

STANISŁAWA SANAK-RYDLEWSKA\*, AGNIESZKA GALA\*\*, ŁUKASZ WAJDA\*\*\*

## **Environmental hazards of the metallurgical wastes dumping sites – barium and arsenic ions elimination with ionits**

### **Introduction**

The metallurgical industry produces wastes of a varying degree of harmfulness. These are low active wastes (turnings from machining operations, slag), onerous wastes (dusts which residue after castings cleaning, spent cores and moulds, sludges from the wet de-dusting process) and hazardous wastes (metals processing sludges, tempering processes by-products) (Florjańczyk, Penczak 1998). The wastes are stored at dumping sites, which may influence the environment. Their presence may adversely affect soil, air and water habitat.

The metallurgical wastes impact on the air manifests in the dusting phenomenon. The steel industry is one of the largest dust producers. These dusts are highly pulverized and with high heavy metals content. Their impact range is much lower than that of gaseous pollutants. Due to their gravity, dusts fall significantly closer to the emitter than gaseous pollutants. At high dusting levels, the adverse effects on green plants are observed, although their harmfulness to trees is various and disputable. Some researchers believe, that even fine particles of dust may slightly penetrate stomata of leaves and needles. Dusts may also cover leaves, which impairs, or even stops photosynthesis.

The heavy metals compounds are deposited in soil as insoluble particles. They may dissolve as a reaction to some physico-chemical and biological agents and then infiltrate into the soil. Also, the process of air erosion (deflation) that occurs on the slopes of settlers

---

\* Prof. dr hab., \*\* Mgr, \*\*\* Mgr inż., Wydział Górnictwa i Geoinżynierii, AGH Akademia Górniczo-Hutnicza, Kraków, e-mail: [ssanak@agh.edu.pl](mailto:ssanak@agh.edu.pl)

should be considered. The following factors influence intensity of this process: the weather conditions in the dumping site, relative humidity of the scarp ground and the material used to build the settler. Actually, only the dusty fraction of settlers has the grain size, which can be lifted by the wind. The dumping sites presence near human habitats might be hazardous for their life and health. The suspended particles containing lead, copper, arsenic, zinc, etc. cause numerous diseases, from minor ailments to acute poisonings and cancers (Podniewski 1979). Introduction of the green areas with grassy lanes by hydro-sowing is one of the methods, which is recommended in air protection against the above mentioned dusts emission. Products of chemical interactions between wastes compounds- liquid or gaseous, might be noxious or even toxic (Tremillon 1970).

The leachates presence in the dumping sites is an effect of water penetration (mostly from the rain), through the waste heaps and chemical substance release. Extraction, hydrolysis and fermentation might occur as well. The above mentioned processes might result in soluble organic and inorganic compounds presence in the leachates (Bodzek et al. 1997) in a wide range of concentrations. Subsequently, they might be transferred to the surface and ground waters affecting their quality. The metallurgical wastes dumping sites leachates are fairly specific. They have high compounds concentration and contain biodegradable or refractive substances. The dumping sites leachates can not be discharged directly into the sewage system (Lema et al. 1988).

In currently built dumping sites, their environmental impact on the ground and surface waters is negligible. They have leak-proof, isolated ground and side scarps that prevent contaminants migration into the ground and water habitat. Such dumping sites also have girdling ditches, which stop surface flushing and leaching from dumping sites. The leachates accumulation demands drainage of the bottom of the dumping site and sewage disposal. All of these actions are often difficult to implement and expensive. Technical solutions unreliability, current control and possible repair unavailability, as well as, huge costs of the pollutants removal from the environment, may also be an issue. All of these aspects lead to the conclusion, that every dumping site should be considered a real threat to the ground waters and other environmental components connected to them. The effects of leachates penetration to the ground waters should always be predicted (Motyka 2005).

The influence on ground waters might be expected not only in case of those dumping sites, which aren't endowed with bottom sealing made from appropriate materials (like some dumping sites in Poland), but also in case of those secured with relevant materials, such as PEHD foil. The most frequent problems are associated with the dumping sites construction (erroneous use, e.g. of horticultural foil, inadequate protection against foil damage) and their exploitation (e.g. leachates effluent from tanks that are intended for their storage, etc.).

