastes are old enough to make possible a full scale evaluation of the predictions on which the stabilization systems behaviour were based [54–56]; this is the case of confined Municipal Solid Wastes Incineration (MSWI) fly ashes [57]. Confronted with some difficulties, deposits needed to be dismantled, which gave the opportunity to observe the final status of polluting metals and understand a major point that slipped out the previsions. Almost all the behaviour models were based on the results of laboratory leaching tests and the confinement systems were proposed and evaluated at this scale, then for proofs that quickly cool down, though large deposits can be submitted for years to temperatures higher than 80°C what leads to the formation of hydro-garnets (Catoïte), ordered CSH (Tobermorite) and calcium zeolites (Gonardite). Similarly, the local increase of pH leads to a timbering-like crown by amphoteric metals hydrolysis where a paragenesis of lead chloride and basic chlorides in a matrix out of anion lamellar exchangers that also fixes chlorides (Hydrocalumite) [57,58].

The stabilization deals with any process where a leachable compound of the waste is incorporated in a stable mineral structure. Vitrifying and ceramization belong to these techniques.

Due to its cost in energy and infrastructures, the stabilization preferentially involves residual matters the dangerousness of which justifies a peculiar and very careful attention. This is the case of asbestos wastes the ceramization of which can be improved by addition of fusers that themselves can be residual materials. Doping with alkaline salts, fluorides or phosphates can lower by hundreds of degrees the melting or phase-transition temperatures the most significant might be the crystallization into pyroxens or spinels, the last one being a structure that can accept many metals.

Usually, ceramization needs a firing to lower temperature than vitrification and theoretically at a lesser cost. However, the vitrification in glass-oven offers the double advantage to avoid the management of dusts and the handling, at least temporarily, of a fluid viscous phase.

In addition, the deposits must be isolated from the environmental media, using combinations of cement, swelling clays, high specific surface materials and polymeric membranes [51].

The long-term behaviour must also be evaluated. This evaluation can be carried on using transfer models and normalized tests; however, it is also possible to make profit of data from experimental petrology [59]. The calculation validation is based on the analysis of similar natural materials.

- Fissions in natural uranium beds (billions years).
- Magmatic intrusions in sedimentary geological series (tens of millions years).
- Natural evolution of basaltic glasses in sea water (thousands of years).
- Analysis of glass fragments buried in soils at the foot of stained glasses (centuries).

5.2. Natural materials for retention and trapping

5.2.1. Cationic traps

Many cationic exchangers are available, as zeolites or smectites, they can trap small cations. After trapping, some light treatments allow to make this process non-reversible (Hofmann Clemens effect). Concerning smectites, the interaction of long-chained cationic reagents allows the internal surface to become hydrophobic, what makes possible the trapping of non-polar organic pollutants on retention materials with high specific surfaces.

5.2.2. Anionic traps

In volume, anionic mineral traps are very rare in natural conditions. To the contrary, some of them can easily be synthesized; among them, lamellar multiple hydroxides as hydrotalcite [60], some of them spontaneously form in brines (hydrocalumite) [52]. Some poly-cationic forms of iron and some compounds with high specific surfaces as aluminium or iron hydroxides are also formed.

5.2.3. Nano-porous traps

Some natural nano-porous materials are available as zeolites mentioned above. However, some compounds, easy to synthesize exist with micro-porosities that can be modulated either choosing the origin, as active carbons, either by synthesis conditions as for pillared clays issued from smectites [61] or thermal treatment of other layered silicates as chlorites [62]. All these nano-porous solids can adsorb micro-pollutants, sometimes specifically, but their use is not popular in industrial communities.

5.3. By products from agro-industries and metal or small molecules trapping

The chemical functionality of barks and sawing powders lead to the property that they are traps for metallic cations, as it is known concerning cellular membranes of bacteria and fungi. It remains that some organic compounds, namely those of barks are soluble and would increase the oxygen demand of treated effluents. Then chemical or biological activation processes are needed, not only to limit this issue, but also to significantly improve the functionality. An impressive result is the trapping of chromium (III and VI) that can reach 200mg per gram of dry bark; the incineration of this product leads to a product that can titrate 77% of chromium oxide and can be beneficiated. This property can be directly applied to the management of tanneries effluents. Another impressive result is the decrease of cadmium content close to 20ppb, which no other method allows [63–66].

Extracting fatty substances with the same by-products or co-products that previously captured metals is also possible. Numerous food or mechanical industries reject lipids, oils or emulsions. It appears that the retention capacity of grafted barks can reach 4 grams per gram of dry substrate, with a weight yield close to at least 95%, in all the considered cases [67–70].

6. CONCLUDING REMARKS

The management and beneficiation of residual materials has already a long history. It concerns questions of public health, general environment impacts and general economy of raw materials and energetic resources. Though many progresses have been done these last years, we are still very far from an optimal management of residues. More worrying is the fact that in developed countries, the consumption of goods produced by the planet resources is reached by early May. Therefore, the question of management and beneficiation of residual materials is a general problem that also implies the social control of consumption with a reference better than the simple economic aspect with the need adapted regulations.

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Chapter 3

THE FLOTATION PROCESS AND CHEMISTRY: A REVIEW

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ABSTRACT

Flotation is as viable and effective a separation technique in environmental technology as it is in mineral processing, where it was developed. Flotation occurs in a three-phase system consisting of water, particles and air. The particles to be separated are usually hydrophobic or altered to behave this way. They are composed of different minerals and ions which are absorbed or precipitated on the particle. These particles then get attached to gas bubbles. The latter are generated by different methods including dispersed-air and dissolved-air. The bubble-particle aggregate then floats to the surface to be removed from the system. Fine particles flotation faces certain limits. Various adsorbents were tested, for example in the case of heavy metals (as Cu, Cr, etc.), either common such as layered double hydroxides or some industrial by-products (such as pyrite) and even biosorbents - the respective process was termed (bio)sorptive flotation. A brief discussion is presented in this paper on selected examples of the electrokinetic behaviour of sulphide minerals as an illustration how chemistry's knowledge and application may help not only flotation research but also in the sustainable development in this area.

Keywords: Pyrite, Fines, Heavy metals, Wastes, Sorption, Zeta-potential

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1. INTRODUCTION

Raw materials constitute a hot topic in EU, due to marked imbalance between the production and consumption; economic activities are in fact dependent on traditional raw materials. However, the supply of minerals to the European industry, with a few noteworthy exceptions, is heavily dependent on import [1]. Flotation is as viable and effective a separation technique in environmental technology as it is in mineral processing, where it was developed. Without this technology, many common metals and inorganic raw materials would be exceedingly scarce and costly, because the high grade ores that could be processed by simple physical and mechanical methods have long since been used up. On the other hand, the food-chain pyramid receives metals through man's activities and on top of the pyramid, man (perhaps) receives preconcentrated metal toxicity.

The varying behaviour of particles at air–liquid interfaces were studied in a historical perspective; particles attached to bubble surfaces act as a steric barrier. Their effectiveness is dependent upon many factors: such as concentration, particle hydrophobicity and size, among others [2]. In the flotation process, bubble velocity and turbulence are the key factors affecting particle-bubble interaction; collision efficiency is used as an indicator to assess the extent of these interactions [3]. A new flotation technology, the Jameson cell, has shown (following development) interesting advantages, such as the consistent fine bubble generation, without use of spargers and intensive slurry mixing with the bubbles without mechanical agitation [4].

The presence of stratified flow was accepted in the separation zone of a dissolved-air flotation (termed as DAF) tank, used for drinking water treatment; the effect of bubble-particle clustering was also included in a computational fluid dynamic model of particle removal [5]. Other notable applications of flotation that should be mentioned, apart from the aforementioned are: the flotation deinking in paper industry [6], the aqueous two-phase flotation (based on solvent sublation) of biomolecules [7], and the recovery of microalgae for biodiesel production [8].

Arsenic-rich auriferous pyrite concentrates (stockpiled in the mine area) were shown to be further enriched by flotation to assist in gold beneficiation [9]. The various applied techniques for metal ions removal have been recently reviewed, including a hybrid one [10,11]. Alternative bubble generation methods were also examined, such as electroflotation and dissolved-air flotation. The contribution of physical chemistry to flotation was investigated, zeta-potential measurements, contact angle etc., examining the role of bubble and particle size played in the process as well [12]; the aforementioned will be further elaborated and extended in the following text, including an update of the recent literature. It should be noted that in this review there is not much focus on the flotation engineering aspects, such as hydrodynamics as this area has been rather well addressed in the literature.

2. SORPTIVE FLOTATION

Adsorption is commonly used for the removal of heavy metals, due to its low cost, efficiency and simplicity; focus of this review was the use of inorganic adsorbents engineered at the nanoscale [13]. However, nanomaterials are expected to act as a froth stabilizer and therefore, detrimental to flotation [14]. On the other hand, the properties, features and role of nanobubbles in (dissolved-air) flotation have been recently investigated, showing potential for the removal of Fe^{+3} ions [15]. Furthermore, the interface between biological and geological materials was elsewhere examined; bacteria can immobilize various components of solutions or suspensions, offering remediation, and recovery applications [16]. The ability of microorganisms to remove metal ions from dilute aqueous solutions (as most wastewaters are) is a well-known property. Various types of biological materials were tested and floated efficiently, such as bacteria, fungi, yeasts, activated sludge, grape stalks, etc. [17].

The application of mineral particles by-products for the induced removal of toxic metals from aqueous solutions was also proposed [18]; nowadays, the problem of industrial wastes handling and disposal is increasing continuously, as more strict environmental considerations have to be taken into account. Success in developing novel technologies will be greatly improved when we can confront the chemical complexity in flotation systems [19].

The impact of chemical speciation was stressed during various flotation applications for metal separation from the effluent [20]. Toxic metals exist in the effluents of many industrial operations. The removal of soluble ionic species, such as heavy metal cations or oxyanions, from dilute aqueous solutions has been in-depth investigated by applying the sorptive flotation technique mainly in laboratory-scale experiments, batch and continuous mode. For the latter, a countercurrent flow is advisable [21]. This innovative separation technique involved the initial abstraction of heavy metal ions onto a sorbent (including a biosorbent), at first. The application of a flotation stage followed, for the efficient downstream separation of metal-laden particles – i.e. a two-stage process. Typically, dispersed-air flotation was mainly used as the bubble generation method. The process yielded a metal-loaded sorbent stream and a clean water underflow.

Figure 1 presents such an example, where chromium oxyanions was removed by a typical inorganic ion exchanger (synthesized and then calcined at 500 °C for 10 h) combined with recovery by flotation, applying different surfactants. Heating hydrotalcite numerous fine pores are formed perpendicular to the crystal surface from which the CO_2 gas vented. This is accompanied by an increase in the surface area and a doubling of the pore volume. Although this favors chromate sorption, it may possibly explain the difficulty faced in floating hydrotalcite particles [22].

Layered double hydroxides are lamellar mixed hydroxides containing positively charged main layers and undergoing anion exchange chemistry. These sorbents usually exist in powder form, thereby exhibiting high surface area and rapid kinetics for adsorption, but presenting appreciable problems in the subsequent solid/liquid separation process.

Biosorption is considered as the attachment of adsorbates (of the metal ions), onto a non-living biomass surface, being usually bacteria, algae or fungi, or onto a material containing natural biopolymers, acting as bio sorbents, e.g. chitin. This process should be distinguished from bioaccumulation. Figure 2 gives an example from this research area. The residual turbidity after flotation was remarkably improved using the polyelectrolyte, from 126 decreased to 0.4 NTU. Effective flocculation is a prerequisite, mainly for dissolved-air flotation. The biomass reuse after elution was examined as well as the multi-cycle tests.

Filamentous fungal biomass was in this case a waste by-product from industrial fermentation (Synpac Ltd, UK) [23].

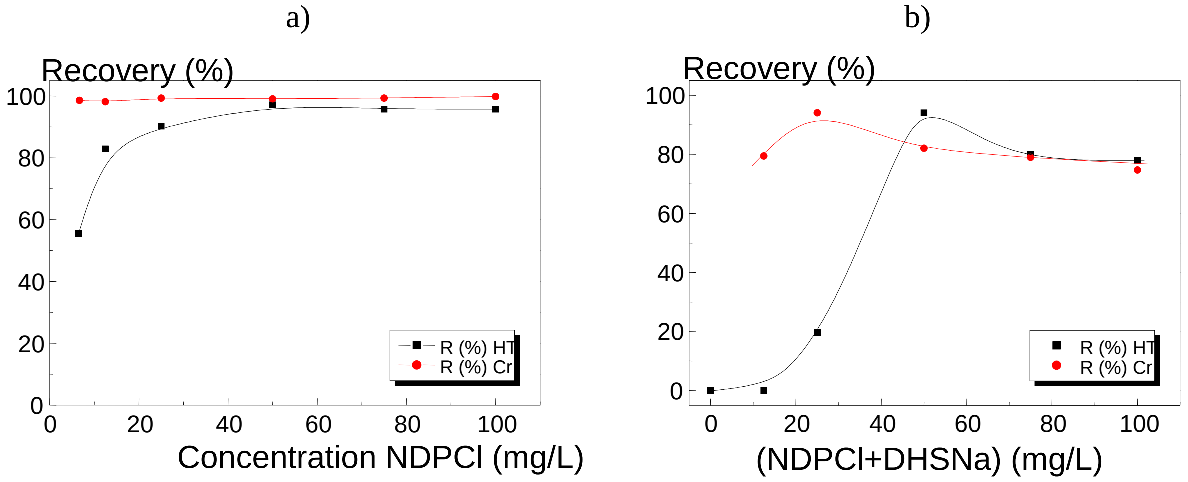

Figure 1 (a) Effect of the concentration of collector lauryl-pyridinium chloride on the separation of hydrotalcite (1 g/L) and chromates (0.2 mM Cr initially), for ionic strength of 0.001 M KNO_3; (b) Flotation by a surfactants mixture of lauryl-pyridinium chloride / sodium lauryl-hydrogen sulphate: at 0.1 M KNO_3 ionic strength, in presence of a frother and also of 50 mg/L cetyl-trimethyl ammonium bromide. Reprinted with permission, copyright Elsevier [22]

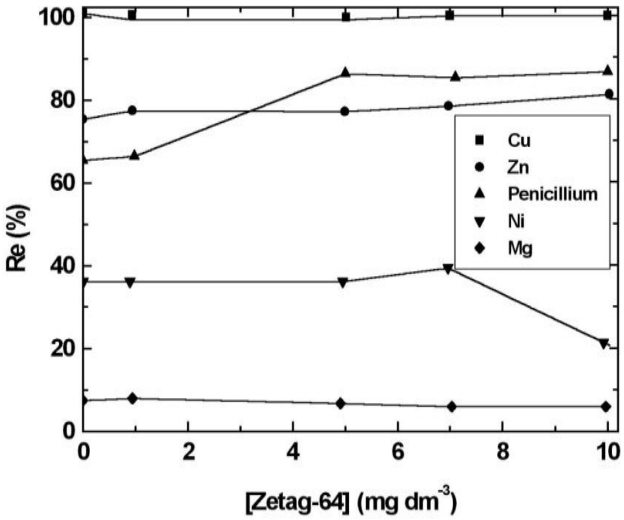

Figure 2 Influence of flocculant concentration on biosorptive (dispersed-air) flotation of Penicillium chrysogenum fungi (6 g dm^{-3}) and on the removal of toxic metals, by dodecylamine ($1 \cdot 10^{-3}$ mol dm^{-3}). Reprinted with permission, copyright Elsevier [23]

It was concluded that biosorptive flotation seemed a viable and effective separation process for the aqueous system under investigation, no matter the type of biosorbent applied. Measurements of surface tension, contact angle and zeta-potential correlated quite reasonably with the observed results of separation by flotation [24].

Activated carbons certainly are among the effective adsorbents in pollution prevention, because of their excellent sorption capacity; their use has been often prohibited due to their relatively high cost, low selectivity and regeneration problems. Powdered activated carbon (PAC) offers, apparently, more surface area for adsorption and is less costly to manufacture. On the other hand, thiourea applied for gold recovery presents an important alternative lixiviant to the commonly used cyanide, especially for cyanide refractory ores, but also as it was then thought due to the severe environmental constraints on cyanide, related to tailings disposal, water quality and environmental impact; the dissolution of gold in acid thiourea solutions is a rather complex process. Motivation for the above was the possible application of the process in gold leach solutions, for instance, after heap leaching. The solution pH, as shown in Figure 3, was not found to be a significant parameter in the acidic pH range, which was of more practical interest.

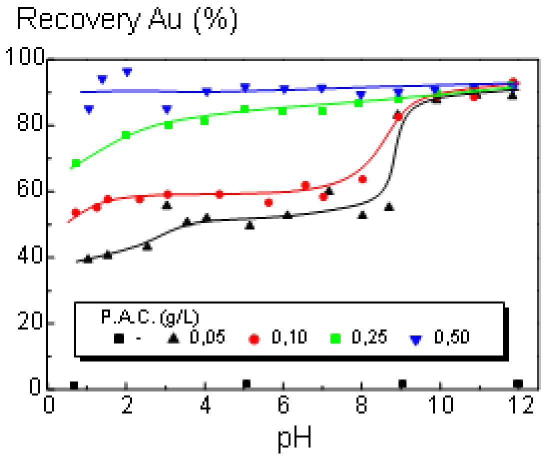

Figure 3 Effect of the solution pH on the gold adsorption process, at various powdered activated carbon additions; Au = 20 mg/L, thiourea = 400 mg/L, contact time = 600 s. Reprinted with permission, copyright Elsevier [25]

As the solution pH was increased above pH 4, formamidine disulphide decomposes irreversibly to elemental sulphur and cyanamide. Flotation of gold from thiourea solutions was also investigated and gave promising results [25]. Nevertheless, after this early work, thiourea has been shown to be a carcinogen in rats.

3. SUSTAINABILITY

Green technologies are environmentally friendly operations which limit the negative impacts of traditional industrial activities and can contribute to solving the challenge of sustainable water management. Apart from the previous comments related with sustainable development, sustainability in the field of water separation processes and its significance for the chemical and process industry is discussed in detail in the literature as the need for fresh sources of drinking water is becoming urgent worldwide [26]. This topic was also addressed in the context of minerals and mining in the plenary lecture at the previous conference in Bor [1].

The mining industry is often criticized for generating large amount of solid wastes, among other, with a significant environmental impact; one study presented a feasible approach of recovering residual coal from its mine waste rocks, and reusing the derived tailings to produce eco-friendly fired bricks [27]. The Raglan mine ore concentrator in Canada produces acid-generating tailings, which contain pyrrhotite (FeS) that need to be properly managed; the option of using desulphurized material as a component of a cover to control acid mine drainage generation was assessed [28]. Various guidance tools and practices have been proposed to improve the sustainability of mining activity while maintaining the economic viability.

Extensive use of electrical and electronic devices in modern life and for industrial purposes produces a large amount of wastes; plastic material (polyvinyl chloride and acrylonitrile butadiene styrene) in this mixed waste accounts for 30-50% of the content, containing brominated flame retardants. Therefore, a selective and sustainable separation was proposed using microwave and/or mild-heat treatment followed by flotation [29]. Water treatment of cyanobacteria and natural organic matter was examined by natural based products, i.e. coagulant and activated carbon, in a process sequence of coagulation/flocculation, dissolved air flotation and adsorption [30].

Two main bubble generation techniques were examined and compared [31]: dissolved-air flotation, which is a common technique in water treatment, and quite different from the dispersed-air flotation. In the latter category electroflotation (or better, electrolytic flotation) is also included. Elsewhere [32], derivatives of modified octyl glucoside were used as flotation collectors to remove various metallic cations from a water phase, due to their excellent biodegradability and the absence of toxic effects (hence, replacing other known surfactants derived from petrochemical industry).

Cheap and plentiful, water was for centuries a manufacturing tool that industry took for granted. But population growth, globalization, and climate change are drivers in a new water-constrained era. Good, clean water just cannot be replaced-and it is getting harder to come by.

4. SULPHIDE MINERALS

The flotation of mixed sulphides is a common application in mineral processing used for selective separation: the encyclopedia of colloid science, as flotation was called [33]. For instance, in the mines at Chalkidiki (Greece) we practiced the consecutively froth flotation separation of mainly galena (PbS), sphalerite ((Zn,Fe)S), and pyrite (FeS_2) (also copper sulphide, arsenopyrite, gold and silver), with the appropriate chemical conditioning (activation or depression) at set conditions; extensive related work was carried out at AUTh [34]. In the mineral processing plant, the first circuit (of six flotation banks in series with at least two stages of cleaning) usually use the zinc sulphate, cyanides, sodium sulphite etc. for sphalerite depression and xanthates as collectors together with frother, pine oil. Xanthates and dithiophosphates are the most commonly used collectors in the flotation of sulphide minerals. Many other collectors have been also developed.

On the other hand, in the second circuit (usually eight banks with two stages of cleaning of the liquid underflow and one stage of the concentrate), copper sulphate is used as activator, with careful pH control (pH 9.5-10) by lime, in order to depress pyrite, is further discussed below. Preceding these circuits (and after the appropriate size reduction, crushing and grinding in order to achieve mineral liberation, there is often one flotation unit that recovers most of the lead (70-80%). It should be noted that the specific gravity of the minerals is different, the gangue minerals usually being quartz or calcite rock. The main properties of modifiers in flotation are their great capability for dispersion, modification of froth properties, control of pH, precipitation of metallic ions which result in modification of collector action.

During galena flotation, the presence of slimes such as lead sulphate or pyrite, which adsorb or precipitate the collector, cause a depletion of the latter and hence, depression. Slime depression occurs when there is no energy barrier to heterocoagulation and is dependent on the zeta-potentials and size of the mineral and slime [35]. The interactions between the amino acid glycine and also a polymer with a glycine functional group and three sulphide minerals (chalcocite, galena and pyrite) were investigated, using settling tests, electrokinetic measurements and dissolution studies [36].

Another study in Melbourne [37] of ZnS and NiS by detailed electrokinetic methods showed that by careful control of experimental parameters much information on sulphide-water interfaces could be obtained. Sphalerite activation with Cu^{2+} ions, including the role of pH in this phenomenon, was examined assisted by zeta-potential measurements; from the flotation point of view, the fast activation was emphasised [38]. The native and induced surface hydrophobicity of several sulphide minerals was published elsewhere [39]; zeta-potential measurements showed that in the presence of EDTA the isoelectric point of the minerals was shifted considerably to lower pH values.

The level of dissolved oxygen concentration is a critical parameter in differential flotation of sulphide minerals, which arises from the instability of the sulphur they contain [40]. A common oxidant, potassium permanganate was used as pyrite modifier; results of electrokinetic measurements are shown in Figure 4. The point of zero charge was at pH 5, and the presence of Na^+ ions did not affect the zeta-potential. Ca^{2+} ions, in contrast, shifted the zeta-potential to less negative values and even changed the sign of it. So, the selection of the pH regulator is important as well.

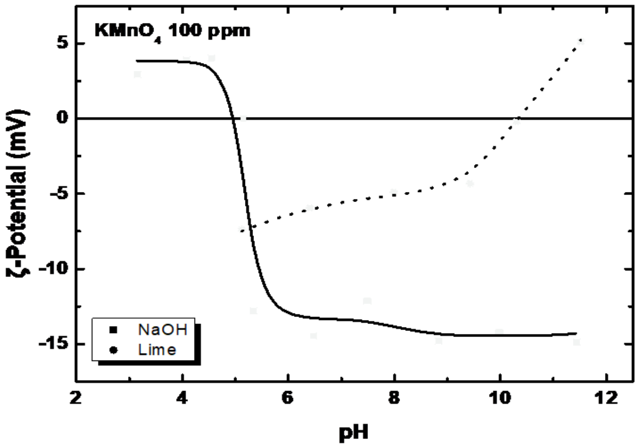

Figure 4 Influence of pH on ζ-potential of pyrite, in the presence of 100 mg/L permanganate, using different pH regulators. Reprinted with permission, copyright Soc. Chem. Ind. [40]

The point of zero charge observed at pH ~10.2 clearly shows that calcium ion is specifically adsorbed on pyrite. It should be noted that the zeta-potential measurements were conducted in the Lab by a particle electrophoresis apparatus (Mark II by Rank Brothers, UK), using a flat cell, with the microscope connected to a video monitor through a camera.

Compared to arsenopyrite, pyrite requires a lower dissolved oxygen concentration to balance the anodic oxidation of xanthate to dixanthogen, which leads to its flotation. This means that pyrite flotation (by xanthate) is possible in a less anodic potential range than that required for the flotation of arsenopyrite. The manipulation of the redox potential of a flotation pulp is possible by electrochemical treatment of the pulp, applying an external potential through metallic electrodes [9].

Electroflotation offers certain advantages over other flotation techniques of bubble generation; among other, the following points are perhaps the most important: (i) the electrode grids can be arranged to provide good coverage of the whole surface area of the flotation tank, avoiding any bypass, (ii) the electric field gradient between electrodes aids flocculation and flotation, even without the presence of any surfactant, (iii) gas production (evolution), flotation time, and the other operating conditions can be checked quickly and are relatively easily controlled [10].

Arsenopyrite (FeAsS) was also selectively floated from pyrite by an unconventional anionic collector, sodium dodecyl-sulphonate, at the pH of ~4. The industrial concentrate, used in this work, was an auriferous bulk pyrite-arsenopyrite flotation concentrate from Olympias Chalkidiki commercial plant, which was considered as a problematic "waste" due to its arsenic content [41]. The separation was further enhanced by the use of methyl isobutyl-ketone as a frother; a synergism of the surfactants was noticed. Based on the experience achieved in the Hallimond tube experimentation, a flotation separation test was designed using a conventional laboratory flotation cell.

In a strongly acidic environment, pyrite was positively charged or about neutral; with the addition of the collector alone, the zeta-potential of pyrite shifted to more negative values and pure arsenopyrite had similar behaviour. Figure 5 shows the comparison of the measurements, while permanganate was also added as modifier.

Arsenopyrite displayed a greater shift at pH range from 3-4 with the addition of collector, indicating stronger interactions with the collecting species. An Eh-pH equilibrium diagram of manganoferous species was also shown in [41]. The manganese oxides are expected to precipitate on the mineral surfaces where the redox process takes place, mainly that of arsenopyrite, altering its surface features.

A possible utilization of an industrial by-product such as iron sulphide, as discussed in the previously, may be as an adsorbent/solid substrate material, which may be followed by their (dissolved-air) flotation as the scavenging mechanism [42]. Copper, among other heavy metals, is a common toxic ion encountered in many dilute leach solutions, spent process streams and liquid effluents in industry. A copper ionic equilibrium diagram was also published. A further aim of that paper was the transfer of mineral processing know-how to environmental technology and vice versa. Ideally, fine mineral particles should be produced only for the purpose for the liberation of valuable materials from gangue minerals.

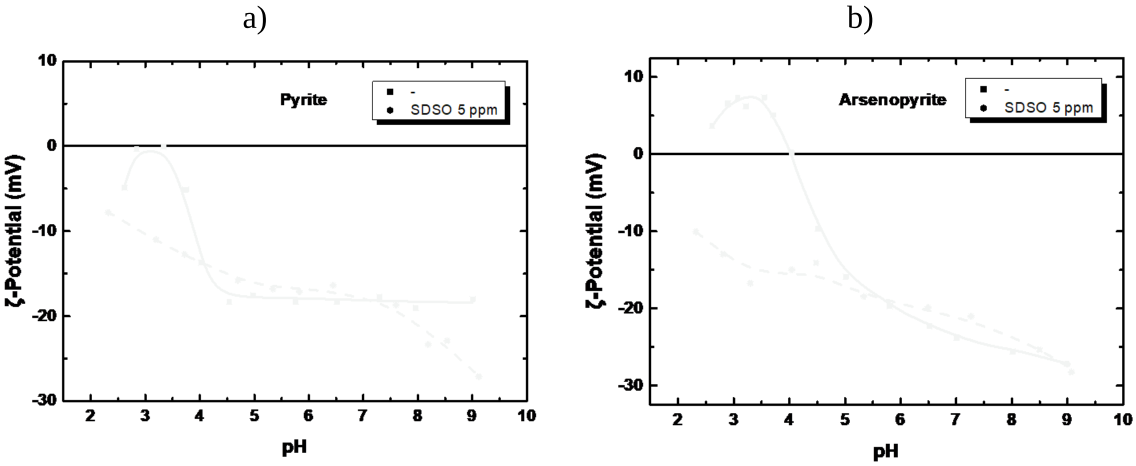

Figure 5 Zeta-potential of modified iron sulphides (with 5 mg/L $KMnO_4$) in the presence and absence of collector dodecyl-sulphonate. Results reprinted with permission, following modification from Kydros *et al.* [41]

The respective electrokinetic measurements, illustrated in Figure 6, had applied increased quantities of copper ions. A reversal of zeta-potential of pyrite was observed around the neutral and slightly alkaline pH region, which was due to the coverage of the mineral surface by hydrolysed copper cationic species. A surface-induced hydrolysis reaction mechanism was suggested. A detailed analysis in the phenomenon of interfacial precipitation was done by Hunder [43].

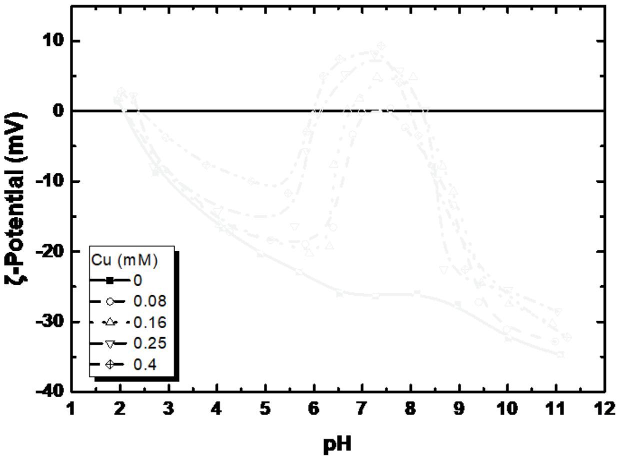

Figure 6 Zeta-potential measurements of pyrite in the presence of copper ions. Reprinted with permission, copyright Taylor & Francis [42]

In another environmental study [44], chromium oxyanions were the target. The latter, particularly in its hexavalent form, is a known highly toxic priority pollutant, used in industry as strong oxidant. A computer-assisted calculated speciation diagram for trivalent chromium was published, too. As shown in Figure 7, in presence of chromium, an excessive positive surface charge of pyrite was observed, indicating a reduction process, since Cr(VI) exists in aqueous solution only as anionic species. For reasons of illustration, the behaviour of chromium hydroxide precipitate ($5\cdot10^{-2}$ M) is also presented. The resulted hydroxo-Cr(III) species were found to be precipitated and removed onto the pyrite particles.

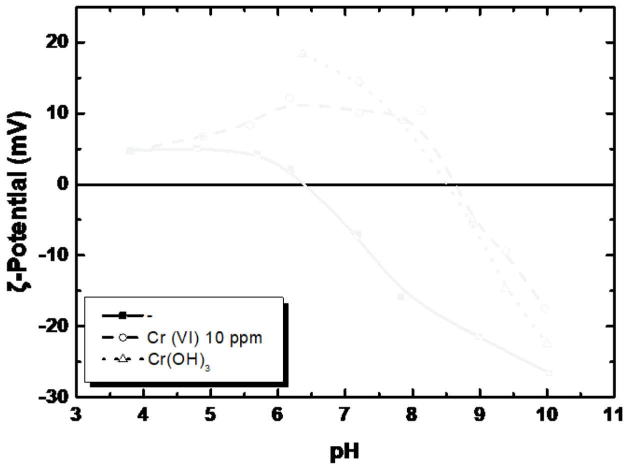

Figure 7 Zeta-potenlial studies of the system Cr(VI)/pyrite and also of chromium hydroxide precipitate ($5 \cdot 10^{-2}$ M dispersion); KNO_3 was applied as conductivity regulator. Reprinted with permission, copyright Elsevier [44]

A comparison between the two removal processes, namely the traditional reduction-precipitation and the present one, was briefly given [44]: (i) conventional reduction-precipitation (use of costly chemical reagents for Cr(VI) reduction and pH control, two-stages process, removal of Cr(III) species only in alkaline pH values (9-10)); (ii) using pyrite fines (-45 μm) (use of an industrial solid waste, possibilities for its reuse, one-stage process, removal of Cr(III)-species even in acidic pH values (4-6)).

5. FINE PARTICLES

In mineral processing, with the increasing demand for minerals, continuously diminishing ore grades and various economic pressures (cost of fuel, energy, etc), the problem of fines processing is becoming more important. Will the field succeed to pass the crossroads [45]? There are numerous examples of processing systems in which the ore must be deslimed, as the conventional separation methods are inadequate in the sub-sieve range. Understanding the limits of fine particle flotation is the key to the selective separation of fine mineral particles. Fine particles have low collision efficiencies with gas bubbles and float slowly. A decrease in the bubble size can increase the bubble–particle attachment efficiency. These factors also increase the flotation rate and recovery of fine particles. Of course, there are drawbacks, such as low rising velocity, long flotation times, etc. - as it might be expected [46].

It was stated that there has been a large body of experimental evidence showing that bubble–particle collection efficiency increases with decreasing bubble size. The published studies concerning the effect of bubble size on flotation of fines are rather limited, in comparison with those on particle size. For instance, in Newcastle, Australia, the flotation rate of fine particles was found to be strongly affected by the bubble size; an increase of up to one hundred-fold was observed when the bubble size was reduced from 655 to 75 μm [47]. In a classical handbook, in fact Volkova and Eigeles [48] were certainly one of the first scientists proposing that fines can be collected more effectively by finer bubbles.

The behaviour of bubble clusters in a well-controlled turbulent flow was also examined [49]. An early work presented plant-site evaluations of six different feeds comprising very fine particles (80% passing sizes 8-23 μm). Five of the streams contained mainly sulphides, and one contained oxide minerals. The testwork was performed using pilot-scale columns. For each stream, column metallurgical performance was compared with plant and laboratory mechanical cells. Column results were better [50]. In wastewater treatment, centrifugal flotation systems have been applied; hydrocyclone mixing was also combined with small dissolved-air flotation bubbles, leading to the development of a hybrid technique [51].

Dissolved-air flotation of magnesite ($MgCO_3$) and dolomite $\{CaMg(CO_3)_2\}$ fine particles was undertaken (using a jar tester by Aztec, UK), in the presence of modifiers (such as carboxymethyl cellulose, sodium hexametaphosphate and sodium pyrophosphate) for their selective recovery with promising results [52]. These two salt-type minerals are by nature hydrophilic; they have the same crystal structure, similar surface characteristics and flotation properties. Salt-type minerals are slightly soluble in water and in aqueous dispersion, ions are transferred to solution and then further hydrolysed, changing the pH. A differential gravimetric bubble separation method has been used for the estimation of the bubble size distribution in dissolved-air flotation [53].

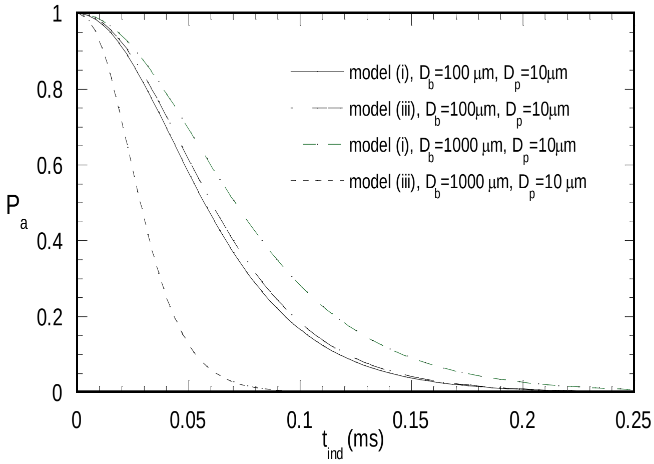

Figure 8 Attachment efficiency, P_a, from models (i) and (iii) versus induction time, t_{ind}, for several pairs of bubble and particle diameters. Reprinted with permission; copyright Elsevier [55]

Inside flotation machines, the operation takes place in a highly turbulent flow [54]; it should be noted that in mineral processing usually there is a larger amount of heavier particles compared to wastewater treatment. Despite the significance of turbulent fluid motion for enhancing the flotation rate in several industrial processes, there is no unified approach for the modeling of the flotation rate in a turbulent flow field [55]. The attachment efficiency computed by two models are shown versus the induction time for two pairs of particle and bubble diameters in Figure 8; where typically, the efficiency P consists of two components (i.e. $P = P_cP_a$), the first (P_c: collision efficiency) expresses the probability of the particles and bubble colliison. Model (i) was a modification of the classical Yoon-Luttrell [56] approach by King [57], and model (iii) was developed by Nguyen [58]. As expected the attachment efficiency (i.e. the probability of the collided particle to drain the thin liquid film and eventually aggregate with the bubble) decreases as the induction time (being a parameter which collectively includes all physicochemical interactions between a bubble and a particle) increases since the time spent by the particle on the bubble surface is not enough for permanent attachment. For small bubbles, where the Reynolds number for the flow around a bubble is small, the predictions of the two models for P_a were very close.

Inverse gas chromatography has been recently studied as a method to determine specific surface free energy components and their distributions of particulate surfaces; the latter being a more fundamental flotation parameter, related to the contact angle via Young's equation [59]. A first principle model was developed to predict flotation from both surface chemistry and hydrodynamic parameters (such as bubble size, particle size, energy dissipation rate, contact angles, etc.) [60]. Very small bubbles, which partially coat the surface of particles, influence if heterocoagulation between a particle and a bubble occurs [61]. Research on the mechanisms of particle-bubble interaction provided valuable information on how to improve the flotation of fine (and coarse particles) with novel flotation machines, which provide higher collision and attachment efficiencies of fine particles with bubbles and lower detachment of the coarse particles [62]. Attention is always required to differentiate, perhaps due to turbulent flow currents, between true flotation and entrainment in the flotation of submicron particles by fine bubbles [63].

6. OBITUARY

Finally, the first time one of the authors (KAM) met with Prof. Zoran Markovic was in 2002, actually twice that year: first time during an international conference in High Tatras, Slovakia and second time in Bor, during one of the October conferences that he organized - the latter was after seeing the ruins in Belgrade, due to the bombing of Yugoslavia. Two more meetings followed, in 2004 in Bor (36th Conf.) and at the XXIII IMPC at Istanbul, as well as our communication with regards to his Journal. Zoran had solid background in Mining and Metallurgy, with an extensive theoretical knowledge, a he was hard-working, intelligent and dedicated scientist/engineer and member of academic staff; a nice character. We were really shocked by his death. May he rest in peace.

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Chapter 4

ASPECTS OF INVESTIGATIONS IN PHYTOREMEDIATION

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ABSTRACT

Worldwide problem of soil pollution with contaminants emitted from the industrial facilities or resulting from disposal of solid waste, requires development of various environmental remediation methods. The best known are phytoremediation techniques such as phytostabilization and phytoextraction, based on the immobilization and extraction of metals/metalloids by plants, respectively. All aspects of scientific investigations in this area rely on the principles of natural interactions between plants and soil components, as well as on the adaptation mechanisms of plants under the increased concentrations of metals/metalloids in soil. Multidisciplinary approaches, and more stringent assessment of the overall criteria established in the scientific researches, must be employed in the process of determining the suitability of plants for use in phytoremediation. The values of Biological factors, certain contents of metals/metalloids in the aboveground plant parts, and plant–soil relationships defined by statistical data analyses, should be simultaneously considered. Phytoremediation techniques in the conditions of natural environment are not commercialized, so improvement of phytostabilization and phytoextraction by various inorganic and organic amendments is of great interest. According to the scientific findings, plants as natural resources could have a great potential for use in green technologies for reduction of soil pollution.

Keywords: Metal, Metalloid, Phytoremediation, Phytostabilization, Phytoextraction, Soil pollution

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1. INTRODUCTION

The presence of polluting substances in the environment affects the ecological stability, and disrupts natural balance of basic life resources. According to the Directive 2004/107/EC and available scientific data, arsenic, cadmium, nickel, as well as some polycyclic hydrocarbons belong to the human genotoxic carcinogens, and there is no minimum concentration below which these substances do not cause adverse effects on human health [1]. One third of the total arsenic content in the atmosphere originates from the smelting of sulphide ores of copper, and that's why this metalloid poses the biggest threat to the environments around the facilities for pyrometallurgical copper production [2–9]. Continuous monitoring, assessment of the limits of transmission, understanding of the biogeochemical cycles of polluting substances, and primarily preventing their occurrence and emissions into the environment, are thus necessary [10,11].

Aboveground parts of plants are in constant interaction with the polluting substances in the air, and their roots with the polluting substances in the soil. The ability of plant species to uptake metals and metalloids from the soil, ensures the basic metabolic functions, but in specific conditions provides their usage in phytoremediation [12]. Plants that grow on naturally metal–enriched soils tend to be genetically tolerant to high metal concentrations, have an excellent adaptation abilities to extreme environmental conditions, thus having the potential for phytoremediation [13–16]. Fernández *et al.* [17] found that the abandoned mining areas could be an important reservoir of a large number of plant species with high potential for phytostabilization or phytoextraction of metals and metalloids from contaminated soil. Also, the use of metal–tolerant and acid–tolerant species in combination with amendments resulted in a rapid and effective revegetation of metalliferous and sulphide–bearing mine wastelands [18]. Grobelak and Napora [19] suggested that remediation activities applied to large–scale areas contaminated with heavy metals should mainly focus on decreasing a degree of metal mobility in the soil profiles and metal bioavailability to non–phytotoxic levels.

The most studied techniques of phytoremediation are phytoextraction and phytostabilization. Phytoextraction is based on the decreasing of metals and metalloids concentrations in soil, or on their complete removal, by absorption in plants. The effects of various amendments for improving phytoextraction technique were studied by many authors [20–24]. Specific substances in the soil can be immobilized by phytostabilization, which prevents their further distribution to other components of the environment [25]. Chemophytostabilization is a process by which soil amendments and plants are used to immobilize metals [19]. It is interesting that depending on the used soil additives, the same plant species could be used for phytoextraction or phytostabilization, as shown in the study by Lambrechts *et al.* [26]. However, Smolinska and Rowe [22] emphasize that potential risk of using the inorganic additives for phytoremediation should be considered.

During the examination of phytoremediation, it is necessary to understand the mechanisms of absorption, translocation and accumulation of metals and metalloids in the plants, which may be achieved only by interdisciplinary approach to the problem [25].

Solar energy is a driving force for functioning and survival of the plant world. Because of that, biomonitoring and phytoremediation belong to „green technologies“, whereby plant material presents ecologically safe and cost–effective resources.

Enell *et al.* [27] pointed out that phyto–technologies do not have widespread usage in practice, and there is a clear requirement of field studies that could provide information on success and failures.

2. PRINCIPLES OF NATURAL INTERACTIONS BETWEEN PLANTS AND POLLUTING SUBSTANCES IN SOIL

Plants have specific and effective mechanisms for nutrients uptake from the soil. However, the same mechanisms are used for uptake, translocation and accumulation of toxic elements whose chemical properties correspond to the chemical properties of essential elements [28]. Uptake of nutrients takes place through complex interactions on the interface soil–roots. Nutrients pass through the cell membrane into the root cells by the active and passive transport. Passive transport is based on the ion diffusion through cell membrane, from the area of higher (soil solution) to the area of lower concentrations (root cells). However, transport through cell membrane, which takes place from the area of lower to the area of higher concentrations with spending of metabolic energy, belongs to active transport [29]. Plants uptake all the elements by passive transport, when biological and structural functions of root cells are disrupted under the concentrations of elements higher than the required [30].

After absorption in plant roots or leaves, nutrients and polluting substances are transported to other plant parts, by the same physiological processes. Main processes of transport are: 1) Transpiration flow: transport of water and dissolved substances from roots to aboveground parts through xylem; 2) Assimilation flow: transport of assimilates and dissolved substances from the leaves to the plant parts below (root) or under (fruit) the leaves through phloem [31].

Transpiration or evaporation of water from the surfaces of leaves is a diffusion process, whose driving force is kinetic energy of water molecule and gradient of water potential in a plant–air system [31]. Plants with a large biomass transport larger quantities of soil solution, thereby transporting the nutrients and toxic elements through a plant. During the transpiration, plants give off water in the form of steam and volatile substances into the environment. Polluting substances from the soil solution are also uptaken and sequestrated, metabolized or evaporated from leaves together with the water, during the transpiration process [28,32]. Some plant species have the ability to increase the intensity of translocation from the roots to the aboveground parts, by increasing the transpiration intensity [33]. Baltrėnaitė *et al.* [34] suggested that deciduous trees have a much higher intensity of transpiration than evergreen trees. Also, these authors determined more intensive translocation of metals through the trees with more intensive transpiration.

The efficiency of uptake, translocation and accumulation of elements from soil in plants depends on the physico–chemical properties of the soil (pH, soil organic matter content, cation exchange capacity, etc.), characteristics of plants (the depth of the root, plant species, age of plant, etc.), form of metal or metalloid (oxidation state, solubility, etc.) interactions with the microorganisms in the soil, climatic factors and many more [30,34–35].

Mobility of metals in soil is related to their toxicity, and depends upon the pH value of soil, particulate size and formation of secondary minerals [36]. Conesa *et al*. [37] found that liming increased pH of the soil solution from 2.9 to 5.5, reduced the content of dissolved salts by more than 75%, and decreased concentrations of soluble metals, resulting in lower metal accumulation in shoots.

Quantity of uptaken metals depends more upon the concentrations of their bioavailable forms in greater extent than on the total concentrations in soil [38]. Bioavailable quantity of a metal is the content in soil which can interact with any part of cell of a living organism [39]. Metal ions which are in a soil solution (in the form of ions, chelates or complexes) have the highest bioavailability, while metal ions which are precipitated have the lowest bioavailability [30,40]. Bioavailability of metals decreases with the increase of cation exchange capacity, organic matter content, content of clay, pH value of soil solution [38,41–42]. Bioavailability of divalent cations for plant roots increases in slightly acid soils, and decreases in alkaline soils due to precipitation in the form of insoluble hydroxides [43]. Results of both greenhouse and field experiments by Li *et al*. [44] indicated that Ni uptake by two *Alyssum* species was reduced at lower soil pH and vice versa. This is contrary to the abovementioned facts. At higher pH, plant yield was also improved. Regarding the bioavailability in soil, three categories of metals/metalloids can be distinguished: readily (Cd, Ni, Zn, As, Se, Cu); moderately (Co, Mn, Fe) and least bioavailable (Pb, Cr, U) [25]. Li *et al*. [45] concluded that plant uptake of Cd and Zn from the soil, caused a decrease in concentrations of these metals in the acid–soluble fraction followed by reducible metals. In their research, oxidisable and residual fractions of Cd and Zn were less available to plants. Plants can increase the bioavailability of metals in soil, by releasing the chelating compounds (phytochelators/phytosiderophore) into rhizosphere, whereby metals are chelated and transformed into the soluble forms. Formation of metals chelating complexes prevents precipitation and sorption, keeping their bioavailability to the required level. Plants can release specific phytochelators as a response to a metal deficit, increasing their bioavailability, which was observed in the case of Fe, Al and Zn [46–49]. Dago *et al.* [50] found that Cd was the most potent inducer of phytochelatins by *Hordeum vulgare*. The main conclusion of these authors was that phytochelatins are induced at different rates depending on the used metal stressor. Increasing of rhizosphere acidity and exudation of carboxylates is one more strategy by which plants increase bioavailability of metals [46–49]. Increasing of rhizosphere acidity is achieved by roots secretion of H^+ ions which replace metal cations adsorbed on the soil particles, whereby concentration of metal ions in soil increases. Capability of plants to uptake a certain metal by roots is increased in this way. Root secretions can decrease the pH value of rhizosphere by one or two units, compared to pH value of the surrounding soil [25]. However, decreasing of pH soil solution can lead to the uptake of metal in concentrations which are phytotoxic [51]. Qasim *et al.* [52] found that rhizosphere soil of poplar (*Populus euramericana* Dorskamp) had a higher pH than the bulk soil, which was the effect of root exudates. Plants have the ability to decrease metals bioavailability and simultaneously to immobilize metals in the root zone. This can be achieved by facilitating formation of a poorly soluble metals compounds (as sulphides, or carbonates ions) by precipitation, by binding metal complexes, by sorption of metals to the surface of the root or inside the roots [49,53].

Doumett *et al.* [54] investigated distribution of Cd, Cu, Pb and Zn between contaminated soil and the tree species *Paulownia tomentosa* in a pilot–scale assisted phytoremediation study. They found that the metal uptake and translocation were not mainly dependent on the content of bioavailable fractions. Also, predominant mechanism for metal accumulation was not the concentration gradient between soil and plant tissues. The plant had a great role in the selection of the metal complexes that were taken up and translocated. According to their opinion, this selection might be based on the structure and the dimensions of the ligand. Lambrechts *et al.* [26] also showed that soil heavy metal mobility and plant uptake were not systematically positively correlated. Enell *et al.* [27] concluded that the growth rate of willow clones on the brownfields depended on the soil texture rather than the contamination level of these sites. Also Li *et al.* [45] found that the coarse soil particles played the most important role in phytoextraction.

Microorganisms (bacteria and fungi) are present in the rhizosphere, and some of them can establish a symbiotic relationship with the plants. According to that, microorganisms can be divided in two groups: 1) microbes which affect the bioavailability and mobility and also the quantity of metals which plants uptake and 2) microbes which improve adaptive ability, releasing the substances which stimulate plant growth. Microorganisms affect bioavailability and movement of metals in soil, by changing pH of soil solution, forming metal chelates, participating in redox reactions, whereby oxidation state of metals is changing, by adsorbing metals. Chelators form complexes with metals, whereby unavailable forms of metals/metalloids become available for the uptake by microorganisms, and indirectly by plants. Adsorption of metal ions on microorganism cells lead to the decreasing of their bioavailability to plants [55]. Symbiotic association of fungi can increase root surface for absorption and stimulates uptake of nutrients including metal ions [47].

2.1. Mechanisms of plant reactions to the increased concentrations of metals/metalloids in soil

Plants use specific defense strategies for tolerance and detoxification, when they are facing stressful conditions, caused by high concentrations of heavy metals, in order to achieve the natural balance (Figure 1).

The first stage of reaction on metal intoxication is avoidance of stress. That can be achieved by controlling the quantity of metal which is uptaken from soil, or by exclusion which relies on the prevention of the root uptake of metals from soil. If these strategies fail and heavy metals are translocated through the plant organs, mechanisms of tolerance for detoxification are being activated. These mechanisms include: sequestration and compartmentalization of metals in different intracellular spaces (vacuoles), transport of metal ions, metal binding to the cell walls, intracellular complexation or chelation of metal ions by secreting certain substances like organic acids, polysaccharides, phytochelatins and metallothioneins. If these processes are not effective, and concentrations of heavy metals in plant tissues become too high, antioxidant defense mechanisms are activated [43,56].

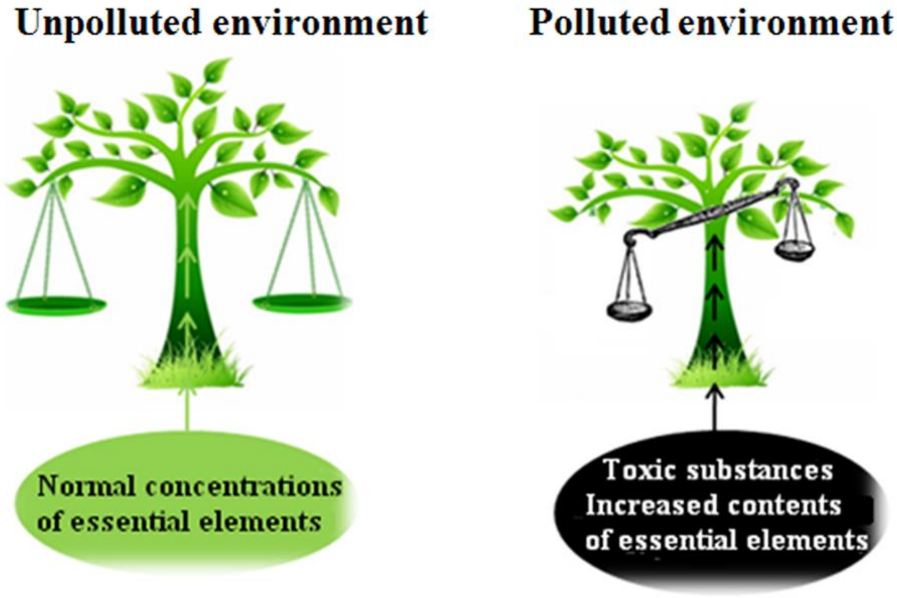

Figure 1 The position of natural balance in plants in unpolluted and polluted environment

Heavy metal stress induces changes in calcium levels, kinase activity and subsequent changes in gene expression. Survival and adaptation strategies of a plant faced with toxic ions are based on the changes in gene expression which initiate survival and adaptation strategies, including plasma membrane exclusion to protect the cytosol as well as chelation and sequestration in the vacuole [57]. To protect the cellular components from oxidative damage by metal contamination, biological systems have developed enzymatic and non–enzymatic antioxidant mechanisms. Another detoxification mechanisms produced in plants are osmoprotectants, which are the compatible solutes which maintain a favorable water potential gradient and protect cellular structures from toxic ions [58].

Baker [59] was among the first researchers who established the classification of plant species on the excluders, indicators and accumulators/hyperaccumulators, according to the mechanisms by which they react to the increased concentrations of metals in soil. In the conditions of a large range of metal concentrations in soil, metal concentrations are constant in aboveground parts of excluders. When certain concentration in soil is exceeded, mechanism of exclusion is disrupted, which leads to the undisturbed transport through a plant. Content of metals in aboveground parts of indicators are in accordance with metal contents in the surrounding environment. Indicators are nowadays more and more implemented in the studies of air pollution, and not only in the assessment of soil pollution [60–64]. Accumulators concentrate metals in aboveground parts both in the conditions of high and in the conditions of low levels of metals in soil [51,59,65].

Hyperaccumulators are the subgroup of accumulators, and are usually endemic species, which grow in the natural mineralized soils, uptaking high amounts of metals in their foliar parts, without toxic symptoms [51]. Typical hyperaccumulators have low biomass and grow more slowly than majority of plants [66].

By examinations in controlled conditions hyperaccumulators were defined only for Ni, Zn, Cd, Mn, As and Se. Hyperaccumulators of Pb, Cu, Co, Cr and Tl were not recognized in such conditions. Determining whether a certain plant has properties of a hyperaccumulator should not be based on the analyses of the whole plant or its underground parts because we cannot be sure if the soil particles are completely removed, and plants which immobilize metals in a root system are very common, so active accumulation in the aboveground parts is a much better indicator of hyperaccumulation [67]. According to Van der Ent *et al.* [67], aerial parts i.e. leaves should be used for defining hyperaccumulators, and studies need to be based on plant organs, and not on plant tissues. Also, accumulation should be regarded only on active accumulation inside leaves from roots, and not on the passive accumulation through atmospheric deposition on the leaves.

Van der Ent *et al.* [67] suggested that plants could be considered as hyperaccumulators if concentrations of a certain element in leaves from the polluted areas are 20–30 times higher than in the leaves from the unpolluted areas, and concentrations of a certain element in leaves from the polluted areas are at least one order of magnitude higher than in the leaves of a plant from the metalliferous soil.

3. DETERMINING THE SUITABILITY OF PLANTS FOR USE IN PHYTOREMEDIATION

Studies of phytoremediation are multidisciplinary and should be based not only on the soil chemistry, biology of plants, ecology, soil microbiology, but also on the environmental engineering [25]. Phytoremediation is classified into “green technologies”, wherein the plants as profitable resources, serve for the remediation of polluted soils with metals and metalloids [12,28,51,68]. Phytoremediation techniques include: phytoextraction, phytofiltration (rhizofiltration, biofiltration), phytostabilization, phytovolatilization, phytodegradation (phytotransformation) [69–71]. Phytoremediation of soil polluted with metals and metalloids is based on the two best known techniques and these are phytostabilization and phytoextraction [72–73].

Figures 2 and 3 show the number of published scientific studies on phytostabilization and phytoextraction, respectively, as well as the research areas of the published articles, according to the scientific base Scopus. Total number of publications about phytoextraction amounted to 2,255, which is a far greater number compared to the total number of the published researches about phytostabilization (794). The area of research with the highest number of published studies is Environmental Sciences for both phytostabilization and phytoextraction.

During the process of phytostabilization, bioavailability of metals is reducing, while phytoextraction leads to the reducing of metal or metalloid concentrations in soil or to their complete removal [74]. The process of phytoextraction can be used for remedial purposes (phytoremediation), or potentially for economic profit (phytomining or phyto−reclamation). Although a promising technique, phytoextraction has yet to see significant commercialization A key factor for successful phytoextraction is that the value of the extracted metal needs to exceed the cost of the recovery method [75]. According to some opinions, in large areas of soil contaminated by very high concentrations of several metals/metalloids, phytoextraction is not an option, and phytostabilization is a viable consideration [76].

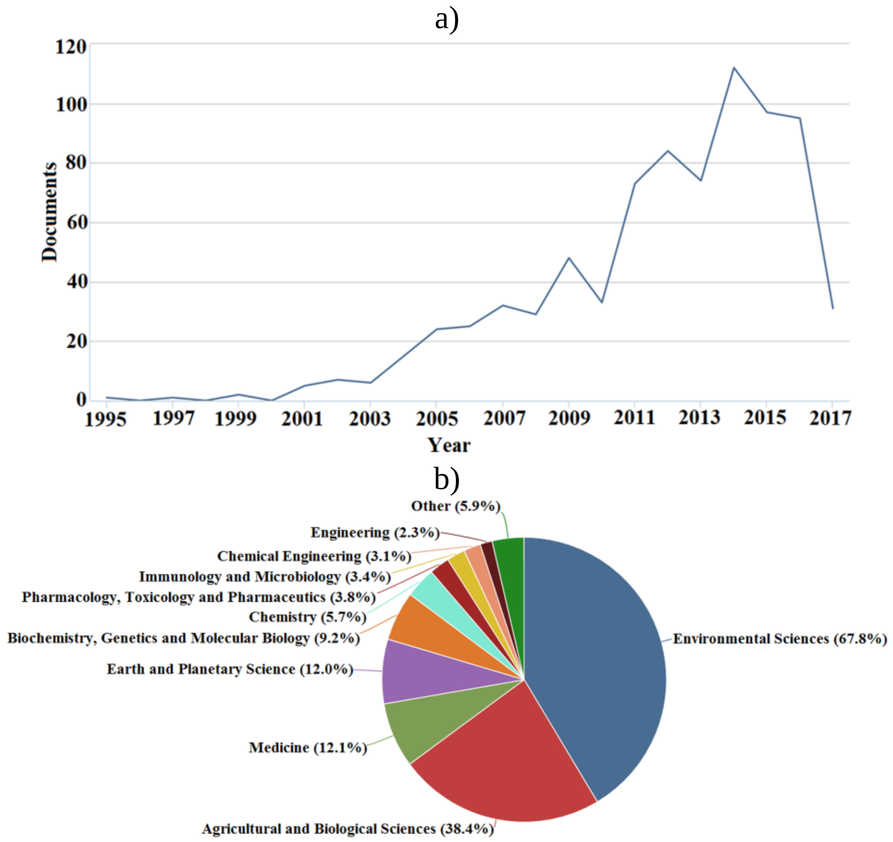

Figure 2 Published investigations about phytostabilization a) Number of publications; b) Published investigations according to the research areas (Data from 1995 to 6 April 2017)

Uptake and translocation of metals and metalloids by plants was usually examined in controlled and real conditions. It is much easier to analyze and interpret experimental results. Nevertheless, examinations on plants which grow in natural environments give more realistic insight in the interactions of polluting substances and biota [64,77].

Possibilities of using certain plant species in phytoremediation are defined in scientific literature according to the Bioaccumulation factor for roots and/or leaves (BAF_{roots}, BAF_{leaves}), Translocation factor (TF), as well as comparing the element concentrations in leaves with concentrations defined for plants hyperaccumulators or excluders (Table 1) [17,53,59, 67,78,79]. It is very important to indicate that the use of element concentrations in washed plant parts for calculating the above–mentioned factors is the most appropriate. Otherwise, the interpretation of the results could be incorrect [17,77].

The value of Bioaccumulation factor is usually calculated for roots and washed leaves according to the Eq. 1 and 2, respectively [59]:

$$BAF_{roots} = \frac{C_{roots}}{C_{soil}} \tag{1}$$

$$BAF_{leaves} = \frac{C_{leaves}}{C_{soil}} \tag{2}$$

where C_{roots} is concentration of a certain element in roots and C_{soil} is concentration of a certain element in soil, C_{leaves} is concentration of a certain element in leaves.

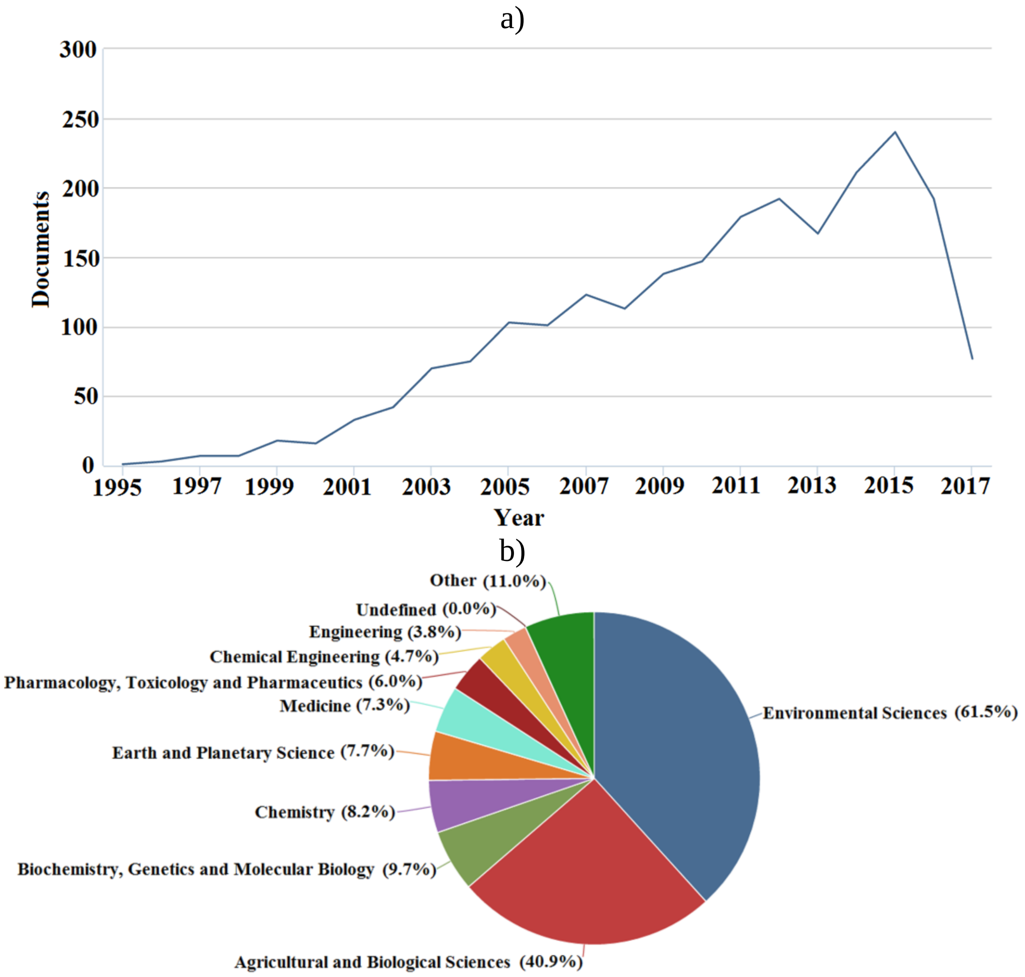

Figure 3 Published investigations about phytoextraction a) Number of publications; b) Published investigations according to the research areas (Data from 1995 to 6 April 2017)

The values of BAF_{roots} and BAF_{leaves} indicate the efficiency of a plant to absorb the analyzed elements from soil into its roots and leaves, as well as the possibility of using certain plant species in phytoremediation. Depending on these values, absorption was classified in the following way: 10–100 intensive absorption, 1–10 strong absorption, 0.1–1 intermediate absorption, 0.01–0.1 weak absorption, 0.001–0.01 very weak absorption [80–81]. The values of these two factors >1, suggest that plants could be used in phytoextraction. Calculations by Robinson *et al.* [82] reveal that plants with the Bioaccumulation factors >10 should reduce the total metal concentration in soil by 50% within 25 years, under conditions that are ideal for phytoextraction.

Translocation factor (TF) is calculated according to the Eq. 3:

$$TF = \frac{C_{leaves}}{C_{roots}} \tag{3}$$

The values of the Translocation factor <1, indicate limited translocation of elements from roots to leaves, which is characteristic of excluders that could be used in phytostabilization. Efficient translocation of elements from roots to leaves defines the values of Translocation factor >1.

Table 1 General characteristics of plants that could be used in phytostabilization or in phytoextraction

Ratio	Phytoextraction	Phytostabilization	Reference
$\frac{[\text{aboveground plant part}]}{[\text{soil}]}$	>1	<1	[53]
$\frac{[\text{aboveground plant part}]}{[\text{root}]}$	>1	<1	
Concentrations in the aboveground plant parts (mg/kg)			
As	≥1,000	≤30	[53]
Cd	≥100	≤10	
Cu	≥1,000–5,000	≤40	
	300		[67]
Mn	≥1,000–10,000	≤2,000	[53]
	≥10,000		
Pb	≥1,000–10,000	≤100	
Zn	≥10,000	≤500	
	≥3,000		
Se	≥100	/	[67]
Co	≥300		
Co	1,000		[47]
Cr	≥300		[67]
Ni	≥1,000		

Significant shortcomings of researches about phytoremediation are based on the incomplete analysis of the obtained results. One of the more comprehensive approaches to the data analysis should be based on the assumption that some criteria are simultaneously fulfilled: aboveground plant parts contain concentration of a certain element defined for the plants hyperaccumulators, $BAF_{roots}>1$, $BAF_{leaves}>1$ and $TF>1$. According to these terms, a plant could be considered as a hyperaccumulator, i.e. could be used in phytoextraction.

If the values of BAF_{roots}, BAF_{leaves} and TF are <1, then a plant has characteristics of an excluder, whereby it should not be disregarded that these plants, however, uptake enough contents of essential elements for the proper functioning of its primary metabolic functions. Excluders can accumulate higher concentrations of a certain element in their roots than in other parts, but translocation to the aboveground parts is limited. These characteristics are also important for the use of plants in phytostabilization. Criteria such as $BAF_{roots}>1$ and $TF<1$ for defining excluders was used by Mahdavian *et al.* [72]. Some researches indicate that calculating the abovementioned relations is not enough to reach the conclusion about the way of uptake and translocation efficiency of metals in plants. Therefore, statistical data analyses like correlation between element concentrations in a plant part and soil, as well as between concentrations in plant parts, were additionally applied [17]. Maisto *et al.* [83] confirmed that the values of Enrichment factor (element concentration in a plant part or soil from a polluted site divided by element concentration in a plant part or soil from the unpolluted site) were higher for leaves than for soil samples. Such results pointed out higher contamination originating from atmospheric deposition than from the soil.

The results of some recent findings about the potential plants that could be used in the natural phytostabilization and phytoextraction are given in Table 2.

Table 2 Potential plant species for phytostabilization and phytoextraction–recent findings

Phytostabilization	**Element**	**Reference**
Ruellia paniculata L., *Combretum leprosum* M.	Cu	[49]
Quercus virginiana	Cd, Pb, Zn	[84]
Salix viminalis, *Salix purpurea*	As, Sb, Pb	[85]
Populus euramericana Dorskamp	Zn, Pb, Cd	[52]
Atriplex atacamensis, *Atriplex halimus*, *Atriplex nummularia*	As	[86]
Holcus lanatus, *Dittrichia viscosa*, *Lotus corniculatus*, *Plantago lanceolata*	As	[87]
Spiraea media Schmidt	Cu	[14]
Karelinia caspica (Pall.) Less	Cd	[14]
Nonnea persica, *Achillea wilhelmsii*, *Erodium cicutarium*, *Mentha longifolia*	Pb, Zn	
Ferula assa–foetida	Pb, Zn, Ag	[72]
Spartina pectinata	Zn	[88]
Phytoextraction		
Coincya monensis	Zn (3,391.31 mg/kg)	[17]
Ageratina sp., *Achyrocline alata* (Kunth) DC., *Cortaderia hapalotricha* Pilg., *Epilobium denticulatum* Ruiz & Pav., *Taraxacum officinale* Weber, *Trifolium repens* Walter	Pb (>1,000 mg/kg)	[13]
Ageratina sp., *Epilobium denticulatum*	Zn (>10,000 mg/kg)	[13]
Pteris vittata L.	As (4,106 mg/kg)	[89]
Viola principis H. de Boiss	Cd (1,201 mg/kg), Pb (2,350 mg/kg), and As (1,032 mg/kg)	[89]
Erigeron canadensis L.	Cd, Zn	[90]
Polygonum aviculare	Cu (>1,000 mg/kg)	[14]
Alyssoides utriculata	Ni (>1,000 mg/kg)	[91]
Hybrid giant Napier	Cd	[92]

3.1. Phytostabilization

During the phytostabilization process, polluting substances in soil are immobilized, absorbed and accumulated in roots without further translocation to the aboveground plant parts, adsorbed on the root surface, and/or precipitated in the root zone of a plant–rhizosphere. Plants used for phytostabilization could have the capacity for creating a binding condition for metals which will be adsorbed to soil particles and will be less available. These plants can also transform some toxic molecules in less toxic forms (e.g., Cr^{6+} to Cr^{3+}) [28,69,93,94]. By phytostabilization, leaching of metals from soil to the underground waters is reduced, as well as the intensity of erosion [31,95]. Plant species used in the process of phytostabilization have the ability to change soil pH, and thus reduce solubility and mobility of metals. Excluders are usually used for phytostabilization purposes [49]. Boisson *et al.* [96] indicated that the selection of plant species for phytostabilization purposes is crucial. Selected plants should have specific characteristics in order to be used in phytostabilization. They should grow under site conditions, to be native and grow quickly. Dense root and shoot systems preventing heavy metal dispersion by water and/or wind erosion are also important, as well as a large quantity of available propagules. Allowing the implementation of phytostabilization on a large scale could be preferentially attained by seed reproduction. Heckenroth *et al.* [97] concluded that a century of soil pollution with metals/metalloids had lead to a significant correlation with plant community dynamics in terms of composition, diversity and structure, causing the co–occurrence of different plant succession stages.

The goal of phytostabilization is (re)establishing a vegetative cap using native plants that stabilize metals in the root zone with little to no translocation to shoots. Standard practice in reclamation of mine tailings is the emplacement of a 15 to 90 cm soil/gravel/rock cap which is then hydro–seeded [98].

Enell *et al.* [27] suggested that the use of bioenergy crops for phytostabilization on brownfields could contribute to preserving and improving ecosystem, as well as to creating economic regeneration of these areas. These authors found that cultivation of brownfields using willow clones reduced the ecological risks, improved the soil quality of the site and reduced the potential risks associated with distribution of metals in environment especially in the food chain.

Perlatti *et al.* [49] evaluated the biogeochemical processes occurring in the rhizosphere of *Pityrogramma calomelanos* L., *Biden pilosa* L., *Ruellia paniculata* L., and *Combretum leprosum* M., growing spontaneously in a copper contaminated soil in an abandoned copper mine site. The results of these authors suggested that the plants had greatly altered the physicochemical characteristics of the soil in the root zone. Slight alkalization in the rhizosphere of *P. calomelanos* and *C. leprosum*, was observed compared to the bulk soil, which was the reason of different distribution of copper. In the bulk soil, copper was mainly distributed in three fractions: carbonates, noncrystalline iron oxides, and sulfides. The highest differences were in the rhizosphere of *R. paniculata* and *C. leprosum*. The concentrations of the more labile copper form (exchangeable) and also the copper associated with carbonates were significantly lower in the rhizosphere soil than in the bulk soil of these species. These results indicated that the plants *R. paniculata* and *C. leprosum* promote phytostabilization of copper in their rhizosphere zone, showing desirable characteristics for use in phytoremediation.

Shi *et al.* [84] conducted a pot experiment to evaluate the feasibility of using tree seedlings for the phytoremediation of lead/zinc mine tailings. Seedlings of *Quercus* spp. (*Q. shumardii*, *Q. phellos*, and *Q. virginiana*) and rooted cuttings of two *Salix* spp. (*S. matsudana* and *S. integra*) were transplanted into the pots containing 50 and 100% lead/zinc mine tailings. All species showed low metal translocation factors (TF). *Q. virginiana* showed the highest tolerance and a low TF, implying that it was a good candidate for phytostabilization of Cd, Pb and Zn in mine tailings.

Phytostabilization (by two willow species: *Salix viminalis* and *Salix purpurea*) of technosols (7,243 µg/L of As; 554.71 µg/L of Sb) from a former gold mining site presenting polymetallic contamination (As, Sb and Pb) was investigated by Sylvain *et al.* [85]. Different soil samples, representing mixtures of the litter and the technosol collected on the mined site and a non–contaminated control garden soil were investigated in a laboratory. Despite the high concentrations of metal/metalloid in technosol, especially As, both willow species were able to develop a root system and aboveground biomass. Biomass production of both plant species growing on the technosol was lower in comparison to the plants growing in the control garden soil. High biomass production of *S. purpurea* on the mixture of control garden soil and technosol, and high accumulation of metal/metalloid in root systems, indicated that this species could be used as a successful phytostabilization plant in the investigated conditions.

Qasim *et al.* [52] found that poplar (*Populus euramericana* Dorskamp) could be used for phytostabilization of technosols contaminated with Zn, Pb and Cd, at the former metallurgical site occupied for over 60 years. The pH value of rhizosphere soil pore water was increased by 0.1 to 0.6 units compared to bulk soil. Concentrations of dissolved organic carbon also increased irrespective of soil type or total metal concentrations compared to the bulk soil. Plant growth reduced the solubility of Zn, Pb and Cd due to increases of pH or by complexation of heavy metals with dissolved organic carbon (effects of root exudates).

In the Chiu Chiu village (Atacama Desert, Chile), a high concentration of As in the soil is a result of natural causes related to the presence of volcanoes and geothermal activity [86]. Arsenic in these soils was a part of highly available fractions, which was attributed to the alkaline pH (8.6), low organic matter and iron oxide content, and sandy texture. Fernández *et al.* [86] found that *Atriplex atacamensis* (native for Chile), *Atriplex halimus*, and *Atriplex nummularia* accumulated higher levels of As in their roots than in the leaves, indicating a phytostabilization capacity. Despite the extreme conditions in these soils, the establishment of plants of the genus *Atriplex* seems to be a good strategy for generation of a vegetative cover that prevents the spreading of As through the soil or by wind.

Obeidy *et al.* [87] investigated the content of As in the rhizosphere of *Holcus lanatus*, *Dittrichia viscosa*, *Lotus corniculatus* and *Plantago lanceolata* grown in an alkaline soil naturally rich in As. These authors found that plant species induced consistent physico−chemical alterations in their rhizosphere that increased As concentration in the soil solution, but decreased As concentration in the easily exchangeable bound fraction on the solid phase. The major part of As (60%) desorbed from the exchangeable bound fraction was likely redistributed on the less available fractions on the soil solid−phase. A second part (35%) corresponded to the fraction of As taken up by plants. The minor part (5%) corresponded to As released in solution. The redistribution of a major part of As from the exchangeable bound fraction to less available fractions in soil could be a protective effect for the biota and the environment in the surrounding of As−rich soil. Obeidy *et al.* [87] highlighted that small but significant increase of As content in soil solution was, however a potential concern for the spread of As through plant uptake and leaching. de Melo *et al.* [99] observed very low root to shoot As translocation in castor beam growing under a range of As concentrations from to 5,000 μg/dm^3. Shoot and root biomass decreased, without severe toxicity symptoms. These authors suggested that castor bean did not have characteristics of a plant suitable for commercial phytoextraction, but could be useful for revegetation of As−contaminated areas.

Liu *et al.* [14] aimed to assess the extent of metal accumulation by 19 plant species found in two mine tailings area in Aletai in the northwest part of China. These authors used

Bioconcentration and Translocation factors in order to define the suitability of the analyzed plants for using in phytoremediation. Among plant species which Liu *et al.* [14] collected from the mining tailing of Cu–Zn and Pb–Zn mines, *Spiraea media* Schmidt was considered as the most effective species for phytostabilization of Cu (BCF=6.77; TF=0.74), and *Karelinia caspica* (Pall.) Less was most effective species for phytostabilization of Cd (BCF =1.38; TF=0.28).

Mahdavian *et al.* [72] investigated the suitability of 40 plant species which colonized a mining area in Yazd Province in Central Iran, for phytoextraction and phytostabilization. The main criteria for determining the suitability of plants for use in phytostabilization was high Bioconcentration factor (BCF>1), and low Translocation factor (TF<1). *Nonnea persica*, *Achillea wilhelmsii*, *Erodium cicutarium*, and *Mentha longifolia* were found to be the most suitable species for phytostabilization of Pb and Zn. *Ferula assa–foetida* was the most suitable species for phytostabilization of Pb, Zn and Ag at the same time.

Korzeniowska and Stanislawska–Glubiak [88] conducted the 2–year microplot experiments in order to assess the suitability of *Miscanthus*×*giganteus* and *Spartina pectinata* for using in Cu, Ni, and Zn phytoremediation. Soil samples were contaminated with Cu, Ni, and Zn in different doses. The results showed that *M.*×*giganteus* had lower tolerance to the soil contaminated with Zn, Cu and Ni, and *S. pectinata* had some potential for phytostabilization of Cu and Ni polluted soil. These authors suggested that because of both its high tolerance to Zn, as well as the ability to accumulate this metal in belowground organs and a small Zn transfer from the belowground to the aboveground organs, *S. pectinata* was very suitable to Zn phytostabilization.

3.2. Phytoextraction

Phytoextraction is achieved by sorption of metals inside root cells and by translocation to the aboveground plant parts. The most suitable plants for use in phytoextraction are hyperaccumulators, which can increase the bioavailability of metals and metalloids in soil [31,51,94]. Among the numerous factors that influence the phytoextraction efficiency of a particularly toxic element from polluted substrates (e.g., mining sludge, flotation tailings, or metalliferous soils), the selection of plants that can survive and effectively accumulate that element is essential. The most effective plant species are characterized by high efficiency in phytoextraction of elements, translocation to aerial parts, easy adaptation to the presence of pollutants, and relatively high biomass as well as simplified collection procedures for plant material after their growth [70]. Many studies of the phytoextraction had focused on the potential use of wild plants that spontaneously colonize the mining areas [13]. Fernández *et al.* [17] suggested that phytoremediation with native species is a low cost technique for recovering contaminated soils, avoiding ecological risks associated to the use of non–native species. About 400 plants are known to be hyperaccumulators, which represents <0.2% of all angiosperms, among which Brassicaceae is the family with the largest number of accumulator species [13,100]. Wan *et al.* [89] indicated that hyperaccumulators which could simultaneously extract multi–metals had been rarely reported.

Fernández *et al.* [17] characterized the species able to spontaneously germinate and survive on six ancient mining tailings from sulfide ore exploitations in the Austrian mountain areas under oceanic climate conditions. 118 samples of plants and the corresponding soils extremely contaminated with heavy metals/metalloids (Pb, Zn, As and Hg) were sampled. These authors identified *Coincya monensis* as a Zn hyperaccumulator with high soil–to–plant transfer factor for Zn (BAC=6.59) and the shoot Zn content of 3,391.31 mg/kg, which falls within the definition of Zn hyperaccumulator levels.

Bech *et al.* [13] analyzed accumulation of As, Cu, Pb and Zn patterns in wild species (i.e. *Ageratina* sp., *Achyrocline alata* (Kunth) DC., *Cortaderia hapalotricha* Pilg., *Epilobium denticulatum* Ruiz & Pav., *Taraxacum officinale* Weber and *Trifolium repens* Walter). Plant samples were collected from the Carolina mining area of Hualgayoc (Cajamarca, Peru), and were growing in a substrate polluted with As (810–1,029 mg/kg), Cu (256–2,070 mg/kg), Pb (3,992–16,060 mg/kg) and Zn (11,550–28,058 mg/kg). These authors found concentrations of Pb (over 1,000 mg/kg) in shoots and TF greater than one for six different plant species (*Ageratina* sp., *Achyrocline alata* (Kunth) DC., *Cortaderia hapalotricha* Pilg., *Epilobium denticulatum* Ruiz & Pav., *Taraxacum officinale* Weber and *Trifolium repens* Walter). Concentrations of Zn (over 10,000 mg/kg) were obtained in *Ageratina* sp. and *E. denticulatum* and the TF values were greater than one for plants from some studied locations. However, the ratio of metal concentration in shoots to that in soil was smaller than one. Therefore, the ratio is maybe not a reliable index when the metal soil concentration is extremely high. According to Bech *et al.* [13] controlled–environment studies must be performed to definitively confirm the Pb hyperaccumulation character of the examined plant species.

In a field survey by Wan *et al.* [89] which was conducted in the four mining sites, it was found that *Pteris vittata* L. and *Viola principis* H. de Boiss were two potential multi–metal extractors. *P. vittata* accumulated 4,106 mg/kg of As, 499.5 mg/kg of Pb, and 321.5 mg/kg of Sb in the aboveground parts. Also, *V. principis* accumulated 1,032 mg/kg As, 2,350 mg/kg Pb, and 1,201 mg/kg Cd in the aboveground parts. The values of Bioaccumulation factor for As, Pb, Zn, and Sb in *P. vittata* were >1. The Bioaccumulation factors for As, Pb, Zn, and Cd in *V. principis* were also >1. Therefore, *P. vittata* could be regarded as an As hyperaccumulator and a Pb and Sb accumulator. By contrast, *V. principis* acted as a Cd, Pb, and As hyperaccumulator. Wan *et al.* [101] suggested that oxidation and chelation reactions contributed to the accumulation of As in *P. vittata*.

Krgović *et al.* [90] explored the feasibility of the use of plant *Erigeron canadensis* L. for phytoremediation purpose on the fly ash landfill of the power plant "Kolubara" (Serbia). These authors found that *E. canadensis* L. could be considered adequate for phytoextraction of Cd and Zn from coal ash landfills at the Kolubara, because the values of BCF and TF were >1.

Liu *et al.* [14] found that plant *Polygonum aviculare* had the properties as a hyperaccumulator (BCF and TF>1), and could be used especially in phytoextraction of Cu, on the tailings of lead–zinc and copper–zinc mines, regardless of Cu content in shoots that was not above 1,000 mg/kg.

Colchicum schimperi, *Londesia eriantha*, *Lallemantia royleana*, *Bromus tectorum*, *Hordeum glaucum*, and *Thuspeinantha persica* were the most promising species for element phytoextraction in sites slightly enriched by Ag, from the area surrounding Pb–Zn mine [72].

Roccotiello *et al.* [91] highlighted for the first time that *Alyssoides utriculata* could be suitable for cleaning Ni−contaminated areas, and therefore for phytoremediation. The concentration of Ni in leaves was higher than 1,000 μg/g, which categorized the plant as Ni−hyperaccumulator and great candidate for Ni−phytoextraction purposes. The BFs and TFs were strongly higher than 1 and generally did not significantly differ between plants from serpentine (higher Ni) and non−serpentine soils (lower Ni). Precisely, these authors suggested that *A. utriculata* could be classified as a facultative hyperaccumulator species, since plants attained leaf Ni concentrations >1,000 μg/g only when grown on Ni−rich soil (serpentine) in contrast to plants growing on non−serpentine soils which attained a maximum leaf Ni concentration of <500 μg/g.

Ma *et al.* [92] aims to determine the potential of *Hybrid giant* Napier (HGN) grass to phytoextract heavy metals from the tailing waste collected from a mine site, predominantly consisting of sand. The obtained results suggested that heavy metals were phytoextracted by fibrous roots, then transported from roots to shoots and stored to all parts of the plant including fibrous roots, tap roots, stem and leaves. The efficiency in extracting 7 heavy metals/metalloids, Zn, Mn, Cu, Pb, Cd, Cr and As, in HGN plant after the two year pot study was 20.44%, 17.97%, 19.16%, 12.37%, 26.24%, 13,55%, 13.32%, respectively, in the tailing waste. The phytoaccumulation/phytoextraction of Cd in HGN was the highest in both the control soil (74.18%) and the tailing waste (26.24%). These authors concluded that *Hybrid giant* Napier grass had good phytoextraction potential in removing heavy metals/metalloids from contaminated tailing wastes.

In the research by Tang *et al.* [102] two different rice lines of Lu527−8 (the high Cd accumulating rice line) and Lu527−4 (the normal rice line) were grown in soils with different Cd concentrations (0, 5, 10, and 20 mg/kg). Rice line Lu527−8 had a higher capability of Cd accumulation and was efficient in extracting Cd from soil. The available Cd content and total Cd content in soils were significantly decreased compared with those in soils before planting.

4. AIDED PHYTOREMEDIATION BY ENVIRONMENTALLY SAFE METHODS

The application of amendments in soil contaminated with heavy metals is considered as an environmentally friendly technique for improving phytoremediation [103]. Acidification is a major limiting factor for revegetation of metal−contaminated soils with sulfides, but the addition of the amendments and the establishment of a plant cover are effective in preventing soil acidification [18]. Bidar *et al.* [104] indicated that the composition and chemical properties of amendments, as well as their impacts on the deeper soil layers were some of the important topics. Amendments should be locally available at low cost, should not cause additional adverse effects on the environment, and be suitable for aided phytoremediation of different contaminants [76].

Some recently analyzed environmentally friendly amendments that potentially could be used in phytostabilization and phytoextraction are given in Table 3.

Phytostabilization Aided phytostabilization is environmentally friendly technique that combines soil amendments, excluder plants and their associated microorganisms [121]. These authors highlighted that soil amendments and vegetation cover must sustainably improve soil structure and fertility parameters, reduce labile contaminant pools and their migration, and limit detrimental effects on living organisms, notably in the root zone.

Yang *et al.* [18] suggested that most of the phytoremediation studies carried out in the field demonstrated that aided phytostabilization was effective for the remediation of moderately to highly acid (pH=3–5) mine soils. However, on a global scale, there are very limited studies that have been conducted to evaluate the potential of this technique for the remediation of extremely acid (pH=3) mine soils.

Aided phytostabilization using trees and fly ashes is a promising technique. Bidar *et al.* [104] investigated the long–term effects of the two fly ashes (silico–aluminous and sulfo–calcic) and the afforestation, on the reduction of Cd, Pb and Zn availability in soil. Their findings highlighted the beneficial effects of aided phytostabilization, as well as the sustainability of this technique 10 years after the fly ash amendment. Pourrut *et al.* [105] also studied the long–term efficiency of aided phytostabilization with silico–aluminous fly ash and sulfo–calcic fly ash on the former agricultural soils highly contaminated by Cd, Pb, and Zn. The data suggested that the tree species studied (*Alnus glutinosa*, *Acer pseudoplatanus* and *Robinia pseudoacacia*) were likely suitable for phytostabilization of highly metal–contaminated soils, unlike *Salix alba* and *Quercus robur*.

Eight years after addition of coal fly ash (CFA) to soil, Lopareva–Pohu *et al.* [106] found that bioavailability and uptake of Cd, Pb and Zn by two plants, *Lolium perenne* and *Trifolium repens*, were reduced.

Kumpiene *et al.* [107] conducted a pilot–scale experiment to study the effects of aided phytostabilization on ore dust–contaminated soil by Cu and Pb. Soil was amended with combination of alkaline fly ashes and peat to reduce mobility of trace elements and vegetated with a proprietary grass/herb mixture. Addition of alkaline fly ashes and peat mixture neutralized soil and the pH values ranged from 6.7 to 7.1. During the experimental period, Cu and Pb leaching was reduced on average by 98% and 97%, respectively.

One of the commonly examined amendments for phytostabilization is biochar. It is charred organic matter, which has shown to immobilize metals due to its high surface area and alkaline nature. Bopp *et al.* [108] performed a pot experiment, and analyzed metal uptake by ryegrass (*Lolium perenne*) from three contaminated soils treated with two biochars, which differed only in their pH (acidic, 2.80; alkaline, 9.33) and carbonate content (0.17% and 7.3 %). Addition of the alkaline biochar reduced toxicity of contaminants, which increased root biomass. However, Zn and Cu bioavailability and plant uptake were equally reduced by both kinds of biochar, showing that surface area played an important role in metal immobilization. These authors suggested that biochar could serve for long–term application, retaining metals immobilization ability even after its alkalinity effect is reduced [108].

Table 3 Environmentally friendly amendments that potentially could be used in phytostabilization and phytoextraction.

Amendment	Plant	Element	Reference
Phytostabilization			
Fly ashes (silico–aluminous and sulfo–calcic)	*Robinia pseudoacacia* L., *Alnus glutinosa* (L.) Gaertner, *Quercus robur* L., *Acer pseudoplatanus* L., *Salix alba* L.	Cd, Pb, Zn	[104,105]
Coal Fly Ash	*Lolium perenne, Trifolium repens*	Cd, Pb, Zn	[106]
Combination of alkaline fly ashes and peat	grass/herb mixture	Cu, Pb	[107]
Biochar	*Lolium perenne*	Zn, Cu	[108]
Biochar (pine woodchip and olive tree pruning)	maize	As, Cu	[109]
Biochar (cane straw)	*Mucuna aterrima*	Cd, Pb, Zn	[110]
Limestone and compost	*Microchloa altera*	Cu	[76]
Ameliorants (lime and chicken manure)	*Cynodon dactylon* L., *Pennisetum purpureum* Schum., *Neyraudia reynaudiana* (Kunth.) Keng., *Panicum repens* L., the non–native *Eucalyptus robusta* (Smith.)	extremely acid (pH<3) polymetallic pyritic mine waste heap	[18]
Sheep manure	*Medicago sativa* L.	Cd, Pb, Zn	[20]
Compost	buffalo grass, arizona fescue, quailbush, mountain mahogany, mesquite, and catclaw acacia	Pb, As, Zn	[98]
Organic amendments (cow and pig manure, and organic fertilizer)	*Eucalyptus camaldulensis*	Cd	[111]
Calcium carbonate and pig manure	*Nerium oleander*	As, Cd, Pb	[112]
Calcium carbonate and pig manure	*Lavandula dentata, Rosmarinus officinalis, Thymus vulgaris*	As, Cd, Cu, Pb, Zn	[113]
Fresh ramial chipped wood	*Phaseolus vulgaris*	Mo, Zn, Cu, Cr, Co	[114]
Slags, alkaline by–products of steel industry	*Agrostis gigantea* L., *Populus trichocarpa*×*deltoides* cv. Beaupré	Cu	[115]
Sewage sludge from food industry and the addition of lime and potassium phosphate	tall fescue	Cd, Pb, Zn	[19]
Lime	*Myrtus communis*	As	[116]
Phytoextraction			
Commercial citric acid	maize and vetiver	Pb	[117]
[*]EDDS, [**]MGDA	*Mirabilis jalapa*	Pb	[118]
[***]NTA	tufgrass	Cu, Pb, Zn	[119]
KCl	*Medicago sativa* L.	Cu, Pb, Zn	[20]
Sewage sludge	*Salix × smithiana*	Cd, Zn	[21]
Sulphur	*Berkheya coddii*	Ni, Co	[120]
Limestone	*Pennisetum sinese*	Cu, Cd	[24]

[*]EDDS–[S,S]–ethylenediaminedisuccinic acid; [**]MGDA–methylglycinediacetic acid; [***]NTA–nitrilotriacetic acid.

The aim of the study by Brennan *et al.* [109] was the assessment of biochar amendment on the uptake of As and Cu from the soil. Investigation was conducted under the experimental conditions, with maize planted in As and Cu–contaminated soil (74 and 404 mg/kg, respectively; pH of 6.8; organic matter content 1.08%), and amendment with two different types of biochar, pine woodchip and olive tree pruning. Soil was collected from the vicinity of the tailings dump of the copper mine. The results by these authors indicated that biochar addition to the contaminated mine soils might enhance plant cover by improving root development and promoting larger biomass both above and below ground. Biochar amendment reduced soil toxicity to plants and might play a role in limiting contaminant dispersion. These results are in agreement with the findings of Bopp *et al.* [108].

Sugar cane straw–derived biochar (BC), produced at 700°C, was applied to a heavy metal contaminated mine soil in the study by Puga *et al.* [110]. Jack bean (*Canavalia ensiformis*) and *Mucuna aterrima* were grown in pots which contained soil and biochar mixtures, and in control pots without biochar. The results by these authors indicated that the application of this kind of biochar decreased the available concentrations of Cd, Pb and Zn at 56, 50 and 54% respectively. Jack bean translocated large amounts of metals to its shoots, especially Cd. *M. aterrima* accumulated large amounts of Cd, Pb and Zn in roots, but translocation to the above ground parts was limited.

Shutcha *et al.* [76] conducted a study of spontaneous and assisted phytostabilization to promote plant establishment on bare soil contaminated by trace metals (total Cu: 42,500 mg/kg in bare soil vs. 220 mg/kg in remote forest). Limestone (0, 2.5, 5, and 10 t/ha) and compost (0, 45, and 225 t/ha) were applied. Plant establishment had been monitored for three years, while leaf trace metal concentration was assessed during the third year. Soil amendments improved bare soil conditions (higher pH, nutrients, lower metal contents), and facilitated spontaneous plant establishment. Compost exhibited the largest positive effects. During the following three years of conducting the phytostabilization experiment, a substantial growth and high survival was observed in *Microchloa altera*. A combination of soil amendments (lime and compost) was the most effective to improve plant fecundity, and reduce metal uptake by leaves.

In the study by Yang *et al.* [18] a combination of ameliorants (lime and chicken manure) and five acid–tolerant plant species (*Cynodon dactylon* L., *Pennisetum purpureum* Schum., *Neyraudia reynaudiana* (Kunth.) Keng., *Panicum repens* L. and the non–native *Eucalyptus robusta* (Smith.) were used in order to establish a self–sustaining vegetation cover on an extremely acid (pH<3) polymetallic pyritic mine waste heap. All the plants survived, grew rapidly and developed a good vegetation cover in the conditions of extremely acid and metal–contaminated mine soil. Vegetation development enhanced nutrient accumulation in the mine soil. The obtained results by these authors suggested that aided phytostabilization could be a promising strategy for the restoration of extremely acid mine soils.

Compost–assisted direct planting phytostabilization technology, as an alternative to standard cap and plant practices, was investigated by Gil–Loaiza *et al.* [98]. The study site was extremely acidic tailings pile with the concentrations of Pb, As, and Zn each exceeding 2,000 mg/kg. Compost amendment and seeding, guided by preliminary greenhouse studies, allowed plant establishment and sustained growth over four years of demonstrating feasibility for this phytostabilization technology.

Meeinkuirt *et al.* [111] conducted greenhouse and field experiments to evaluate the influence of three different organic amendments (cow manure, pig manure, and organic fertilizer) on the Cd phytostabilization potential of *Eucalyptus camaldulensis* grown on Cd–contaminated soil. Plants grown on the amended soils had lower Cd content than those grown on the Cd soil without amendments. Translocation factor was <1 and Bioconcentration factor for the roots was >1, for soil that was amended with organic fertilizer, which was an indication of the potential of this species to stabilize Cd in the roots.

Calcium carbonate and pig manure were also studied as amendments for improving phytostabilization in the research by Parra *et al.* [112]. Greenhouse pot experiment was conducted to evaluate the potential use of *Nerium oleander*, *Cistus albidus* and *Pistacia lentiscus* for phytostabilization of acidic mine soils. The selected species were grown in mine tailing soil, unamended, amended, and in a unpolluted control substrate. These authors found that the application of amendments reduced the concentrations of the studied elements (mainly for As, Cd and Pb) in exchangeable and extractable fraction in the amended soil. The tested species directly contributed to the immobilization of trace elements in the soil. Trace element concentrations in plants grown in the unamended tailing soil were similar to those reported for the amended soil, with levels below toxicity thresholds. Therefore, these species in combination with the amendments fulfill the criteria to be used in phytostabilization. Parra *et al.* [112] suggested that *N. oleander* seemed to be the best choice, since it directly contributed to trace element immobilization in the soil, while lower quantities of trace elements were translocated in the aerial tissues, with the increased accumulation in roots.

The similar investigation of the use of three Laminaceae species (*Lavandula dentata*, *Rosmarinus officinalis* and *Thymus vulgaris*) for phytostabilization of acid soil contaminated by trace elements was conducted by Parra *et al.* [113]. These species were grown in mine tailing soil with concentrations of As, Cd, Cu, Pb and Zn of 178, 13.28, 42.31, 1,142, 3,878 mg/kg, respectively, unamended and amended with calcium carbonate and pig manure. Application of amendments reduced concentrations of trace elements in exchangeable and extractable fractions in the amended compared with the unamended soil. The studied plant species fulfilled the criteria for phytostabilization purposes, aided by amendments.

Hattab *et al.* [114] aimed to assess the effect of two different organic amendments (composted sewage sludge, CSS) and fresh ramial chipped wood, RCW) on the phytoremediation of contaminated technosols by *Phaseolus vulgaris*. RCW significantly reduced the Mo, Zn, Cu, Cr and Co dissolved concentrations in the soil pore water (SPW) whereas it did not have any effect on the As contents. In contrast, the application of CSS significantly increased the concentrations of Zn, Cu, Co and As in the dissolved form in the SPW, while it decreased the concentrations of Mo and Cr. Consequently, RCW was more effective than CSS for reducing elements mobility and phytoavailability in the contaminated technosols.

Le Forestier *et al.* [115] found that the addition of slags, alkaline by–products of the steel industry, in the contaminated soil increased Cu concentration in the residual fraction and thus reduced its potential mobility to the plants (*Agrostis gigantea* L. and *Populus* *trichocarpa*×*deltoides* cv. Beaupré). Total concentration of dissolved Cu in soil pore water remained identical, but speciation changed as the real dissolved fraction diminished and lowered the Cu bioavailability. These authors concluded that the addition of a small amount of basic slags was beneficial for this Cu–contaminated soil in the context of aided phytostabilization.

Grobelak and Napora [19] investigated the effects of organic and inorganic amendments on phytostabilization of Cd, Pb and Zn in contaminated soil, seeded with grass (tall fescue), under the experimental conditions. The contaminated soil was collected from the area surrounding a zinc smelter in the Silesia region of Poland (pH 5.5, Cd 12 mg/kg, Pb 1,100 mg/kg, Zn 700 mg/kg). The results confirmed that the combined application of sewage sludge from the food industry and the addition of lime and potassium phosphate had the highest impacts on the decreasing of the Zn, Cd and Pb concentrations in mobile fractions.

Moreno–Jiménez *et al.* [116] also tasted the effects of lime on the phytostabilization efficiency of four plant species: *Myrtus communis*, *Retama sphaerocarpa*, *Rosmarinus officinalis* and *Tamarix gallica*. A pot experiment was carried out under semi–controlled conditions with a mine–impacted soil mainly with As and Zn, by applying 5% of pyritic sludge. These authors found that liming induced an effective immobilization of metals and As. Plant establishment, mainly *M. communis*, decreased labile As in the substrate by 50%, although the levels of extractable metals were not affected by the plants.

Phytoextraction Chelating agents increase the solubility of heavy metals in soil and enhance phytoextraction. Evangelou *et al.* [122] gave an overview of the chelating agents applied in different studies. They indicated that most studies dealt with the application of synthetic aminopolycarboxylic acids, such as ethylene diamine tetraacetic acid, and natural ones such as, ethylene diamine disuccinate and nitrilotriacetic acid, as well as naturally low molecular weight organic acids, such as citric and tartaric acid. They concluded that the effectiveness of chelating agents varied according to the plant and the heavy metals used. Although some inorganic chelating agents are more efficient for the use in phytoextraction [123–124], the main focus should be directed towards the fate of chelating agents fate after the application and towards its toxicity to plants and soil microorganisms, as well as its degradation. Najeeb *et al.* [124] showed that environmentally safe chelates compared to inorganic compounds recovered the plant biomass.

Effects of citric and tartaric acids on Cu and Zn mobilization in naturally contaminated mine soils were assessed in column study by Pérez–Esteban *et al.* [125]. Their results showed that higher concentrations of organic acids increased metal desorption from soil. Citric acid was more effective in Cu desorption from soil than tartaric acid. Concentration of citric acid of 10 mM significantly promoted Cu mobilization, from 1 mg/kg to 42 mg/kg Cu. These authors suggested that citric acid could be used in the assisted phytoextraction with minimal environmental risk, because of high biodegradability.

Freitas *et al.* [117] studied the effect of commercial citric acid on the phytoextraction of Pb from soil contaminated by battery recycling activities. Applying 40 mmol/kg of chelating agent, promoted a 14–fold increase in the Pb concentration in maize shoots as compared to the control. The citric acid induced a Pb concentration in vetiver shoots that was 7.2–6.7–fold higher than the control. It was concluded that the use of citric acid substantially increased the uptake and translocation of Pb to the shoots of vetiver and maize.

De Melo *et al.* [126], unlike Pérez–Esteban *et al.* [125] and Freitas *et al.* [117], found that neither citric acid nor gallic acid was efficient for Cd, Pb, Cu, and Zn phytoextraction, by velvet bean (*Stizolobium aterrimum*). According to Evangelou *et al.* [127] natural low molecular weight organic acids (NLMWOA) such as citric acid, oxalic acid and tartaric acid could be degraded by the fungi, *Cordyceps* sp., *Paecilomyces* sp. and the bacteria *Burkholderia* sp. Biodegradation of NLMWOAs increased the natural pH value of the soil by approximately 1 unit, and decreased the bioavailability of Cu from 175 mg/kg to approximately 140 mg/kg. That could be the reason for the inefficiency of three NLMWOAs in enhancing phytoextraction.

Two easily biodegradable chelating agents [S,S]–ethylenediaminedisuccinic acid (EDDS) and methylglycinediacetic acid (MGDA) were tested for the application in the assisted phytoextraction process, using *Mirabilis jalapa* [118]. EDDS and MGDA have demonstrated to be efficient chelating agents with a mobilizing capacity that can be considered comparable with EDTA. These authors assumed that Pb content was probably increased by the use of chelating agents up to the limit that overcame the physiological barriers in roots. This allowed transport of Pb through xylem in leaves. The chelating agents had a positive influence on bacterial communities of bulk soil and rhizosphere.

In the study by Zhao *et al.* [119], the use of biodegradable chelator nitrilotriacetic acid (NTA) was effective for enhancing metal phytoextraction from municipal solid waste compost. Adding NTA to soil before each harvest of tufgrass, lead to the gradually removing of Cu, Pb and Zn from compost.

Elouear *et al.* [20] evaluated the effects of the use of KCl and sheep manure, on the growth of alfalfa (*Medicago sativa* L.) in contaminated mine soil with Cd (53 mg/kg), Pb (970 mg/kg) and Zn (9,641 mg/kg), and on the heavy metal accumulation. Results of this study suggested that KCl could be a useful amendment for phytoextraction of metals by accumulator species, while sheep manure could be very useful for phytostabilization.

Fast–growing clones of *Salix* and *Populus* species have been studied for phytoremediation of soils contaminated by Cd, Pb and Zn, using short–rotation coppice plantations. Biomass yield, accumulation and removal of these elements by highly productive willow (S1—(*Salix schwerinii*×*Salix viminalis*)×*S. viminalis*, S2—*Salix*×*smithiana*) and poplar (P1—*Populus maximowiczii*×*Populus nigra*, P2—*P. nigra*) clones were investigated with and without sewage sludge (SS) application. Kubátová *et al.* [21] found that application of SS reduced concentrations of studied elements in shoots had been compared to the control treatment. The removal of elements was significantly higher in the second harvest for all the clones (except the P2 clone) and elements, and the biomass yield was the major driving force for the amount of element concentrations removed by shoots. From the four tested clones, S2 showed the best removal of Cd (up to 0.94 %) and Zn (up to 0.34 %) of the total soil element content, respectively, and this clone was a good candidate for phytoextraction.

Sulphur, and the addition of acid mine tailings in the study by Robinson *et al.* [120], caused a highly significant increase in Ni and Co uptake by the South African nickel hyperaccumulator *Berkheya coddii*, relative to the controls. These authors indicated that sulphur could be used as a low–cost soil amendment to enhance the metal uptake of crops grown on ultramafic soils.

Cui *et al.* [24] investigated the possibilities of metal removing from acidic contaminated soils using five plant species in combination with limestone application. Results indicated that *Pennisetum sinese* and *Sedum plumbizincicola* were most effective for Cu and Cd removal from the contaminated soils in the first growing season, respectively. *P. sinese* was the best species for overall Cu and Cd removal. These authors recommend that intercropping *Elsholtzia splendens* with *P. sinese* may be a useful approach both to remove heavy metal from soil and to improve its biological properties.

5. CONCLUDING REMARKS

Abilities of plants to survive in the conditions of extreme soil pollution were used in the researches of various phytoremediation techniques. The focus is on the immobilization of polluting substances in soil by phytostabilization, or their content reduction/total removing from soil by phytoextraction. There are many studies about the plant species which have naturally developed mechanisms for uptake, accumulation or exclusion of metals and metalloids from soil. Great attention was also paid to the assisted phytoremediation techniques. Amendments that potentially could be used in phytostabilization and phytoextraction must be environmentally friendly, which means that they should have a good influence on the soil characteristics and fertility, as well as on the vegetation cover development. The most analyzed amendments for phytostabilization in the resent findings were fly ashes, biochar, limestone, compost, chicken, pig, cow and sheep manure and sewage sludge. Natural low molecular weight organic acids and easily biodegradable chelating agents showed the best results in phytoextraction processes.

The conducted examinations were done in the controlled and real conditions. Flotation tailing ponds, overburden dumps or soils in the vicinity of the copper smelters with high contents of As, Cd, Ni, Pb, Cu and Zn usually represented the main investigated areas.

It has been shown that determining the suitability of plants for use in phytoremediation is not easy. It should be based on the multidisciplinary approaches of uptake and translocation efficiency of metals in plants. It was concluded that soil physico–chemical, as well as plant characteristics, had important role in plant–metal/metalloid interactions. Most of the researchers used different biological factors based on the relations between concentrations in plant parts, as well as between contents in plant parts and root zone soil. A lot of authors suggested that the used plant parts should be washed, in order to avoid element concentration error due to the attached soil particles. Metal/metalloid contents in aboveground parts of hyperaccumulators or excluders were also defined. Statistical analyses of the obtained research data were implemented. There are a lot of criteria that should be met at the same time, in order to define some plant species as an excluder or an accumulator/hyperaccumulator.

The number of published researches of phytoextraction is higher compared to the number of researches of phytostabilization. This is maybe related to the fact that the phytoextraction technique could be used for obtaining the metals/metalloids from the polluted land with low content of valuable elements that is not suitable for classic exploitation.

Different aspects of investigations were made in order to contribute to the development of potential economically profitable phytoremediation methodologies with minimal environmental risks. However, it should not be forgotten that minimizing the emission of polluting substances should be the first line of the environmental balance and human health preservation.

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Chapter 5

EXPIRED ANTIBIOTICS AS POSSIBLE SOLUTION FOR CORROSION OF METALS CAUSED BY ACID RAIN

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ABSTRACT

Environment protection is a matter of global concern of scientists dealing with various research topics since the state of the environment is important for the existence of all living beings. Numerous phenomenons might have detrimental effects on the environment and some of them are acid deposition, metal release due to dissolution, uncontrolled release of pharmaceutical compounds etc. These phenomenons are connected to some extent. For instance acid rain is one of the causes of metal corrosion that leads to dissolution, and it is important to find appropriate means to prevent it. On the other hand, some pharmaceutical compounds can react with metals or adsorb on their surface, which as the result might diminish their corrosion. Hence, it is interesting to use pharmaceutical compounds, especially antibiotic suspensions since they are only used for short time and afterwards disposed, as corrosion inhibitors in order to prevent or reduce at least two potential risks for the environment. Metal and antibiotics release to the environment can be in this way reduced. Hemomycin is commercially available antibiotic with azithromycin as the active component. It is tested as brass corrosion inhibitor in simulated acid rain. It is concluded that azithromycin gets strongly adsorbed on brass surface and protects it against corrosive ions from simulated acid rain solution. The adsorption mechanism can be described by Langmuir adsorption isotherm. Azithromycin acts as mixed-type inhibitor and it is possible to achieve inhibition efficiency degree as high as 98%.

Keywords: Expired antibiotics, Acid rain, Brass, Corrosion inhibition, Hemomycin

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1. INTRODUCTION

The impact of acid deposition has been investigated for over a century. This impact is recognized on stone monuments made of marble and limestone, also on building materials which contain carbonate [1–4]. The current problem that arises from the devastation of acid rain is the deterioration and corrosion of metals and alloys. Air pollution and acid rains are very important problems and must be solved in the near future because such pollution has a significant influence on environment [5]. Acid rain, or acid deposition, is a broad term that includes any form of precipitation with acidic components, such as sulphuric or nitric acid that fall to the ground from the atmosphere in wet or dry forms. This can include rain, snow, fog, hail or even dust that is acidic [6]. Acidity is determined on the basis of the pH level of the water droplets. Normal rain has pH value of about 5.6 and it is slightly acidic because carbon dioxide (CO_2) dissolves into a rain and forms carbonic acid. If pH value of rain water falls below 5.6 it becomes acid rain. Acid rain, a kind of acidic deposition is very corrosive medium containing not only H^+ but also other species including NH_4^+, Mg^{2+} and SO_4^{2-} ions [7].

A large number of studies dedicated to deterioration of metals under the climatic conditions, natural and artificial [8,9]. Acid rain corrosion of outdoor-structures made of galvanized steel has become an actual problem [10]. Atmospheric corrosion of galvanized steel has been investigated in several studies and it is concluded that SO_2 is a major component which increasing the corrosion rate [11–13]. Further, SO_4^{2-} and H^+ ions react with ZnO, which is a component of protective film, forming $ZnSO_4$ [14]. Similar results were presented by Spence *et al.* [15] suggesting that atmospheric corrosion of galvanized steel structures is conditioned by SO_2, H^+ and HCO_3^- as major contributors to corrosion. Also it has been established through investigations that SO_2 adsorbed on the zinc surface is oxidized to SO_4^{2-} with reduction of pH of solution [16]. On the other hand large number of studies investigated corrosion behaviour of copper and its alloys under similar conditions i.e. corrosion in acid rain and corrosion in simulated acid rain solutions [17–20]. Many objects made of copper or copper alloys often suffer significant corrosion damage by acid rain, specially statues and roofs [10]. Exposed to atmosphere, copper and its alloys form a thin layer of corrosion products called patina [21]. Bronze sculpture with patina are not just protected with this film, patina also enhances the aesthetic of art objects. Coloured patinas form spontaneously on copper alloys as result of very slow and controlled corrosion. Corrosion processes take place in the presence of moisture, carbon dioxide, oxygen or in seawater. Colour of formed patina depends on the corrosion products formed and depends partly on the alloy and partly on the media. First, a thin cuprite layer forms (Cu_2O) and then this layer oxidizes to copper(II)oxide, that forms hydroxide in humid conditions [22]. A secondary patina, also, can occur, and as a result a thick layer of corrosion products is present [23,24]. These patinas could be soluble and washed out from the metal or alloy surface.

In order to preserve metal objects it is also necessary to have very good knowledge of the corrosion mechanism and the corrosion inhibitory mechanism. To preserve metal works from corrosion suitable treatments with coating substances are often required [25]. Many organic compounds can be used for this purpose, and provide protection to the exposed surfaces by the formation of thick barrier layers or thin films [26,27]. Some of organic compounds act as inhibitors and normally form very thin films, which can be very persistent. Those films could be physically or chemically adsorbed on metal surface and lead to a remarkable decrease in the corrosion rate due to the slowing down of the anodic and/or cathodic reaction. One of the best organic inhibitors for protection of copper and copper alloys from both underwater and atmospheric corrosion in various media is 1H-benzotriazole (BTAH) [28–30]. Its effectiveness as an inhibitor is good in basic and near-neutral solutions, it is rather poor in acidic solutions due to the higher solubility of 1H-benzotriazole layers at lower pH values [31]. This problem can be solved using the 1H-benzotriazole derivative that has a greater inhibitory activity for copper. Also, heterocyclic compounds which contain a mercapto group have been explored as copper corrosion inhibitors [32]. Beside benzotriazole derivatives 2-mercaptobenzimidazole showed grate effectiveness probably due to sulphur atom presumably involved in forming a thick polymeric film that is strongly adsorbed on the surface of copper [20,33].

Today, special attention is paid to organic compounds such as antibiotics as corrosion inhibitors in different media. Such investigations are especially important because in this way antibiotics are used which can no longer be used for the treatment of people. In order to minimize the damage caused by corrosion in terms of economic costs, but also in terms of environmental pollution it is very important to understand the mechanism of metal corrosion as well as the possibility of its suppression by using the appropriate inhibitors. Taking into account the markedly increasing the air pollution, additional protection for metals and alloys exposed to urban environment is recommended.

1.1. Pharmaceutical compounds as potential risk for the environment

The pharmaceutical compounds that either passed the expiration date or are unsuitable for further human usage, can also pose a threat to the environment if they are improperly disposed. However, results of numerous studies, carried out all over the world, indicate that there is still a low level of consciousness among people regarding the treatment of unused medications. In numerous cases researchers came to the conclusion that unused pharmaceuticals are being disposed through household waste or sink or toilet [34–36].

Similar behaviour is displayed by some pharmaceutical industries as well, as can be seen in paper published by Ngwuluka *et al.* [37] on pharmaceutical waste management in Nigerian industries. On the other hand, as a result of a study on disposing pharmaceutical waste in school, it is found to be easy to introduce a proper way of disposal into a well-organized system by collecting it and transporting it to a local hospital disposal system [38].

In the areas that have poor wastewater treatments pharmaceutical compounds are becoming the contaminants that through wastewaters reach ambient waters and raise concern about environmental effects [39]. For instance, in the region of Western Balkan, detailed analysis of composition of different waters from various sources from three different countries, led to conclusion that numerous pharmaceutical compounds and among them numerous antibiotics are found in detectable amounts. One of them is azithromycin and it is interesting to mention that based on the water composition the variation in the medicine of choice is observed between the studied region and the countries of Western Europe. It is noticed that different medicines from the macrolide group are found in significant amounts in these regions. It is also important to have in mind that an additional problem with the occurrence of these compounds in waters is that the conventional methods for their removal provide very low elimination efficiency [39].

Recently, it has been reported by Terzic *et al.* [40], that enriched activated sludge can be used for efficient removal of macrolide antibiotics. The authors used activated sludge from aeration tank of wastewater treatment plant and modified it with several components among which was high dosage (10 mg/l) of azithromycin. This treatment enabled the sludge adaptation to high dosages of macrolide antibiotics and the use of this process for removal of not only azithromycin but also erythromycin and clarithromycin. This process of biotransformation enabled very high removal efficiencies and showed pronounced positive ecotoxicological outcomes.

Another reason for concern is presented by Resende *et al.* [41] who discovered correlation between drug-resistance and toxic metal tolerance of medically important bacteria isolated from and aquaculture system. For example, the resistance to azithromycin was observed in the group of Gram-positive cocci, and bacteria were also tolerant to nickel, zinc, chromium and copper. These results indicate the need to strictly control the exposure of aquaculture systems to antimicrobials and toxic metals. Based on the literature sources mentioned above and a few others [39,41–45], the interest in the effect of pharmaceutical compounds on the environment, firstly waters and afterwards sediments, is increasing in the last few years.

The most important conclusion drawn from all those studies is that most of the frequently used pharmaceuticals find their way from pharmacies and our homes to the environment where they will definitely impose a threat if this trend continues. One of the possible solutions is to find a new way to utilize antibiotics and other drugs, for instance as inhibitors of metals corrosion.

1.2. Pharmaceutical compounds as corrosion inhibitors

Numerous literature deals with the problem of corrosion that is acknowledged as technical, economic and environmental problem. Due to its relatively high stability towards corrosion processes brass is one of the most frequently used metal materials. However, under certain conditions brass also undergoes corrosion [46,47,48]. Hence, there is a need to find adequate corrosion inhibitors. There are several reviews describing the possibility of application of different compounds as inhibitors of copper or it alloys corrosion [49–51]. Generally, most often, the compounds from group of azoles are considered very efficient corrosion inhibitors and a large number of studies is dedicated to them [52–54]. On the other hand, many of them that are proven very efficient are compounds that have adverse effects on the environment such as benzotriazole [55–62].

Hence, the number of studies on the possibility of application of environmentally friendly compounds as copper and its alloys corrosion inhibitors is increasing over the past few years. There are numerous results indicating that amino acids such as cysteine [63–65] can be used for that purpose. Also, purine and its derivatives such as adenine, 6-benzylaminopurine, mercaptopurine are investigated as potential inhibitors of copper corrosion [66–73] in various media such as chloride, nitrate and sulphate solutions as well as complex media such as artificial seawater and uterine fluid. It is shown that purine and its derivatives also enable efficient copper corrosion inhibition, whereas, their nontoxic characteristics are of the highest importance when they are used as inhibitors of corrosion of materials inserted in human body [68,74].

Some purine derivatives are found also in medications used for targeted tumour treatment [75] or antiviral therapy [76], so it can be interesting to see how they may interact with biomaterials containing copper [77] and conduct research from that point of view as well. This might bring out the other questions such as the effect of other pharmaceutical compounds on metals found in human body.

Numerous research results indicated that pharmaceutical compounds act in the manner that suppresses corrosion of metals. The results are summarized within the reviews published by Pathak and Mishra [78], Karthikeyan [79], Abdel Hameed [80] and Verma *et al.* [81]. It can be seen that this class of products can provide very good results, also with multiple benefits rising from previous discussion. The main focus so far has been on steel, however, there are some tests on other metals as well. The literature survey regarding the use of various medications as corrosion inhibitors enabled the formation of Table 1 where the values of inhibition efficiencies are summarized.

It can be concluded that drugs poses huge potential for application as corrosion inhibitors. However, research regarding copper corrosion inhibition is rather scarce. According to the previously published review [50], a few compounds that are used as diet supplements or can be found in pharmaceutical products are studied as copper corrosion inhibitors such as vitamin C [102], vitamin B_1 [103], potassium folate [104], 6-chloro-1,1-dioxo-3,4-dihydro-2H-1,2,4-benzothiadiazine-7-sulphonamide, 1-((s)-3-mercapto-2-methyl propanoyl) pyrrolidine-2-carboxylic acid and 3-(2-methoxy phenoxy) propane 1,2-diol [105]. However, as can be seen from the values of inhibition efficiency presented in Table 1 they don’t provide adequate protection of copper against corrosion in the tested media. Only few pharmaceutical compounds in the form of medications are studied in that manner such as levetiracetam and meropenem in nitric acid, septazole and metronidazole in hydrochloric acid and cephradine in sodium chloride solutions. It can also be seen from the Table 1 that somewhat different results are obtained by the application of these drugs used for treatment of epilepsy and bacterial infections. The results indicate that they can effectively inhibit copper corrosion under tested conditions. One of the possible candidates for further research is azithromycin that is an active compound of hemomycin – antibiotic frequently used in treatment of bacterial infections.

Azithromycin is broad-spectrum macrolide antibiotic which relevance and mode of action have been extensively described by Parnham *et al.* [110]. On the other hand, as it is previously reported by several researchers [111,112] azithromycin is electrochemically active. It is also reported that the interaction between azithromycin and copper ions occurs and leads to complexation [113,114].

Table 1 Literature data on metals corrosion inhibition efficiencies obtained by pharmaceutical compounds

Inhibitor	Metal	Media	Concentration	Inhibition efficiency	Reference
Streptomycin	carbon-steel	seawater 25ºC	$0.52\cdot10^{-3}$ M	40.48^{pp}	[82]
Tetracycline			$0.52\cdot10^{-3}$ M	30.95^{pp}	
Streptomycin			$21.2\cdot10^{-6}$ M	40.07^{EIS}	
Tetracycline			$21.2\cdot10^{-6}$ M	23.74^{EIS}	
Streptomycin		seawater 305 K	$0.34\cdot10^{-3}$ M	82.23^{WL}	
Tetracycline			$0.45\cdot10^{-3}$ M	52.33^{WL}	
Ampiclox	mild steel	0.1 M H_2SO_4	0.5 g/dm^3	85.57^{WL}	[83]
Ampicillin				80.93^{WL}	
Cloxacillin				84.07^{WL}	
Chloramphenicol				34.33^{WL}	
Tetracycline				88.75^{WL}	
Levetiracetam	copper	0.5 M HNO_3 303 K	300 ppm	94.99^{WL} 92.61^{EIS} 91.70^{pp}	[84]
Moxifloxacin	carbon steel	1 M HCl 25°C	300 ppm	94.1^{WL} $92.5^{H2\ evolution}$ $93.9^{thermometric\ method}$ 92.0^{pp} 92.0^{EIS} 92.3^{EFM}	[85]
Streptomycin	mild steel	1 M HCl	500 ppm	88.50^{WL} $85.2^{polarization\ resistance}$ $84.8^{Tafel\ data}$ 83.9^{EIS}	[86]
Amoxicillin	carbon steel	20% acetic acid	$2\cdot10^{-4}$ M	61.6^{pp}	[87]
Cefaclor				64.9^{pp}	
Cefradine				87.7^{pp}	
Amoxicillin				52.1^{EIS}	
Cefaclor				63.5^{EIS}	
Cefradine				84.6^{EIS}	
Amoxicillin				67.04^{WL}	
Cefaclor				69.18^{WL}	
Cefradine				92.27^{WL}	

Inhibitor	Metal	Media	Concentration	Inhibition efficiency	Reference
Doxycycline	stainless stell 316L as-received	1% KCl	1 mg/ml		[88]
	stainless stell 316L abraded				
	titanium as-received			+	
	titanium abraded			+	
	vitallium (chromium-cobalt alloy) as-received			-	
	vitallium abraded			-	
Oxytetracycline hydrochloride	stainless stell 316L as-received				
	stainless stell 316L abraded				
	titanium as-received			+	
	titanium abraded				
	vitallium as-received			-	
	vitallium abraded			-	
Oxytetracycline dihydrate	stainless stell 316L as-received			+	
	stainless stell 316L abraded			+	
	titanium as-received			+	
	titanium abraded				
	vitallium as-received			-	
	vitallium abraded			-	
Neomycin tri sulphate	mild steel	1 M KCl	$5\cdot10^{-4}$ M	64.7^{WL} 66.95^{pp}	[89]

Inhibitor	Metal	Media	Concentration	Inhibition efficiency	Reference
Ceftriaxone	nickel	1 M HCl	60 ppm	92.2^{pp} 86.9^{EIS} 85.4^{EFM}	[90]
Cefazolin				91.2^{pp} 75.7^{EIS} 77.7^{EFM}	
Ceftazidime				85.9^{pp} 65.1^{EIS} 65.7^{EFM}	
Cefotaxime				84.1^{pp} 47.2^{EIS} 45.2^{EFM}	
Cephradine	copper	0.9% NaCl	$5\cdot10^{-3}$ M	92.4^{pp} 91.24^{EIS}	[91]
Dicioxacillin	mild steel	0.1 N HCl		92.59^{WL}	[92]
		0.01 N HCl		92.59^{WL}	
		0.001 N HCl		43.22^{WL}	
		0.1 N HNO_3		56.77^{WL}	
		0.01 N HNO_3		17.82^{WL}	
		0.001 N HNO_3		65.88^{WL}	
		0.1 N H_2SO_4		84.55^{WL}	
		0.01 N H_2SO_4		51.38^{WL}	
		0.001 N H_2SO_4		39.50^{WL}	
Cefuroxime		0.1 N HCl		90.74^{WL}	
		0.01 N HCl		81.88^{WL}	
		0.001 N HCl		66.10^{WL}	
		0.1 N HNO_3		83.20^{WL}	
		0.01 N HNO_3		53.04^{WL}	

Inhibitor	Metal	Media	Concentration	Inhibition efficiency	Reference
Amoxicillin		0.1 N HCl		85.18^{WL}	
		0.01 N HCl		85.18^{WL}	
		0.001 N HCl		78.38^{WL}	
		0.1 N HNO_3		31.38^{WL}	
		0.01 N HNO_3		76.52^{WL}	
		0.001 N HNO_3		93.50^{WL}	
		0.1 N H_2SO_4		80.03^{WL}	
		0.01 N H_2SO_4		48.95^{WL}	
		0.001 N H_2SO_4		19.61^{WL}	
Paromomycin	zinc	1 M HCl	500 ppm	93.03^{pp} 91.59^{EIS} 91.96^{WL}	[93]
Streptomycin				91.46^{pp} 89.90^{EIS} 90.70^{WL}	
Spectinomycin				89.66^{pp} 88.98^{EIS} 88.44^{WL}	
Cefixime	mild steel	1 M HCl 303 K	$8.8 \cdot 10^{-4}$ M	90^{WL} 91.6^{pp} 91.8^{EIS}	[94]
Ampicillin	mild steel	1 M HCl 30°C	$5 \cdot 10^{-3}$ M	75.85^{WL}	[95]
Amoxicillin	mild steel	1 M H_2SO_4	0.001 M	60.95^{WL}	[96]
Cefixim				80.06^{WL}	
Cephalexin				76.94^{WL}	
Esomeprazole	galvanized steel	5% NaCl	100 ppm	98.32^{WL} 98.34^{pp} 98.32^{EIS}	[97]
Cephalothin	API 5L X52 steel	1 M HCl	200 ppm	89.6^{EIS} 88^{pp}	[98]

Inhibitor	Metal	Media	Concentration	Inhibition efficiency	Reference
Melatonin	carbon steel	0.5 M H_2SO_4	500 ppm	94.76^{pp} 93.90^{EIS}	[99]
Irbesartan	mild steel	1 M HCl	300 ppm	95^{pp} 91^{EIS}	[100]
		0.5 M H_2SO_4		84^{pp} 81^{EIS}	
Carbamazepine	carbon steel	0.1 M H_2SO_4	$5\cdot10^{-3}$ M	90^{pp}	[101]
Paracetamol		0.25 M acetic acid 0.25 M sodium acetate buffer		85^{pp}	
Vitamin C	copper	4% HCl	3 g/dm^3	61.93^{WL}	[102]
		3% NaCl		66.01^{WL}	
Thiamine hydrochloride	copper	30 min 30°C	$2\cdot10^{-3}$ M	69.9^{WL}	[103]
		2.5 M HNO_3			
Potassium folate	copper	1 M Na_2SO_4 15°C	0.01 M 0.006 M	73.9^{pp} 60.9^{pp} 63.57^{EIS}	[104]
6-chloro-1,1-dioxo-3,4-dihydro-2H-1,2,4-benzothiadiazine-7-sulphonamide	copper	2 M HNO_3	$1.1\cdot10^{-5}$ M	82.6^{WL} 89.7^{pp} 60.5^{EIS} 80.6^{EFM}	[105]
1-((s)-3-mercapto-2-methyl propanoyl) pyrrolidine-2-carboxylic acid				79.4^{WL} 85.6^{pp} 43.5^{EIS} 67.1^{EFM}	
3-(2-methoxy phenoxy) propane 1,2-diol				75.9^{WL} 64.8^{pp} 32.2^{EIS} 63.9^{EFM}	
Ranitidine hydrochloride	mild steel	1 M HCl	400 ppm	89^{WL} 90^{pp} 92^{EIS}	[106]
Meropenem	copper	1 M HNO_3	300 ppm	94.6^{WL} 93.7^{pp} 96.7^{EIS} 98.7^{EFM}	[107]

Inhibitor	Metal	Media	Concentration	Inhibition efficiency	Reference
Septazole	copper	0.1 M HCl	900 ppm	84.8^{pp} 82.4^{EIS} 84.3^{EFM}	[108]
Metronidazole	copper	1 M HCl	$1\cdot10^{-3}$ M	91.8^{Tafel} 87.6^{Rp}	[109]

WL - weight loss; pp - potentiodynamic polarization; EIS - electrochemical impedance spectroscopy; EFM - electrical frequency modulation.

Azithromycin is generally slightly soluble in aqueous environments and so are its complexes. IUPAC name of azithromycin is (2R,3S,4R,5R,8R,10R,11R,12S,13S,14R) -11-[(2S,3R,4S,6R)-4-(dimethylamino)-3-hydroxy-6-methyloxan-2-yl]oxy-2-ethyl-3,4,10-trihydroxy-13- [(2R,4R,5S,6S)-5-hydroxy-4-methoxy-4,6-dimethyloxan-2-yl] oxy - 3,5,6,8,10,12,14-heptamethyl-1-oxa-6-azacyclopentadecan-15-one and the structure of azithromycin molecule is presented in Figure 1 which is drawn by ArgusLab 4.0 [115]. As it can be seen it possesses numerous heteroatoms, nitrogen and oxygen, that are known as very important in the processes of organic compounds adsorption on metal surface. The compounds that have in their structure those kind of molecules are usually expected to be able to provide high corrosion inhibition efficiency due to strong adsorption of organic compound molecules on copper surface [49,50,52]. Based on the previous facts it might be interesting to test the electrochemical behaviour of azithromycin in the presence of brass and see if it possesses inhibiting characteristics.

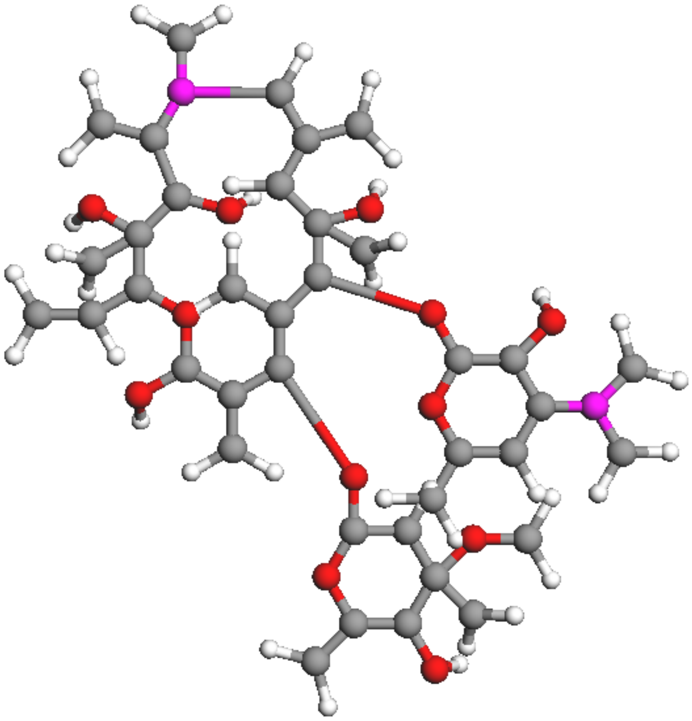


Figure 1 Azithromycin molecule structure

2. MATERIALS AND METHODS

2.1. Electrochemical measurements

All electrochemical measurements were performed using potentiostat (IVIUM XRe, IVIUM Technologies) with supporting software. The brass electrode was working electrode and it was made by the method of casting upward and then sealed using sealing material based on methyl methacrylate. In addition to the working electrode in the experiments were used two more electrodes i.e. platinum electrode as auxiliary one and saturated calomel electrode (SCE) as reference electrode. Before each measurement working electrode was polished by alumina paste 0.3 μm (Al_2O_3, Buehler USA), then was rinsed with distilled water and dried.

Electrochemical methods such as open circuit potential (OCP), potentiodynamic polarization measurements and electrochemical impedance spectroscopy measurements were applied. Open circuit potential was recorded during 30 minutes after which potentiodynamic polarization measurements were conducted. Potentiodynamic polarization measurements were recorded from OCP to -0.5 V vs. SCE in the cathodic as well as from OCP to 0.25 V vs SCE in anodic direction. These measurements were conducted with scan rate 1mV/s. Electrochemical impedance spectroscopy (EIS) measurements were performed at OCP over a frequency range 10 kHz–0.01 Hz with a single amplitude perturbation of 10 mV using IVIUM soft.

The test solution was simulated urban rain which was prepared from Na_2SO_4 (0.2g/l) (Zorka Pharmacy, Šabac, Serbia), $NaHCO_3$ (0.2 g/l) (Zorka Pharmacy, Šabac, Serbia) and $NaNO_3$ (0.2 g/l) (Zorka Pharmacy, Šabac, Serbia). The pH 2.42 of the test solution was achieved by the addition of H_2SO_4 (Zorka Pharmacy, Šabac, Serbia). In bulk solution azithromycin was dissolved at a concentration of $8 \cdot 10^{-3}$ M, afterwards these solutions were diluted to concentrations of $4 \cdot 10^{-3}$ M, $8 \cdot 10^{-4}$ M and $4 \cdot 10^{-4}$ M.

3. RESULTS AND DISCUSSION

3.1. Open circuit potential and potentiodynamic polarization measurement

Figure 2 illustrates the open circuit potential curves of brass in simulated acid rain solution (SAR) in the absence and presence of different concentrations of azithromycin. According to these curves, the open circuit potential is shifted into negative direction in the presence of inhibitor in regard to uninhibited solution. In the blank solution, the OCP value decreases with time due to the formation of adsorbed layer of sulfate, nitrate and carbonate ions at interface brass/electrolyte [116]. The addition of azithromycin in SAR leads to the displacement of OCP toward negative values. The maximum shift in the OCP value was 79 mV in regard to inhibitor-free solution. This preliminary result points to ability of azithromycin to hinder both anodic and cathodic reactions and it may be classified as mixed type inhibitor.

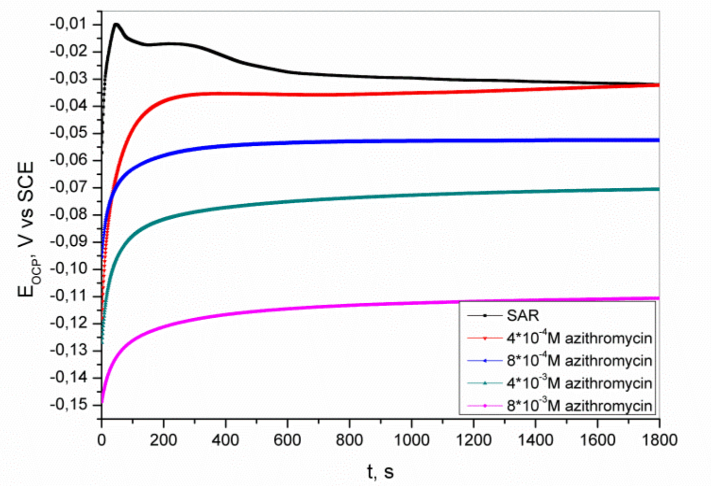


Figure 2 Open circuit potential measurements of brass in simulated acid rain without and with the addition of azithromycin

Further, the ability of azithromycin to inhibit corrosion of brass in simulated acid rain solution (at pH 2.42) was investigated by potentiodynamic polarization measurements. Figure 2 shows the obtained polarization curves of brass in SAR without and with the addition of different concentrations of azithromycin. Corrosion parameters including corrosion potential (E_{corr}), corrosion current density (j_{corr}), anodic (b_a) and cathodic (b_c) Tafel slopes and inhibition efficiency (IE) derived from these curves are presented in Table 2. The inhibition efficiency is calculated according to the following equation:

$$\%IE = [(j_{corr} - j_{corr(inh)}) / j_{corr}] \cdot 100 \tag{1}$$

Where j_{corr} and $j_{corr(inh)}$ are corrosion current densities without and with the addition of azithromycin.

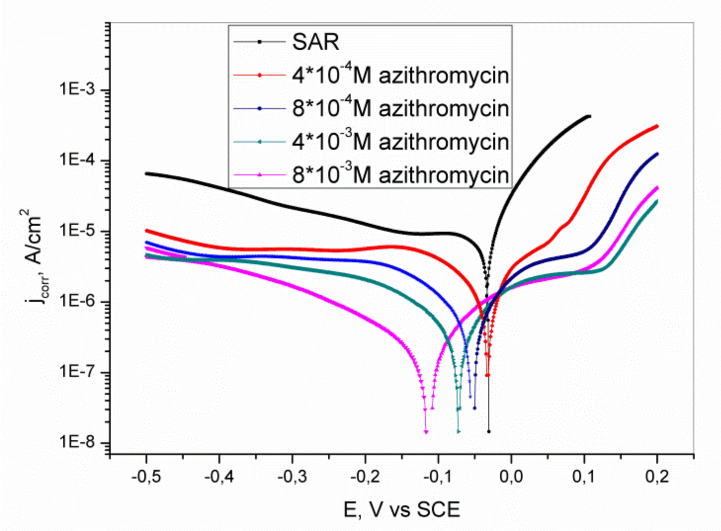


Figure 3 Potentiodynamic polarization curves for brass recorded in simulated acid rain without and with the addition of different concentrations of azithromycin

Based on relevant literature, the reduction of oxygen presents the cathodic reaction in acidic solution according to the reactions (2 and 3) [117]:

$$O_{2,\ bulk} \rightarrow O_{2,\ surf} \rightarrow O_{2,\ ads} \qquad (2)$$

$$O_{ads} + 2H^{+} + 2e^{-} \rightarrow H_2O \qquad (3)$$

Magaino [10] also suggest that initial step of the copper dissolution process is a charge transfer reaction and a result of this is the formation of an adsorbed Cu^{+} species (reaction 4) while the initial step for zinc dissolution is the charge transfer reaction resulting in formation of Zn^{+}_{ads}. Further, the formed Zn^{+}_{ads} is oxidized to Zn^{2+} directly or through the formation of Zn^{2+}_{ads}.

$$Cu \rightarrow Cu^{+}_{ads} + e^{-} \qquad (4)$$

After which Cu^{+}_{ads}associated with anion species X^{n-}_{surf} which diffuses from the bulk solution on the electrode surface and reacts with Cu $^{+}_{ads}$ according to reaction (5):

$$nCu^{+}_{ads} + X^{n-}_{surf} \rightarrow [(Cu^{+})_nX^{n-}]_{surf} \qquad (5)$$

Then $[(Cu^{+})_nX^{n-}]_{surf}$ diffuses into the bulk solution.

By comparing polarization curves (Figure 3) it can be seen that in the presence of azithromycin comes to noticeable reduction of both anodic and cathodic current densities in regard to the uninhibited solution. It is assumed that the protective layer is formed in the presence of inhibitor. As can be seen from Table 2 the inhibition efficiency increases with inhibitor concentration rise. Therefore, the obtained results indicate the adsorption of inhibitor molecules on the brass surface and formation of protective layer. Both anodic and cathodic Tafel slopes are changed in the presence of azithromycin in regards to SAR so it can be thought that azithromycin has influence on the kinetics of metal dissolution and of hydrogen evolution. This is in agreement with the literature dealing with relevant topic [118,119]. Also, in the presence of azithromycin, the E_{corr} values are moved into negative direction with maximum shift 78 mV. According to literature [120], azithromycin can be classified as mixed-type inhibitor which is in agreement with results obtained by open circuit potential measurements.

Table 2 Electrochemical parameters of brass corrosion in simulated acid rain without and with the addition of different concentrations of azithromycin

Inhibitor concentration, M	**E_{corr}, V vs SCE**	**j_{corr}, μA/cm^2**	**b_a, V/dec**	**$-b_c$, V/dec**	**IE, %**
Inhibitor free solution	-0.034	4.95	0.041	0.173	/
$4\cdot10^{-4}$	-0.033	0.392	0.044	0.075	92.1
$8\cdot10^{-4}$	-0.052	0.196	0.044	0.053	96.0
$4\cdot10^{-3}$	-0.072	0.142	0.054	0.049	97.1
$8\cdot10^{-3}$	-0.112	0.0917	0.056	0.090	98.2

3.2. Electrochemical impedance spectroscopy measurements

Besides the potentiodynamic polarization, the electrochemical impedance spectroscopy measurements were carried out in order to obtain more information about corrosion behavior of brass in the absence and presence of azithromycin in SAR. The equivalent circuits used for fitting the electrochemical impedance spectroscopy data obtained in SAR without and with the addition of inhibitor are presented in Figure 4 (a, b). The corresponding Bode and Nyquist plots are shown in Figure 5 (a-c).

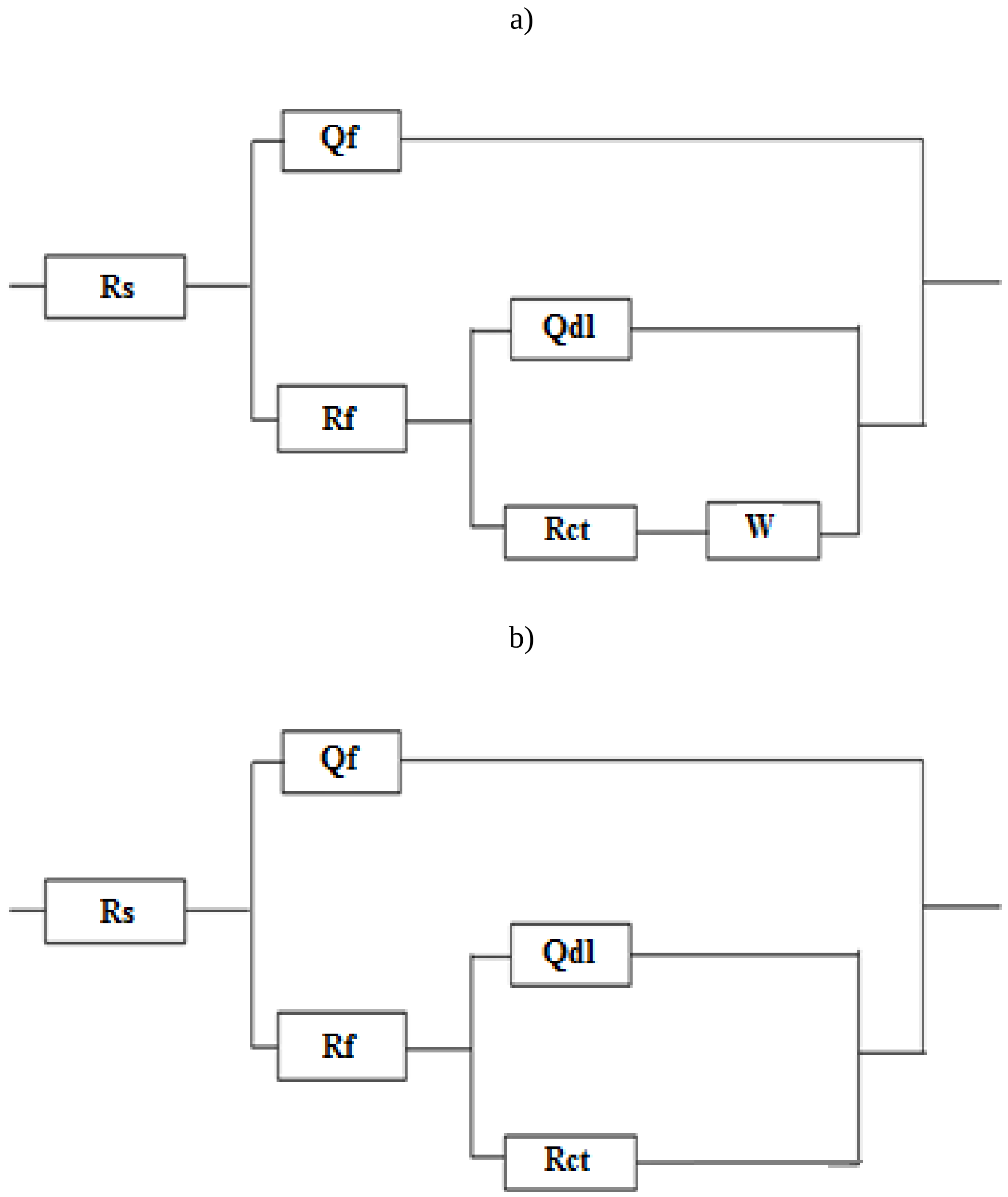
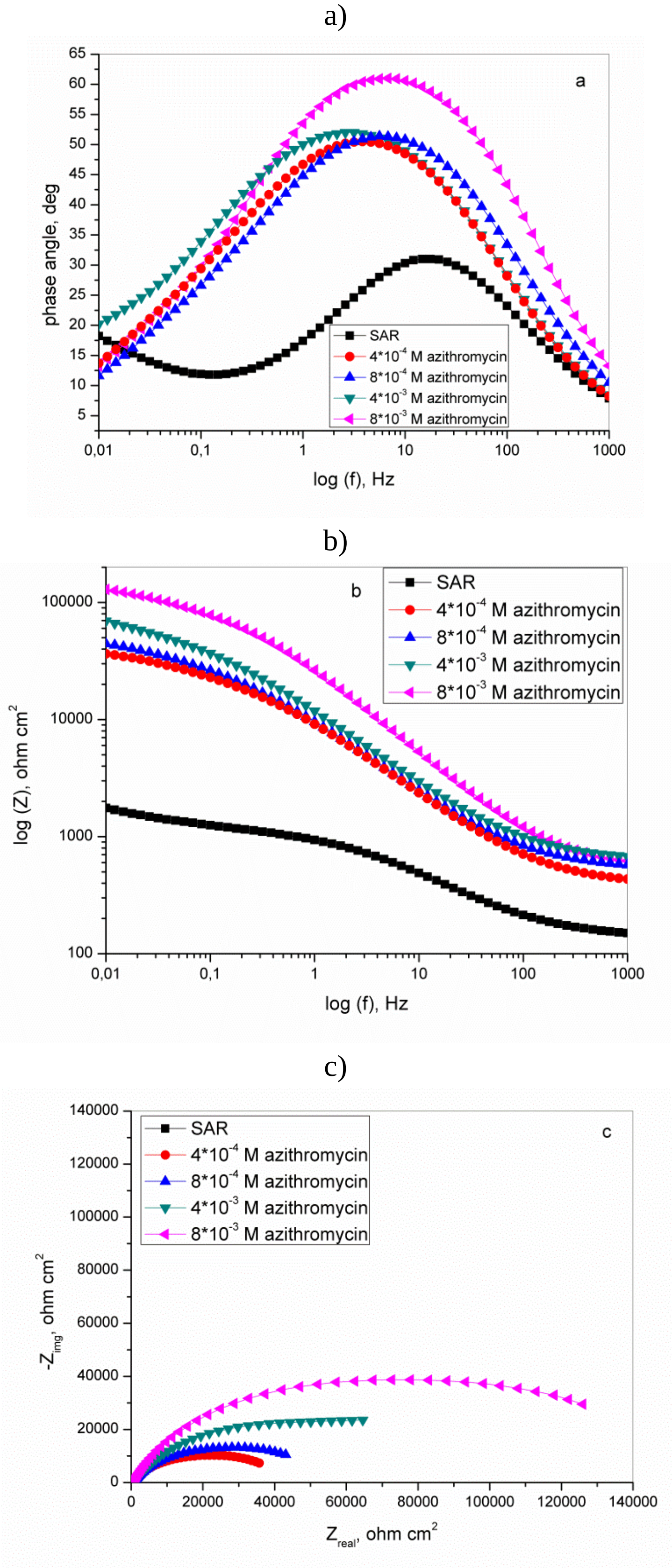


Figure 4 Electrical equivalent circuits for brass in simulated acid rain (a) and with the addition of azithromycin (b)


a)

b)

c)

Figure 5 EIS diagrams for brass in simulated acid rain in absence and presence of different concentration of azithromycin; Bode phase angle (a); Bode modules (b) and Nyquist plots (c)

Corrosion kinetic parameters derived from EIS method are given in Table 3. The inhibition efficiency is calculated according to equation (6):

$$\%IE = [(R_{ct} - R_{ct}^{o}) / R_{ct}] \cdot 100 \tag{6}$$

Where R_{ct}^{0} and R_{ct} ($\Omega \cdot cm^2$) represent the charge-transfer resistance of brass in simulated acid rain solution without and with the addition of azithromycin.

Table 3 Electrochemical impedance spectroscopy parameters for brass in simulated acid rain without and with the addition of different concentration of azithromycin

Inhibitor, M	R_s, Ω cm^2	R_f, Ω cm^2	R_{ct}, Ω cm^2	C_f, µF cm^{-2}	n_1	C_{dl}, µF cm^{-2}	n_2	W, Ω^{-1} cm^{-2} s$^{0.5}$	IE, %
Inhibitor free solution	116.9	1311.0	911.7	0.0994	0.675	0.7470	0.400	38.9	/
$4 \cdot 10^{-4}$	385.6	25340	17920	0.0349	0.700	0.0329	0.620	/	94.9
$8 \cdot 10^{-4}$	523.8	33780	21390	0.0270	0.700	0.0316	0.625	/	95.7
$4 \cdot 10^{-3}$	614.0	62980	45450	0.0227	0.710	0.0262	0.635	/	97.9
$8 \cdot 10^{-3}$	648.6	83750	67900	0.0517	0.780	0.0404	0.695	/	98.6

Figure 4 (a, b) shows the electrical equivalent circuits employed to analyse the obtained results using the IVIUM soft program, where R_s is the solution resistance, R_f is the resistance of the film formed on the brass surface while R_{ct} represents the charge transfer resistance. Q_f and Q_{dl} represent the constant phase elements (CPE), where Q_f is composed of the capacitance of the film formed on the electrode surface C_f and the deviation parameter n_1, and Q_{dl} is composed of the double-layer capacitance C_{dl} and the deviation parameter n_2. W is the Warburg impedance. The C_f and C_{dl} values are calculated according to the following equations [121]:

$$C_f = (Q_f \cdot R_f^{1-n})^{\frac{1}{n}} \tag{7}$$

$$C_{dl} = (Q_{dl} \cdot R_{ct}^{1-n})^{\frac{1}{n}} \tag{8}$$

In the presence of azithromycin the Warburg element is removed. It can be observed that an increase in the concentration of inhibitor causes an increase in R_p and R_{ct} values and a corresponding decrease in C_f and C_{dl} in regards to uninhibited solution. This is a result of increasing surface coverage by the inhibitor, leading to an increase in inhibition efficiency. The Bode phase plot (Figure 5a) shows the change in the phase angle as a function of inhibitor concentration which indicates the improvement in the smoothness of the metal surface with gradual increase in the inhibitor concentration. Besides, obtained phase angles in inhibited solutions move to lower frequencies indicating the increasing coverage of electrode surface with the adsorption of azithromycin molecule and/or with the deposition of corrosion products [122]. Also, the impedance modulus (Figure 5b) is increased with the addition of inhibitor which points to the dissolution of brass in SAR is reduced. Therefore, the increase in the R_p and R_{ct} values with simultaneously decrease in the C_f and C_{dl} upon increasing concentration of inhibitor shows the formation of the protective layer on the brass surface which is supported by the continuous rise in the phase angle thereby confirming the corrosion inhibition performance of azithromycin. As can be seen in Table 3, n values increase with increasing the concentration of inhibitor, which indicates the decrease of the surface inhomogeneity due to the adsorption of inhibitor [123]. Nyquist curves of metal in inhibited and uninhibited SAR solutions containing different concentrations of azithromycin are presented in Figure 5c. EIS spectra data consists of one depressed capacitive loop. The higher diameter of loop obtained in SAR medium with AZ indicated that this compound acts as an efficient corrosion inhibitor of brass.

The results obtained from EIS yield good agreement with the data derived from potentiodynamic polarization method, which is illustrated in Figure 6.

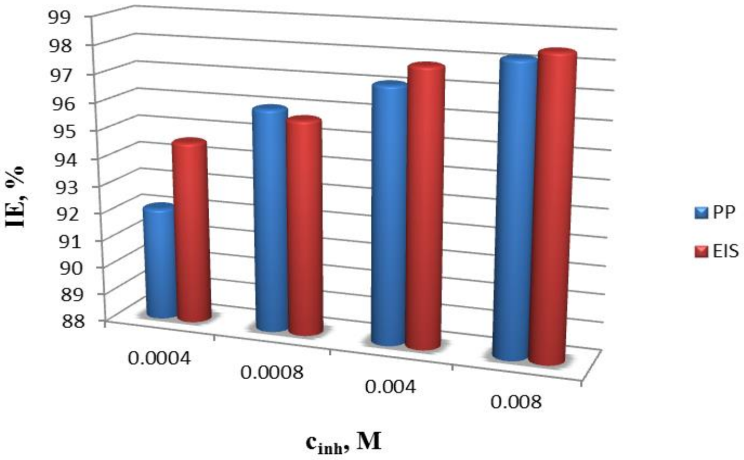


Figure 6 Comparison of inhibition efficiency (IE) of azithromycin obtained by potentiodynamic polarization (PP) and electrochemical impedance spectroscopy (EIS) measurements

3.3. Adsorption isotherm

According to the literature [124], organic inhibitors may achieve their effect due to adsorption on the metal surface. Having that in mind, adsorption isotherm provides useful information about adsorption mechanism of tested inhibitor. The adsorption process can be described by following isotherms: Langmuir, Frumkin, Temkin, and Dhar-Flory-Huggins [125]. In order to investigate the adsorption mechanism of azithromycin on brass surface Langmuir isotherm is applied. This isotherm can be presented according to the equation (9):

$$\frac{c}{\theta} = \frac{1}{K} + C \tag{9}$$

Adsorption energy is calculated using the following equation:

$$-\Delta G = \left[\ln K - \ln \frac{1}{55.5} \right] RT \tag{10}$$

where K is the constant of the adsorption process (dm^3/mol), 55.5 is the molar concentration of water, ΔG is the adsorption energy (J/mol), R is the universal gas constant (J/K·mol) and T is the thermodynamic temperature (K). The obtained plot of c/θ as function of inhibitor concentration (c) yield a straight line as is illustrated in Figure 7.

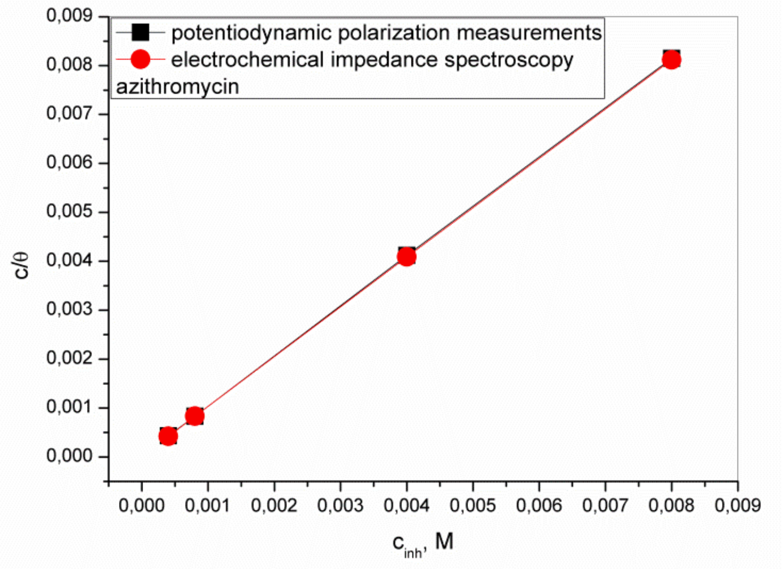


Figure 7 Langmuir adsorption isotherm of azithromycin on brass surface

Table 4 Adsorption parameters for brass in simulated acid rain with different concentration of azithromycin

Technique	R^2	slope	$-\Delta G_{ads}$, kJ/mol
Potentiodynamic polarization measurements	0.9999	1.02	35
Electrochemical impedance spectroscopy	0.9999	1.01	36

Based on the value of Gibbs free energy, the adsorption process can be classified as physisorption and chemisorption. When the $-\Delta G_{ads}$ is around 20 kJ/mol or lower, the adsorption represents physisorption while $-\Delta G_{ads}$ values in range of 40 kJ/mol or higher point to chemisorption [126]. According to presented values of Gibbs free energy in Table 4 it can be assumed that azithromycin gets adsorbed spontaneously and strongly on the brass surface. Therefore, the adsorbed layer provides protection of the brass surface from the attack of aggressive ions in SAR. The obtained value of correlation coefficient (R^2) confirms that the adsorption obeys according to Langmuir adsorption isotherm. Similar behaviour is already noticed when azithromycin was used as inhibitor of copper corrosion in 0.9% NaCl solution [127].

4. CONCLUDING REMARKS

Acid rain presents huge environmental concern. Among other devastating effects is the effect on metal surfaces where it induces corrosion processes. Another potential threat for the environment is the uncontrolled release of antibiotics. Possible way to prevent metals corrosion is the use of corrosion inhibitors. Most often various organic compounds are used for that purpose. According to the numerous literature data antibiotics unsuitable for further human usage are found to be promising corrosion inhibitors. Our data are in agreement with those results. In previous sections the results of the examination of the influence of azithromycin on the corrosion behaviour of brass in simulated acid rain solution are presented. According to the potentiodynamic polarization and electrochemical impedance spectroscopy measurements azithromycin is efficient corrosion inhibitor for brass. It can be classified as mixed type inhibitor. The value of inhibition efficiency increases with the concentration of azithromycin. The calculated Gibbs free energy indicates the strong and spontaneous adsorption of inhibitor molecules, which provides good protection of brass surface.

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Chapter 6

ELECTROCHEMICAL BEHAVIOUR OF AgCu ALLOY

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ABSTRACT

Corrosion processes cause changes in the characteristics of metallic materials during their exploitation. At the same time, these processes can lead to the formation of products harmful to the environment. All metals including precious metals and their alloys subject to corrosion, which is why a large number of researchers is engaged in their systematic extensive studies. This chapter shows the results of tests carried out on an alloy of silver-copper with high (50 mass.%) silver content in an alkaline medium in the presence of ions known as activators of corrosion, as well as in the presence of substances that are supposed to act as inhibitors of oxidation of metals and alloys.

Keywords: Silver, Copper, AgCu alloy, Corrosion, Chloride, Anodic oxidation, BTA

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1. INTRODUCTION

1.1. Literature data

Corrosion mechanisms of metals and alloys in some medium are closely related to their behaviour during anodic polarisation. Silver-copper alloys are characterised with good resistance to corrosion, high electrical and thermal conductivity and good workability. That makes them suitable for a large area of application.

The mechanical properties of copper can be most easily improved by alloying, but the addition of the smallest amount of any other element reduces its thermal and electrical conductivity. The only exception is silver, which does not affect the conductivity of copper, and provides an excellent relationship of good mechanical properties and conductivity [1–3]. Results of investigations of electrochemical characteristics of AgCu alloys are presented in numerous scientific journals, as well as the results obtained on pure copper and pure silver.

Electrochemical literature provides a large amount of data relating to electrochemical behaviour of pure copper and pure silver [4–14]. Silver and copper influence electrochemical behaviour of gold alloys and their corrosion characteristics have been investigated as well [15–19].

Electrochemical and other scientific journals give insight into the big corrosion-related issues [20–32]. Mechanism of anodic oxidation of pure copper was the topic of some our earlier works [33–35]. Investigating anodic oxidation of copper in alkaline medium in presence of chloride ions Modestov came to the conclusion that, first Cu_2O is formed followed by formation of CuCl and CuO on more positive potentials [4].

During their investigation of the effect of chlorides on the initial stages of anodic oxidation of Cu (111) in alkaline solutions for $[Cl^-]/[OH^-] = 0.01$, Kunze *et al.* [5,31] found that the same ordered precursor phase of adsorbed OH is observed in the underpotential region of oxidation as in Cl^- free solutions. For $[Cl^-]/[OH^-] = 0.1$, threadlike nanostructures resulting from the reaction of the ejected Cu atoms with chlorides are formed before agglomeration with the 2D Cu ad-islands formed in the final stage of the hydroxide adsorption process. For $[Cl^-]/[OH^-] = 10$, the step edges, which are normally the preferential sites of the reaction with hydroxide, are blocked by the formation of non-ordered surface chloride complexes.

Our first systematic investigations relating to the corrosion behavior of the silver-copper alloys were performed on alloy with silver content of 4 at. %. This alloy exhibited anneal hardening effect after appropriate thermomechanical treatment. The electrochemical characteristics of the alloy have been tested after different stages of the process which results in this unusual effect, wherein the samples of the alloy were synthesized by two different metallurgical methods: ingot metallurgy and powder metallurgy. The results were published in the relevant scientific journals [36–41]. This chapter summarizes the results obtained by testing an electrochemical behavior of AgCu with a high silver content (50 mass.%) [42–61]. The alloy with 50 mass.% Cu and 50 mass.% Ag is used for solders in industry [62].

1.2. Theoretical background

The AgCu alloys belong to characteristic eutectic type of alloys. Phase diagram for Ag-Cu binary system is presented in Figure 1. It shows the full solubility of components in the liquid state and mutual restricted solubility in the solid state [63].

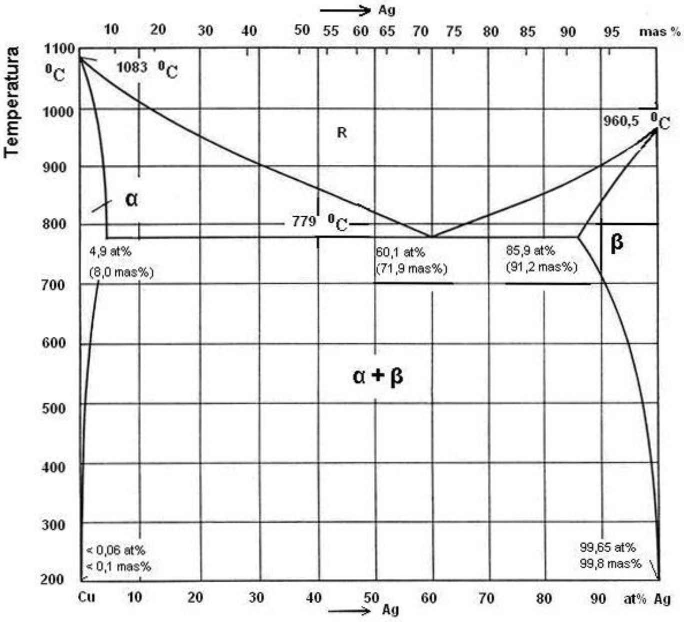


Figure 1 Phase diagram for Ag-Cu binary system [63]

Solid AgCu alloy with 50 mass.% Ag is composed of primary Cu crystals, named α crystals, surrounded by eutectic solid mixture. Eutectic solid mixture is composed of 28.1% Cu and 71.9% Ag in a form of finely distributed small grains of two solid solutions - small amount of copper in silver and small amount of silver in copper. The solubility of both copper in silver and silver in copper is maximal at the eutectic temperature. β crystals solidified at the eutectic temperature are composed of 91.2 mass.% Ag and 8.8 mass.% Cu. With further decrease in temperature, the mutual solubility of the alloy's components decreases rapidly. The boundary lines in the phase diagram show that silver is precipitated from the α crystals and simultaneously the excess copper content will be eliminated from the β crystals.

Corrosion characteristics of metals in water solutions can be predicted from their potential-pH diagrams [64]. From the E-pH diagram for Ag-H_2O system it can be seen that in alkaline water solutions the following reactions can take place during anodic oxidation:

$2Ag + H_2O = Ag_2O + 2H^+ + 2e^-$ (1)

$Ag_2O + H_2O = 2AgO + 2H^+ + 2e^-$ (2)

$2AgO + H_2O = Ag_2O_3 + 2H^+ + 2e^{-`}$ (3)

From the E-pH diagram for Cu-H_2O system it can be seen that during anodic oxidation of copper in alkaline water solutions the following reactions may occur [64,65]:

$2Cu + H_2O = Cu_2O + 2H^+ + 2e^-$ (4)

$Cu_2O + H_2O = 2CuO + 2H^+ + 2e^-$ (5)

$$Cu + H_2O = CuO + 2H^+ + 2e^- \quad (6)$$

At more positive potentials following reaction can take place, as well:

$$Cu_2O + 3H_2O = 2CuO_2^{2-} + 6H^+ + 2e^- \quad (7)$$

2. MATERIALS AND METHODS

Experiment described in this chapter were carried out using a system for electrochemical measurements fully developed by Technical Faculty in Bor. The system is precisely described in our previous works [42–44,66]. Standard electrochemical cell used in the experiments consisted of working electrode formed from pure refined metals (silver and copper) or from AgCu50 alloy, saturated calomel electrode (SCE) as reference electrode and a platinum foil (2 cm^2 surface area) as counter electrode. The alloy is formed by smelting the mixture of equal quantities of pure copper and pure silver in a quartz furnace at 1250 ºC, casting and subsequent cooling. The oxides formed during cooling were removed by aqueous solution of nitric acid (50 vol.% HNO_3). After that the alloy was subjected to rolling and drawing to obtain wires with 1mm diameter. The wires was subjected to recrystallisation annealing at 600 ºC for 30 min.

The working electrode surface represented a vertical intersection of the 1 cm long part of that wire. Figure 2 represents the microstructure of surface of the electrode made from AgCu50 alloy. The microphotography shows a brighter phase rich in silver and a darker phase rich in copper. Crystal grains are elongated in the direction of rolling.

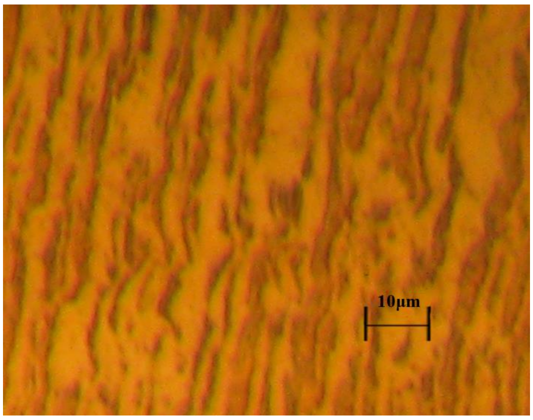


Figure 2 Microstructure of surface of the electrode made from AgCu50 alloy

Optical and scanning electron microscopy (SEM) were used for surface analysis of the alloy AgCu50. Metallographic microscope EPY TIP 2 was used for optical images. A JEOL JSM-6610LV scanning electron microscope (SEM) coupled with an Oxford X-Max large area SDD energy dispersive X-ray spectrometer (EDX) was employed to obtain back-scattered electron (BSE) images, secondary electron (SE) images and EDX spectra for elemental analysis. Acceleration voltage was 20 kV. The samples were gold-coated using a Leica EM SCD005 sputter coater.

All electrochemical measurements were performed at 25 ºC.

3. RESULTS AND DISCUSSION

3.1. Electrochemical behaviour of AgCu50 alloy in 0.1 M NaOH

Investigation of the electrochemical behaviour of AgCu50 alloy was first performed in 0.1 M NaOH. The same measurements were performed with pure silver and pure copper in a goal to distinguish effects that originate from each component of the alloy. Anodic polarisation curves for AgCu50 alloy, pure silver and pure copper recorded in the range of potential from -1.6 V vs. SCE and 1 V vs. SCE with the scan rate 20 mV/s are presented in Figure 3.

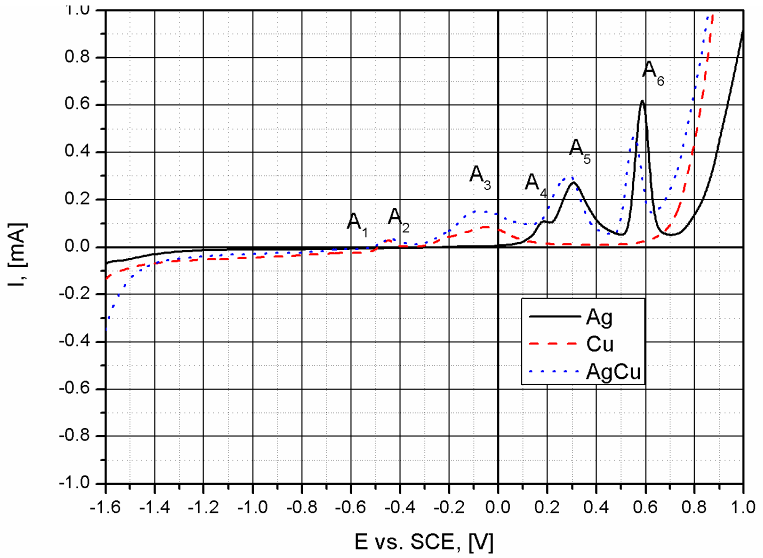


Figure 3 Anodic polarisation curves for pure metals Ag and Cu and AgCu50 alloy in 0.1 M NaOH at v = 20 mV/s

At the beginning on all three anodic curves given in Figure 3 a small peak appears. Many authors who investigated anodic behaviour of copper and silver proved that this peak originates from adsorption of hydroxyl ion on electrode surface. The same process performs on AgCu alloy and corresponds to current peak marked as A1:

$$AgCu + OH^- = AgCu(OH)_{ads} + e^- \quad (8)$$

On polarisation curves for the alloy six current peaks apper. To each of these peaks a suitable electrochemical reaction is assigned. After the adsorption of hydroxyl ions (peak A1), the first monolayer of lower oxides is formed. In case of pure copper it is Cu_2O (reaction 4) and in case of silver it is Ag_2O (reaction 1). Since reaction 4 takes place at lower potential than reaction 1, current peak corresponding to the reaction 4 is marked as A2. Next peak A3 is very wide and corresponds to reaction 5, i.e. to formation of CuO.

Current peaks A4, A5 and A6 are ascribed to the formation of oxides of silver. Silver oxide Ag_2O is formed by two-step reaction. Comparing our results with extensive literature information for those processes, we have concluded that at the potential corresponding to current peak A4 occurs formation of Ag_2O–type one, while at the potential corresponding to current peak A5 formation of the oxide Ag_2O–type two takes place. Current peak A6 is assigned to reaction 3, which results with formation of higher silver oxide, AgO.

Current peak A4 is more pronounced on the voltammogram for pure silver than on the voltammogram for AgCu50 alloy, where it is barely noticeable. Also, anodic and cathodic peaks on the voltammogram for the alloy related to silver appear on more negative potentials than current peaks on the voltammogram for pure silver, while current peaks related to copper appear at approximately the same potential as the ones on the voltammogram for pure copper. Oxygen evolution begins on more negative potentials on the alloy than on pure silver, as a result of the copper content in the alloy, which is more active than silver for this reaction [42].

Potentiostatic oxidation of the alloy in 0.1 M NaOH was first performed at -0.1 V vs. SCE corresponding to current peak A3, i.e. to formation of Cu_2O for 100 s. BSE image of the electrode surface after that treatment is presented in Figure 4. BSE image is obtained from the intensity of backscattered electrons and shows the morphology of the sample's surface. The obtained SEM results can be properly explained by considering a phase diagram of the Ag-Cu binary system.

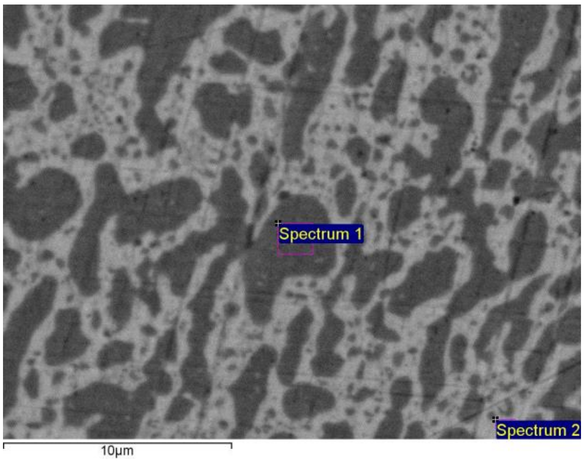


Figure 4 BSE image of AgCu50 alloy after potentiostatic oxidation at -100 mV vs. SCE for 100 s in 0.1 M NaOH [43] (with permission Elsevier, Licence No. 4344210096582)

In Figure 5 primary crystals rich with copper and named the α phase, are clearly visible as large dark grains. Eutectic mixture of α and β crystals appears as a light phase rich with silver in which small crystals of darker phase rich in copper (secondary α crystals) are uniformly distributed. At room temperature under equilibrium conditions the solubility of Ag and Cu in each other becomes less than 0.1 mass.% [43].

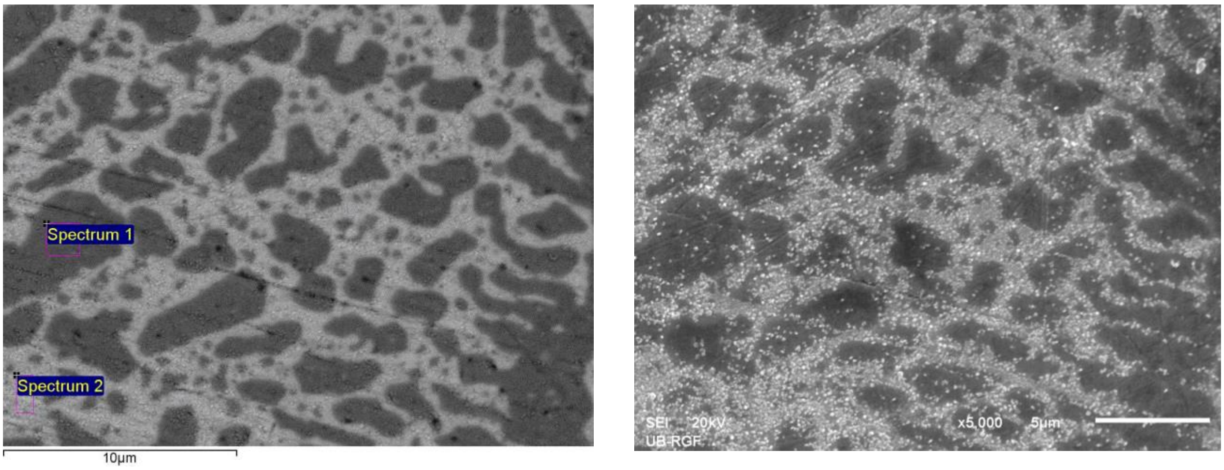
Data about the chemical composition at the points marked as spectrum 1 and spectrum 2 in Figure 4 were obtained using EDS analysis (EDS or EDX: energy-dispersive X-ray spectroscopy), based on characteristic X-radiation from an investigated sample stimulated with an X-ray beam focused on a marked point on the sample. The first EDS recording was performed at the point on the electrode where primary crystals appear on the surface, while the second EDS spectrum was obtained from the part where Figure 4 shows the presence of eutectic structure. Chemical compositions derived from the recorded EDS spectra are given in Table 1.

Table 1 Chemical composition of AgCu50 alloy after potentiostatic oxidation for 100 s in 0.1 mol dm^{-3} NaOH solution derived from EDS spectra [43]

Potential	Spectrum	O	Cu	Ag	Total	Units
-100 mV vs. SCE	Spectrum 1	1.08	92.10	6.81	100.00	mass.%
	Spectrum 2	3.12	14.55	82.33	100.00	mass.%
380 mV vs. SCE	Spectrum 1	1.26	92.30	6.44	100.00	mass.%
	Spectrum 2	3.83	14.62	81.54	100.00	mass.%
620 mV vs. SCE	Spectrum 1	0.77	92.59	6.64	100.00	mass.%
	Spectrum 2	5.14	10.25	84.61	100.00	mass.%

Spectrum 1 shows that the content of silver in α crystals is much higher than that expected from the equilibrium phase diagram. This may be a consequence of insufficient annealing time or fast cooling from 600 ^{o}C where the solubility of silver in copper is still relatively high (about 2 mass.%). A comparison of the oxygen contents in spectra 1 and 2 indicates its much higher concentration on the part covered with the eutectic mixture (spectrum 2). The ratio of copper and oxygen concentrations on this part of the surface (14.55 : 3.12) is near the stoichiometric ratio of these elements in the compound CuO (about 4). Knowing that at -100 mV vs. SCE there are no conditions for oxidation of silver, it can be concluded that the entire amount of copper in the surface layer covered by the eutectic mixture is oxidized, mainly in form of CuO. Spectrum 1 shows that the part of the surface occupied by primary α crystals is considerably less oxidized. The oxygen concentration on that part is only a bit higher than 1 mass.% [43].

The changes on the alloy surface after potentiostatic oxidation in 0.1 M NaOH at 0.38 V vs. SCE, corresponding to current peak A5 in Figure 3, i.e. to formation of Ag_2O–type two, for 100 s are presented by corresponding SEM images presented in Figure 5, BSE view is presented in Figure 5a and SE image in Figure 5b.


a)

b)

Figure 5 SEM images of surface of alloy AgCu50 alloy after potentiostatic oxidation at 380 mV vs. SCE for 100 s in 0.1 M NaOH: a) BSE view; b) SE image [43] (with permission Elsevier, Licence No. 4344210096582)

The BSE image, which shows the distribution of primary crystals and the eutectic mixture, is not changed significantly by the formation of silver oxides at that potential. However, SE image indicates the presence of a new phase. It is clearly visible from the this picture that silver oxides form inside the primary crystals too, pointing that precipitation of silver from α crystals performs during cooling. In Figure 5a, the points at which the EDS spectra were recorded are marked. The elementary composition derived from these spectra is given in Table 1 [43].

EDS does not give information about the compounds present, but the value of the potential at which oxidation was performed suggests that silver oxide should be formed. The SE image shows that oxides mostly appear over the eutectic area, rich in silver, confirming the previous conclusion. More detailed analysis of the data from the Table 1 led to conclusion that passivity can be achieved without complete coverage of the alloy's surface with oxides.

A BSE image of the surface of the AgCu50 alloy after potentiostatic oxidation at 620 mV vs. SCE (corresponding to peak A6 in Figure 3) for 100 s in 0.1 M NaOH is presented in Figure 6. The image shows that after this experiment the surface is smoother and more homogenous than that obtained after oxidation at the potential of peak A5. On the same image, the positions where EDS spectra were recorded are marked. Just as in the previous case, spectrum 1 was first recorded at a primary crystal, and then at the eutectic surface. The obtained chemical composition is given in Table 1.

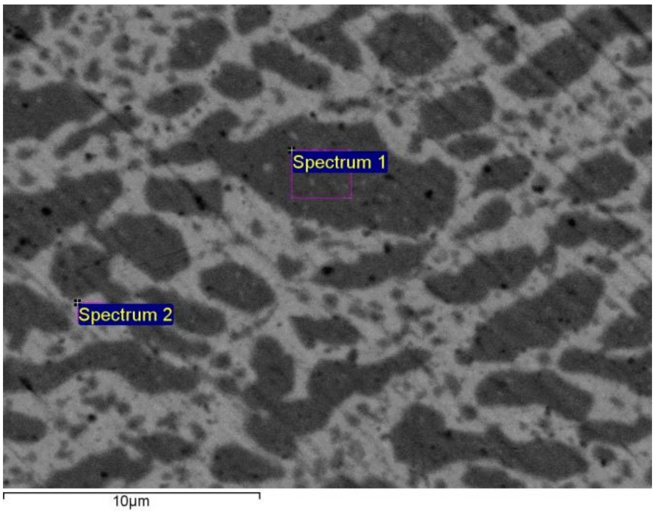


Figure 6 BSE image of surface of alloy AgCu50 alloy after potentiostatic oxidation at 620 mV vs. SCE for 100 s in 0.1 M NaOH [43] (with permission Elsevier, Licence No. 4344210096582)

From the date presented in Table 1 it can be concluded that concentration of oxygen in the primary crystal is lower than after oxidation at the potential of peak A5, which is a bit surprising. On the contrary, spectrum 2 shows a much higher concentration of oxygen that confirms the presumption of formation of the higher silver oxide, AgO. The oxide film formed at the potential of peak A6 exhibits the least protective effect against further oxidation.

3.2. Electrochemical behaviour of AgCu50 alloy in 0.1 M NaOH in presence of chloride ions

3.2.1. Pure metals

Potential – pH diagrams for systems Ag-Cl^--H_2O and Cu-Cl^--H_2O can be helpful in interpreting the results obtained by electrochemical and microscopic analysis. These diagrams are presented in Figures 7 and 8.

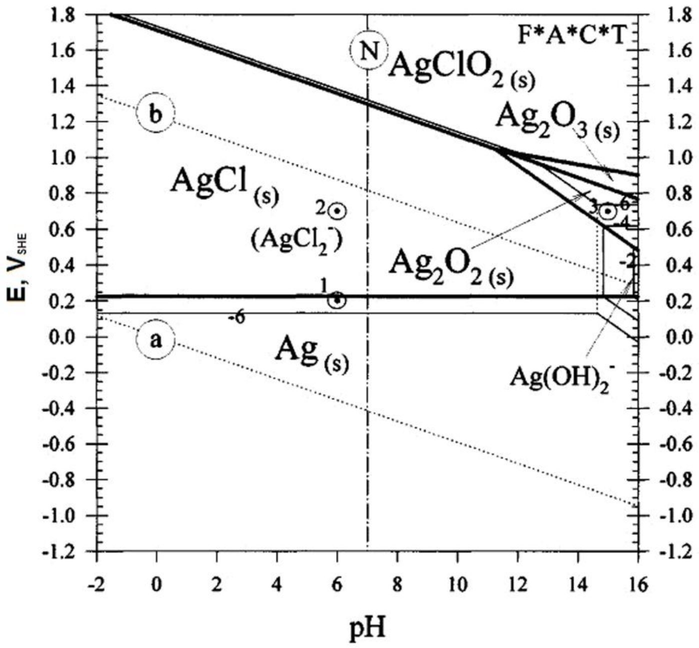


Figure 7 The E-pH diagram for system Ag-Cl^-- H_2O at 25°C in chloride solution at 1 M concentration of Cl^- [67]

Oxidation of silver in solution containing chlorides leads to formation of AgCl by the following reaction [12–14,68–71]:

$Ag + Cl^- \rightarrow AgCl + e^-$ (9)

Prior to the formation of the monolayer AgCl, an adsorption of Cl^- ions occurs [12,14,69]. Afterwards, three-dimensional growth of AgCl takes place and leads to formation of compact layer. To support the continuous formation of AgCl, there must be a transport of Ag^+ from the electrode surface toward the electrolyte and Cl^- from the electrolyte toward the silver electrode. In the newly formed layer ion transport is conducted through pores between AgCl particles, while in thick AgCl layers, this process is more likely to take place through micro-channels.

Mechanism of copper electrodissolution in presence of chloride ions with chloride concentration lower than 1 M can be presented with following equations [6,20–23,72]:

$Cu + Cl^- = CuCl + e^-$ (10)

$CuCl + Cl^- = CuCl_2^-$ (11)

It is mostly accepted that anodic dissolution of copper under the influence of chloride is not dependant of pH [6,24,72].

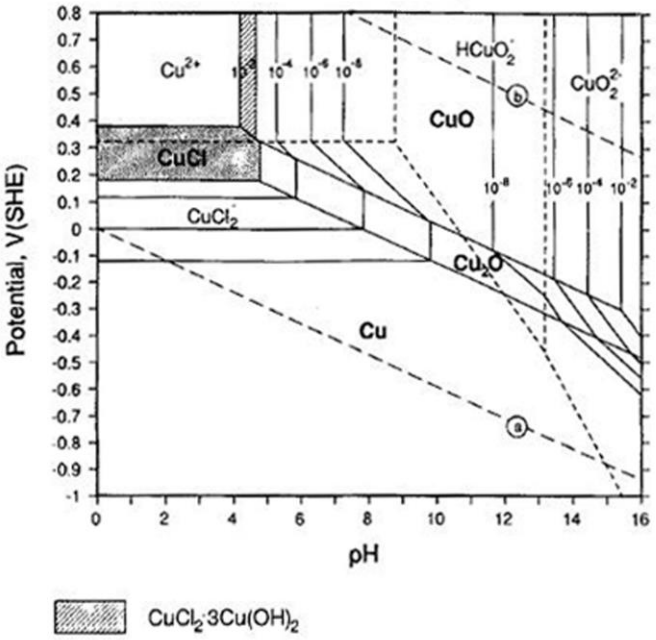


Figure 8 Cu-Cl^--H_2O equilibria at 25 °C in the presence of 0.078 activity of Cl^- ions. Situation equivalent to 0.1 M NaCl [6]

Electrochemical behaviour of copper in a solution containing chloride ions is seen as a competition between the formation of Cu_2O film which leads to passivity, and nucleation and growth of CuCl layer resulting with pitting [6,20–24,72–75]. From the E-pH diagram for Cu-Cl-H_2O system (Figure 8) it can be concluded that in alkaline medium formation of Cu_2O is favoured in comparison to the formation of CuCl layer [6,75].

3.2.2. AgCu50 alloy

The addition of Cl^- ion in solution results with formation of $CuCl_2 \cdot H_2O$, $CuCl_2 \cdot 3[Cu(OH)_2]$ and AgCl on the surface of AgCu alloys during anodic polarisation due to following reactions [31,32]:

$$Cu_xAg_y + Cl^- \rightarrow Cu_xAg_{y-1} + AgCl + e^- \quad (12)$$

$$Cu + Cl^- \rightarrow CuCl + e^- \quad (13)$$

$$CuCl + Cl^- + H_2O \rightarrow CuCl_2 \cdot H_2O + e^- \quad (14)$$

$$2Cu_2O + 2Cl^- + 4H_2O \rightarrow CuCl_2 \cdot 3[Cu(OH)_2] + 2H^+ + 4e^- \quad (15)$$

In Figures 9(a) through (d), the anodic polarisation curves for the alloy were compared with voltammograms recorded for pure copper and pure silver at a scan rate of 20 mV/s in 0.1 M NaOH with the addition of 0.005, 0.01, 0.05, and 0.5 M NaCl. Comparison with the voltammograms obtained under the same conditions without the presence of chloride ions, shows that first three current peaks, A1, A2, and A3, appear at approximately the same potentials and with the same current densities in solution with the Cl^- ion concentration of

0.001 M. Current peaks A4, A5, and A6 appear at more positive potentials and at higher current density values, which means that Cl^- ions have an activation effect. Peak A1 is more pronounced on the curves recorded in the solutions which contain chloride ions because adsorption of not only OH^- ions, but also Cl^- ions occurs. With chloride ion concentrations higher than 0.001 M, in the potential region of current peak A4, a new current peak A′ appears which corresponds to the formation of AgCl as a result of reaction (12). Increase in current density of the anodic peaks of A1, A2, and A3 in solutions with Cl^- ion concentration higher than 0.001 M can be attributed to reactions (13) through (15).

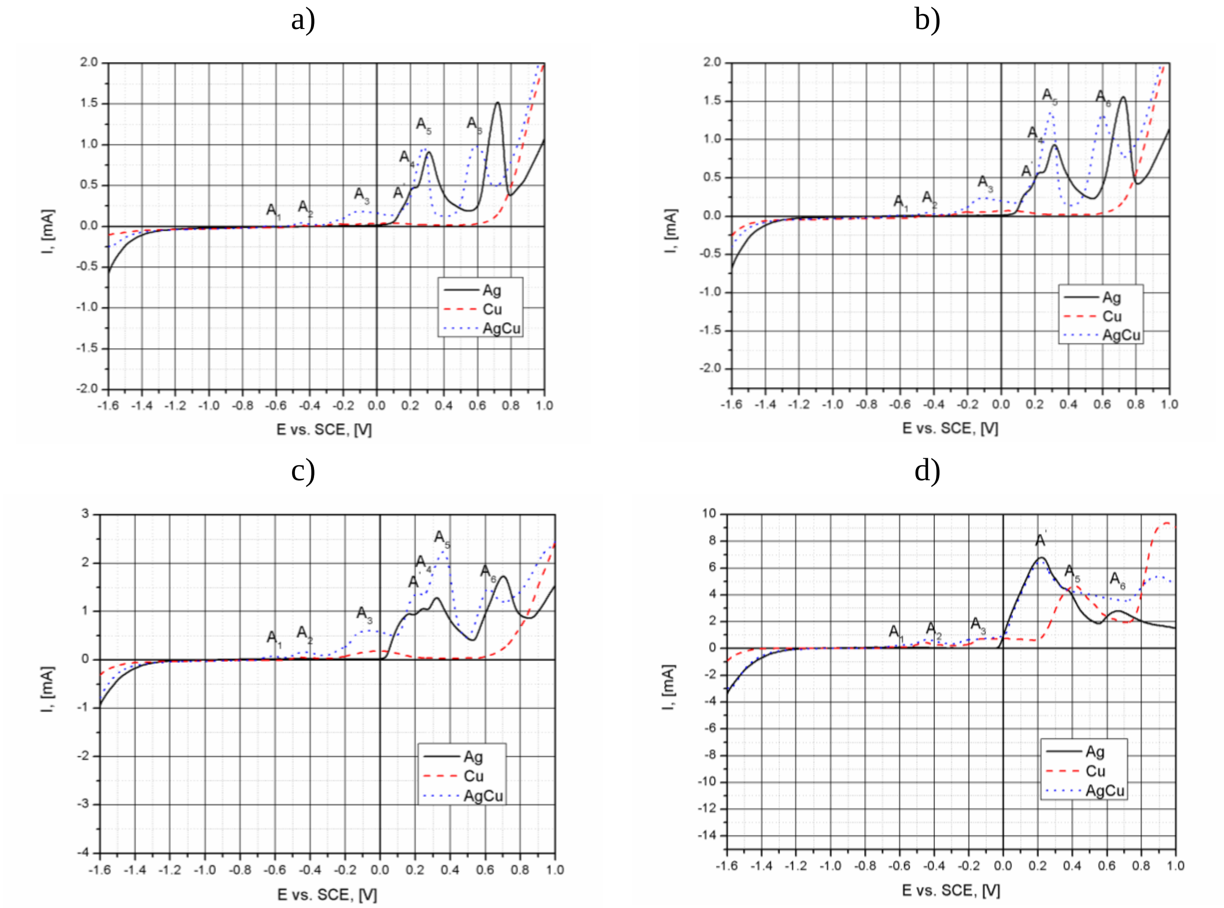

a) b) c) d)

Figure 9 Anodic polarisation curves for pure metals Ag and Cu and AgCu50 alloy in:
a) 0.1 M NaOH + 0.005 M NaCl; b) 0.1 M NaOH + 0.01 M NaCl; c) 0.1 M NaOH + 0.05 M NaCl; d) 0.1 M NaOH + M NaCl at *v* = 20 mV/s

Considering that the formation of copper oxide and chloride occur at approximately the same potentials, new current waves, except A′, do not appear on voltammograms recorded with the presence of Cl^- ions. There is only an increase of current density in the whole region of the potential. With Cl^- concentration of 0.5 M, current peaks attributed to the formation of copper chlorides and oxides appear on the voltammogram for the alloy on approximately the same potential as on the voltammogram for pure metal, while the current peak related to the formation of AgCl is appearing on the more positive potential on the voltammogram recorded for the alloy than on the voltammogram for pure silver.

Potentiostatic curves obtained for the alloy in 0.1 M NaOH with different concentrations of NaCl at 620 mV vs. SCE, corresponding to the peak A6, are presented in Figure 10. Time - current density curves are decreasing monotonously until they reach a stationary state. When the Cl^- ion concentration is up to 0.005 M, the presence of these ions has no significant influence on the oxidation process of the investigated alloy. When the concentration of chloride ions is from 0.01 to 0.1 M, they have an obvious activation effect on processes performing on the electrode surface. In that concentration area a more intensive formation of chlorides of both present metals occurs. The chloride concentration increase over 0.1 M does not lead to a suitable increasing of chloride formation rate [42].

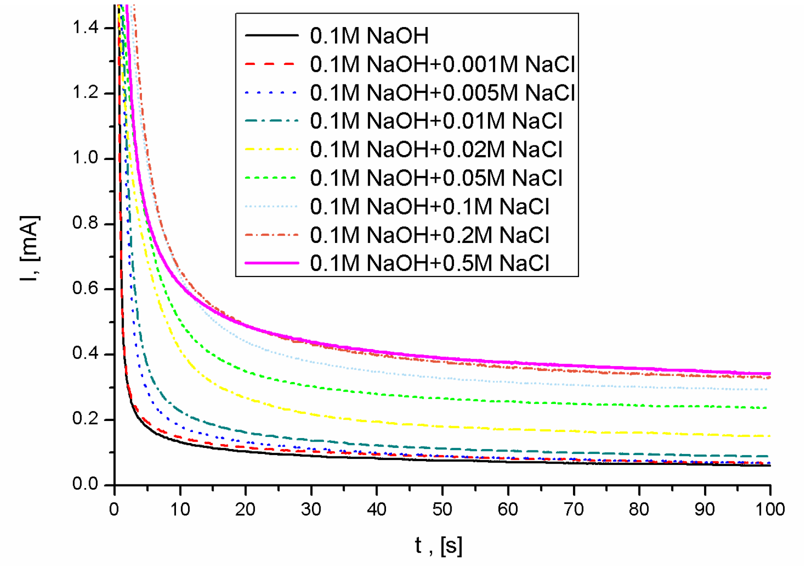


Figure 10 Current–time dependences obtained for the AgCu50 alloy in 0.1 M NaOH at 620 mV vs. SCE with different concentrations of chloride ions; electrode surface area 0.1 cm^2

Potentiostatic oxidation of the AgCu50 alloy is performed at the potentials corresponding to current peaks A3, A’ and A5, i.e. at -100 mV, 200 mV and 300 mV, all vs. SCE. Figure 11a shows a BSE image of the alloy’s surface after potentiostatic oxidation at -100 mV vs. SCE for 100 s in 0.1 M NaOH + 0.02 M NaCl solution, while the corresponding SE image is given in Figure 11b. There is an obvious difference compared to the results obtained under the same conditions without the presence of chloride ions. Namely, the specific groups of rod-shaped crystals appearing here are not present on any image obtained without the presence of chloride. The crystals’ concentration is much higher on the portion of the surface covered with the eutectic mixture, but they also appear inside primary α grains. Knowing that there is a high affinity between silver and chlorine, this may be another confirmation of the presence of precipitated silver inside the primary formed α crystals. Very inhomogeneous structure of the products could be a consequence of a changed mechanism of the crystals growth [43].

EDS analysis was performed at the positions marked on the BSE image in Figure 11a. Results showing the corresponding chemical compositions are presented in Table 2.

Table 2 Chemical composition of AgCu50 alloy after potentiostatic oxidation for 100 s in 0.1 mol dm^{-3} NaOH + 0.02 mol dm^{-3} NaCl solution derived from EDS spectra [43]

Potential	Spectrum	O	Cl	Cu	Ag	Units
-100 mV vs. SCE	Spectrum 1	2.11	0.16	82.69	15.04	mass.%
	Spectrum 2	3.84	0.00	48.33	47.83	mass.%
200 mV vs. SCE	Spectrum 1	4.27	1.84	45.51	48.38	mass.%
	Spectrum 2	4.81	1.59	49.50	44.11	mass.%
620 mV vs. SCE	Spectrum 1	2.49	0.33	22.02	75.16	mass.%
	Spectrum 2	1.40	0.09	84.04	14.47	mass.%
	Spectrum 3	3.08	0.24	24.68	72.0	mass.%

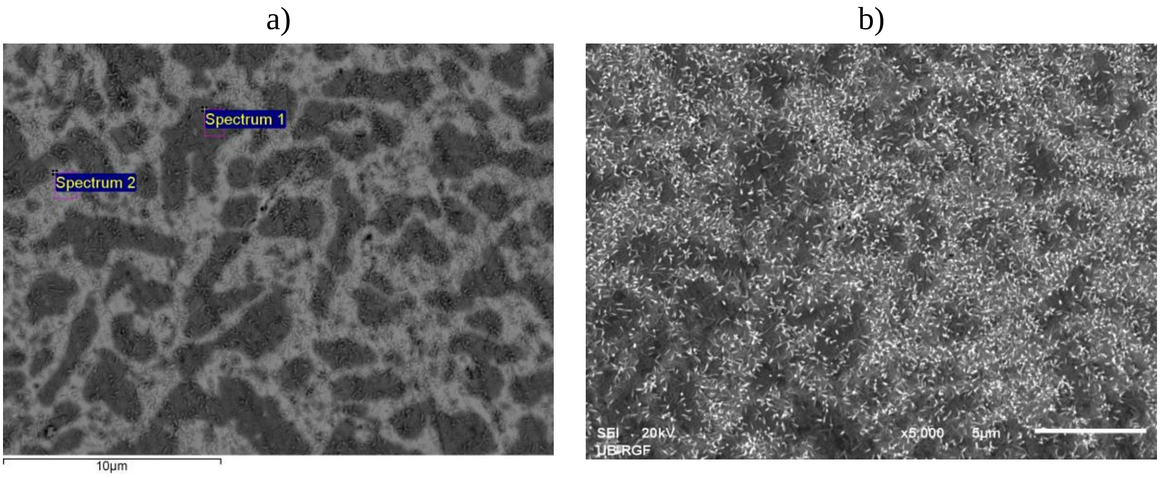


Figure 11 SEM images of surface of alloy AgCu50 after potentiostatic oxidation at -100 mV vs. SCE for 100 s in 0.1 M NaOH + 0.02 M NaCl: a) BSE view; b) SE image [43] (with permission Elsevier, Licence No. 4344210096582)

Comparing these results to the ones obtained under the same conditions without the presence of chloride ions (Table 1), it can be noticed that much higher oxygen concentration appears in both positions pointing that chloride ions at a concentration of 0.02 M considerably disrupt the protective characteristics of copper oxides.

The experiment performed at a potential of +200 mV vs. SCE, corresponding to current wave A`, resulted in voluminous deposit covering the whole eutectic area. It expands towards the middle of the primary crystals. EDS spectra were recorded at the two points marked in Figure 12. Taking into account that the potential of current peak A`, which is connected with the formation of chlorides, overlaps with the beginning of the current peak ascribed to the formation of silver(I) oxide type (II), it is clear that at 200 mV vs. SCE both reactions will proceed in parallel. This is confirmed by the high concentrations of both oxygen and chlorine at both investigated places on the surface (Table 2).

Figure 13 represents BSE image recorded after potentiostatic oxidation of AgCu50 alloy at 300 mV vs. SCE for 100 s in 0.1 M NaOH + 0.02 M NaCl solution. A voluminous product similar in structure to that obtained at the potential of current peak A` covers a remarkable portion of the alloy’s surface. The corresponding EDS spectra were recorded at three points marked in Figure R13 as spectrum 1, spectrum 2 and spectrum 3. The resulting chemical compositions are given in Table 2 [43]

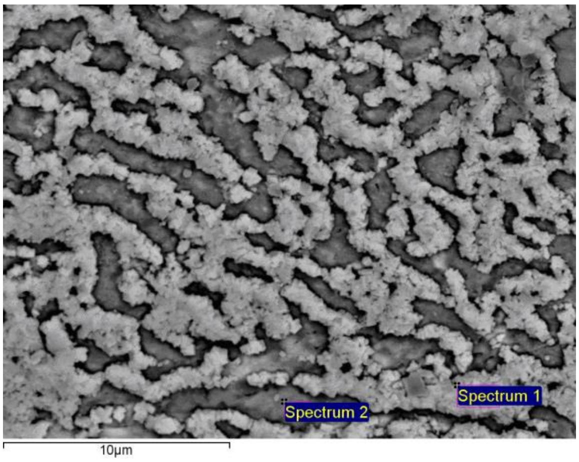


Figure 12 BSE images of surface of alloy AgCu50 alloy after potentiostatic oxidation at 200 mV vs. SCE for 100 s in 0.1 M NaOH + 0.02 M NaCl [43] (with permission Elsevier, Licence No. 4344210096582)

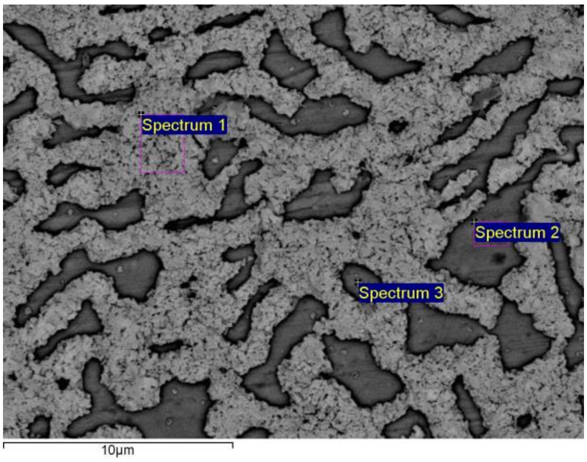


Figure 13 BSE images of surface of alloy AgCu50 after potentiostatic oxidation at 300 mV vs. SCE for 100 s in 0.1 M NaOH + 0.02 M NaCl [43] (with permission Elsevier, Licence No. 4344210096582)

Spectrum 1 is recorded on the lightest part of the surface and exhibits the greatest roughness. This field contains the highest concentration of silver and the highest concentration of chlorine, although considerably lower than that obtained after potentiostatic oxidation at the potential of peak A`. This means that formation of chlorides was not completely finished and that at 300 mV vs. SCE current waves A` and A5 still partly overlap, i.e. oxides and chlorides are being formed simultaneously. On the surface where copper dominates (spectrum 2), the presence of both oxygen and chlorine is lowest because copper is passive at that potential. This field is dark on the BSE image, which means that the morphology there did not change greatly during the experiment. Spectrum 3 was recorded at the darkest point on the SEM image. It indicates a point with very high silver content inside the area rich in copper. At this point the content of oxygen is highest and the content of chlorine is also quite high, indicating an active spot inside a primary α grain.

3.3. Electrochemical behaviour of AgCu50 alloy in 0.1 M NaOH in presence of BTA

Benzotriazole (1-H-benzotriazole, $C_6H_4N_3H$, BTA) is an anodic copper corrosion inhibitor, whose protective mechanism involves the chemisorption on copper surface, followed by formation of Cu(I)BTA complex [6,8,20,25,26,76]. Neutral molecule of benzotriazole has been commonly denoted by BTAH or BTA acronym, where 1-H signifies H atom attached to the N1 atom in the triazole group. Adsorption of BTA on copper surface is governed by the Langmuir isotherm and can be described with the following reactions [27,28,76]:

$$\mathrm{Cu + BTA \rightarrow (Cu\text{-}BTA)_{ads}} \tag{16}$$

$$\mathrm{BTA_{aq} + xH_2O_{ads} \rightarrow BTA_{ads} + xH_2O_{aq}} \tag{17}$$

Reaction (16) takes place on unoccupied spots, while a BTA molecule replaces water molecule already adsorbed on copper surface by the reaction (17).

Formation of a complex with protective characteristics during anodic polarization of copper Abdulah described with the following mechanism [77]:

$$\mathrm{Cu_{(s)} + BTAH_{(aq)} = Cu{:}BTAH_{(ads)}} \tag{18}$$

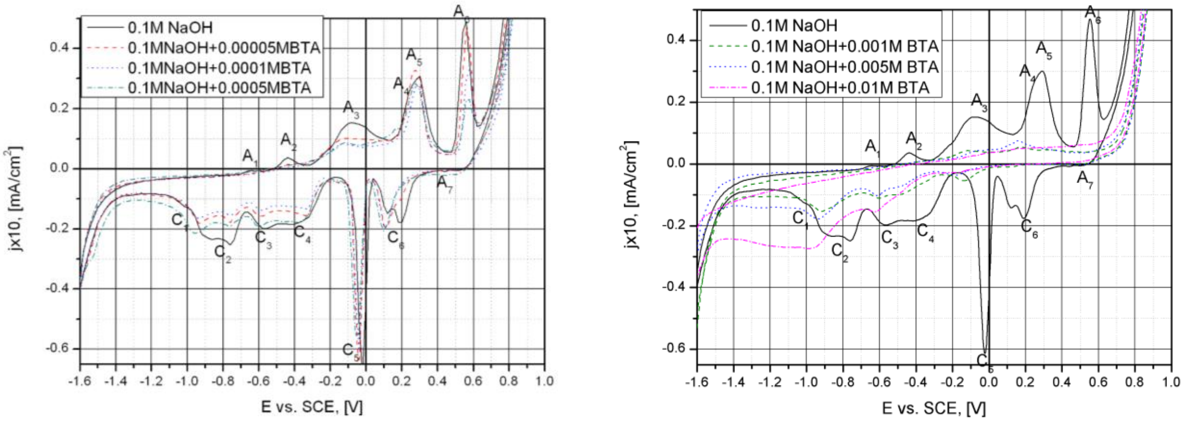
$$\mathrm{Cu{:}BTAH_{(ads)} = Cu(I)BTA_{(s)} + H^+_{(aq)} + e^-} \tag{19}$$

Modestov *et al.* [8] suggest that the formation of copper oxides Cu_2O and CuO is also occurring in parallel with the formation of CuBTA film.

Inhibition of silver is less investigated. Formation of AgMBT complex is confirmed in cyanide solution in the presence of 2-mercaptobenzothiasole [30]. Also, studying the crystalline structure of silver-benzotriazole nanoprecipitates Rajeswaran found that highly insoluble AgBTA complex forms [78]. So, it can be assumed that in the presence of benzotriazole in alkaline solutions the AgBTA complex is formed in parallel with the oxides of silver.

Behavior of AgCu50 alloy in 0.1 mol dm^{-3} NaOH in the presence of benzotriazole was first investigated by using cyclic voltammetry method. The results are presented in Figure 14.

Figure 14 shows that no new current peak appears in the presence of BTA, so it can be assumed that there are no new electrochemical reactions either. The same reactions are ascribed to the current peaks marked with the same numbers as in the part 3.1 of this chapter. It can be seen from Figure 14a that for BTA concentrations at $5.0 \cdot 10^{-4}$ M and below, all current peaks appear at nearly the same potentials as those obtained in the absence of BTA. In the higher concentration range of BTA (Figure 14b) all anodic current peaks flattened out to significantly lower levels. The cathodic currents, although also reduced, are distinct and somewhat shifted in negative direction. Taking into account that there are no new electrochemical reactions, it can be concluded that the BTA influences the oxidation processes by blocking the active sites on electrode surface.


a)

b)

Figure 14 Cyclic voltammograms of AgCu50 recorded in 0.1 M NaOH at scan rate 20 mV/s with the absence of BTA (full lines) and with the presence of BTA in the concentration range of: a) $5.0\cdot10^{-5}$-$5.0\cdot10^{-4}$ M; b) $1.0\cdot10^{-3}$-$1.0\cdot10^{-2}$ M [44]

Since the pH of 0.1 M NaOH is about 12, BTA^- species is to be considered as a stable form in the investigated system [75]. Therefore, it can be presumed that with the addition of BTA a CuBTA film is formed on copper and on Ag-Cu alloy by the following reactions:

$$Cu_{(Ag\text{-}Cu)} + BTA^-_{aq} \rightarrow (Cu_{(Ag\text{-}Cu)}\text{-}BTA)_{ads} + e^- \quad (20)$$

or

$$(Cu_{(Ag\text{-}Cu)}\text{-}H_2O)_{ads} + BTA^- \rightarrow (Cu_{(Ag\text{-}Cu)}\text{-}BTA)_{ads} + H_2O_{aq} + e^- \quad (21)$$

Copper and silver oxides form at the same time on unoccupied sites. On silver rich sites of the alloy, it could be expected that AgBTA is formed by similar reactions:

$$Ag_{(Ag\text{-}Cu)}+BTA^-_{aq} \rightarrow (Ag_{(Ag\text{-}Cu)}\text{-}BTA)_{ads} + e^- \quad (22)$$

or

$$(Ag_{(Ag\text{-}Cu)}\text{-}H_2O)_{ads} + BTA^- \rightarrow (Ag_{(Ag\text{-}Cu)}\text{-}BTA)_{ads} + H_2O_{aq} + e^- \quad (23)$$

Simultaneously with reactions (20) - (23) silver oxides Ag_2O and AgO are formed, but the mechanism of formation of Ag_2O has changed in comparison with the one taking place in the absence of BTA. The oxides of copper and silver are formed on unoccupied sites until the whole surface is covered with CuBTA and AgBTA complexes.

Potentiostatic oxidation of AgCu50 alloy in presence different concentrations of BTA was performed at potentials corresponding to the anodic current peaks A3, A5 and A6 during 100 seconds. All obtained results are presented in our previous work [44]. Here, the results obtained at 300 mV vs. SCE, which corresponds to potential of the peak A5 are presented in Figure 15.

The current peak A5 is related to oxidation of silver to silver(I)-oxide. However, it must be taken into account that in the potentiostatic measurements, becuase the alloy is immediately imposed to the set potential, there was no time for prior formation of copper oxides. It means that at this potential the conditions exist for copper to be oxidized sumultaneously with silver.

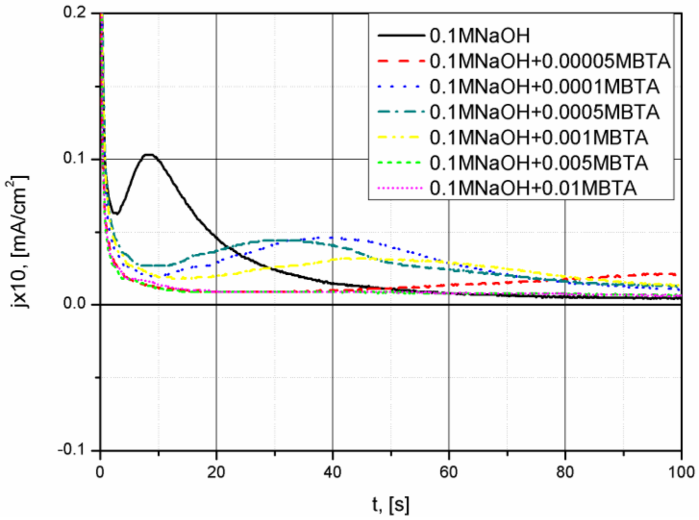


Figure 15 Potentiostatic curves of AgCu50 as a function of benzotriazole concentration in 0.1 M NaOH. Potential held constant at 300 mV vs. SCE [44]

The shape of potentiostatic curves in Figure 15, consisting of electrode discharge and overlap of diffusional zones, strongly indicate the typical nucleation and 3D growth mechanisms. In the absence of BTA, the nucleation stage (first few seconds) and the diffusion zone overlap stage (at about 10 seconds) are sharply defined for the process of oxidation in 0.1 M NaOH (BTA is absent). In the presence of benoztriazole, the characteristic stages for nucleation and 3D growth are broad, nevertheless distinguishable, except for very high concentration of BTA ($5 \cdot 10^{-3}$ M and $1 \cdot 10^{-2}$ M). The low and constant transient current for the high concentrations of BTA demonstrate the efficacy of corrosion protection by Cu(I)BTA and AgBTA films [11,44].

The SEM photomicrograph of surface of Cu50Ag50 alloy after potentiostatic oxidation at 300 mV (SCE) for 100 seconds in the solution of 0.1 M NaOH + 0.001 M BTA is presented in Figure 16.

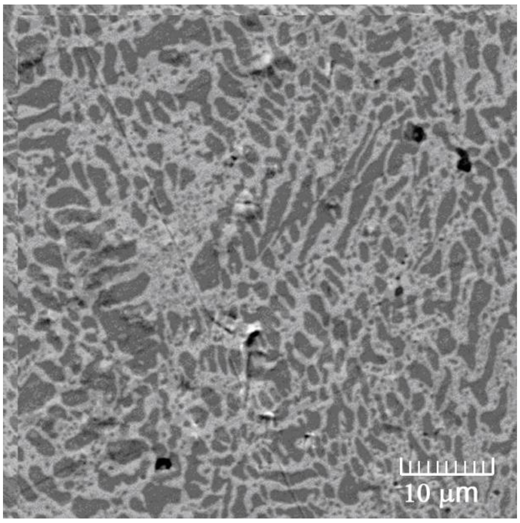


Figure 16 SEM image of AgCu50 alloy after potentiostatic oxidation at 300 mV vs. SCE for 100 s in 0.1 mol dm^{-3} NaOH + 0.001 mol dm^{-3} BTA [44]

Results of the energy dispersive X-ray spectroscopy performed at that surface are presented in Table 3. It can be seen that the concentration of oxygen on electrode surface is low, which confirms that CuBTA and AgBTA films do not allow copper and silver oxides to be formed.

Table 3 Results derived from EDS analysis [44]

Element	Decon	Atomic Ratio	Cone	Units	Bkg Error 2-sig
O	Gauss	1.0000	0.159	wt.%	0.314
Cl	Gauss	0.0000	0.000	wt.%	0.464
Cu	Gauss	56.1395	35.472	wt.%	0.298
Ag	Gauss	60.0140	64.369	wt.%	0.570

3.4. Electrochemical behaviour of AgCu50 alloy in 0.1 M NaOH in presence of chloride ions and BTA

Chloride ions are supposed to accelerate corrosion processes of metals and alloys. On the other hand, it was proved that BTA has an inhibition effect on those processes. It is important to find out how BTA influences corrosion processes in presence of chlorides. Cyclic voltammograms of AgCu50 in 0.1 M NaOH with addition of 0.1 M NaCl with and without the addition of BTA (0.00005-0.01 M) at a scan rate of 20 mV/s are presented in Figure 17.

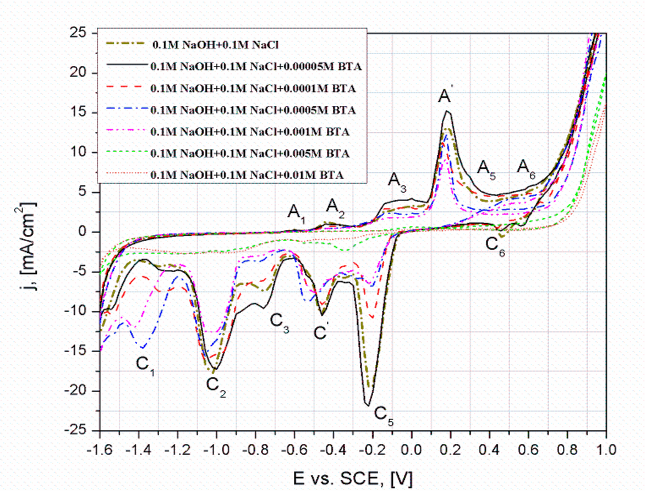


Figure 17 Cyclic voltammograms of AgCu50 in 0.1 M NaOH with addition of 0.1 M NaCl with and without the addition of BTA (0.00005-0.01 M) at a scan rate of 20 mV/s

By comparing curves from Figures 14 and 17 it can be concluded that in the presence of chloride ions inhibition effect of BTA is more pronounced because corrosion processes are more intensive. Potentiostatic curves presented in Figure 18 confirm previous conclusion. Potentiostatic measurements were performed at 620 mV vs. SCE during 100 s. This potential corresponds to the current peak A6 on cyclic voltammograms.

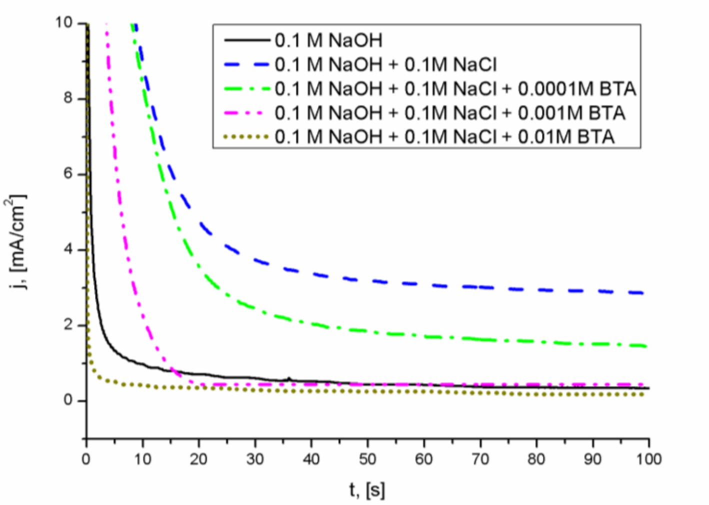


Figure 18 Current density – time transients for AgCu50 alloy in 0.1 M NaOH+0.1M NaCl at 620 mV vs. SCE at various concentrations of BTA

Figure 18 shows that in a 0.1 M NaOH + 0.1 M NaCl solution current density is higher than the value of the current density in the absence of NaCl in the whole course of potentiostatic curve. With the addition of 0.0001 M BTA in solution of 0.1 M NaOH + 0.1 M NaCl, current densities after16 s become lower compared to those obtained in the presence of chloride ions without benzotriazole, but higher than the current density in 0.1 M NaOH. In the presence of 0.01 M BTA, current density after the initial sharp decline remains constant until the end of the measurement. This means that a film composed of CuBTA and AgBTA formed on the surface of the alloy protects it against oxidation. Taking into account the results obtained by Pillard *et al.* [47,79], it should be noticed that the effective corrosion protection could be reached with BTA concentrations near to the toxicity limit.

Optical microscopy of the alloy surface was performed after potentiostatic treatment at 620 mV vs. SCE for a period of 100 s, first in 0.1 M NaOH, then in 0.1 M NaOH with the addition of 0.1 M NaCl and, finally in 0.1 M NaOH + 0.1 M NaCl with the addition of various concentrations of benzotriazole. Recorded photomicrographs are presented in Figures 19a to 19e.

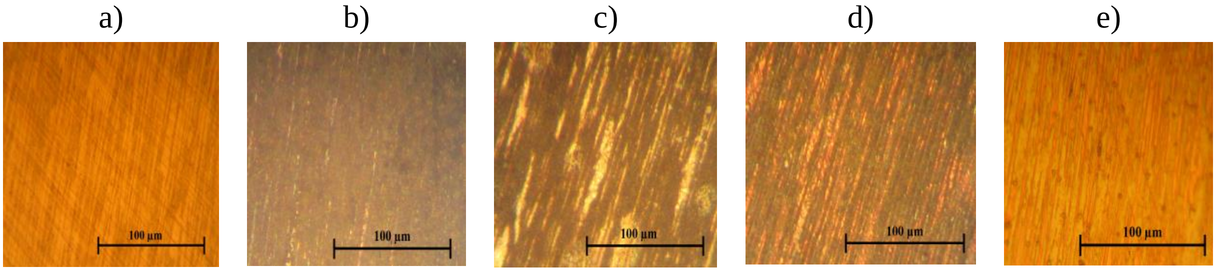


Figure 19 Microphotographs of AgCu50 surface after potentiostatic treatment for 100 s in: a) 0.1 M NaOH; b) 0.1 M NaOH + 0.1 M NaCl; c) 0.1 M NaOH + 0.1 M NaCl + 0.0001 M BTA; d) 0.1 M NaOH + 0.1 M NaCl + 0.001 M BTA; e) 0.1 M NaOH + 0.1 M NaCl + 0.01 M BTA

From the micrographs it can be seen that, after that treatment in pure NaOH solution a dark phase appears. That phase is assigned to oxides of copper and silver. With the addition of chloride ions (Figure 19b) a green phase and a small amount of white phase appear. The green phase originates from the formed copper chloride and the white phase originates from formed silver chloride. The dark phase composed of the oxides of copper and silver is still present. The addition of benzotriazole leads to its adsorption on the surface of the alloy and to formation of CuBTA and AgBTA complexes, which protect the alloy against corrosion. From the microphotographs given in Figures 19c to 19e, it can be seen that with increasing concentration of BTA, the amount of formed oxides and chlorides is decreasing, which means that BTA protects well the AgCu50 alloy surface from corrosion.

4. CONCLUDING REMARKS

Electrochemical and microscopic (SEM and optical) investigations of AgCu50 alloy behaviour during anodic polarisation, closely related with its corrosion characteristics, were performed in three different kinds of solutions: pure alkaline solution, the same alkaline solution containing chloride ions in different concentrations, the same alkaline solution containing benzotriazole in different concentrations and in the alkaline solution containing both chloride ions and BTA.

Obtained results point that in all these solutions first reaction is adsorption of anions and BTA molecules on the alloy surface. Reaction mechanism in pure alkaline solution comprises five reaction steps beside adsorption. In presence of chloride ions one additional anodic current peak appears at anodic part of voltammograms pointing that new reactions take place. The presence of Cl^- significantly intensifies anodic processes. The influence is biggest in the Cl^- concentrations over 0.01 M.

The presence of BTA in alkaline solution has no effect on reaction mechanism, but the intensity of current peaks decreases rapidly with increasing BTA concentration. The inhibition is achieved with CuBTA and AgBTA species formed on surface of the alloy. Inhibition effect of BTA is more important if chloride ions are present in the solution.

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