What's more, many dumping sites were designed many years ago, and they do not meet modern requirements for the protection of the environment. These objects may cause problems with pollutants migration, mainly to water and soil. This results in increased concentrations of heavy and toxic metals, such as: cadmium, lead, arsenic, chromium, nickel, molybdenum, antimony, tin, and others. Also, radioactive elements, like strontium may

appear. Near those “unprofessional” wastes dumping sites high concentrations of iron, sulphates and chlorides are measured. The pH levels around metallurgical dumping sites change from highly acid to highly alkaline, depending on their concentrations. As described above, the impact of dumping sites on the water habitat is extremely important. Metallurgical wastes dumping sites often cause far-reaching economic and environmental effects. Monitoring of all of the environmental spheres around the dumping sites is a tool that might be supportive for the negative impact identification and determination of the landfills' influence on the environment (Górski 1999; Mikołajczak 2006). In this field, Poland is still not experienced enough and should learn from the principles of monitoring in the United States (Jesionek, Sadurski 1991).

The metallurgical wastes impact on soil due to their heavy metals content such as: lead, cadmium, zinc, bar, copper and arsenic is also significant. These metals migrate into the soil by several media, like: rain water, water that infiltrates settlers, and dust which is leaped up from the scarps slopes during deflation and after some time falls on the surface of the ground. The increased metal concentration in leachates is enhanced by their low pH values.

Sulphates might be reduced in anaerobic conditions to the poorly soluble sulphides (Spinosa et al. 1991). Chromium occurs at the third stage of oxidation in reduction terms, and is slightly soluble in such conditions, so in this form it occurs as a sediment.

Complex compounds of those metals play significant role as well, but the most harmful complex compounds are those that contain lead, cadmium, zinc, arsenic, nickel and copper. Heavy metals ground pollution causes that soils, which were previously highly classified in the soil bonitation classification, must be transformed into wastelands or rarely afforested. It is explained by the fact that crops (for example cereals or sugar – beets) absorb heavy metals significantly, and therefore they can not be used for consumer purposes. At the same time, reclamation of heavy metals contaminated soils doesn't bring intended results, because it is impossible to separate complex compounds from soil complex, and soil can not be the source of miogens for plants. Except for nickel, all metals have large susceptibility to biocumulation. That is why metals are potentially hazardous for crops. A. Kabata-Pendias summarized maximum permissible concentrations (MPC) and the maximum allowable loads (MAL) of the above mentioned metals in soils (Table 1).

The pollution impact on the soil can be direct or indirect. Plants by drawing up calcium, magnesium, potassium or ammonium ions from the soil, release hydrogen ions into it and thus cause its acidification. This is called “indirect acidification”. While a direct acidification is caused by penetration of acidic contaminants into the soil and oxidation of ammonia to nitrates(III) and (V) ions, and a displacement of calcium or magnesium ions from the sorption complex and their leaching into the soil. The acidification process begins in the surface layer of soil, and then proceeds downwards. Any increase in soil acidity is reflected by the composition of exchangeable cations in sorption complex. Then, the proportion of alkali metal ions such as calcium, magnesium, sodium and potassium decreases in favour of the increase of hydrogen ions. This results in soil degradation which can be prevented by fertilization. The intensity of these processes also depends on the type of soil (e.g. less, clay or clay-dusty soils).

TABLE 1

Metals content in soils of selected European countries (Kabata-Pendias, Pendias 1993)

TABELA 1

Zawartość metali w glebach w wybranych krajach Europy (Kabata-Pendias, Pendias 1993)

No.	Metal	MPC [mg/kg]	MAL [kg/ha]		
			Great Britain	European Union	Republic of Poland
1	Zinc	2 000	15	30	10
2	Chromium	1 000	–	–	15
3	Lead	1 000	15	15	10
4	Copper	1 000	7.5	5	5
5	Nickel	150	3	3	3
6	Cadmium	20	0.15	0.15	0.2
7	Mercury	10	0.1	0.1	0.2

### 1. Materials and methods of the study

The study was performed on metallurgical wastes samples collected from the inactive dumping sites. The aim of the study was to determine the negative impact of wastes on the aquatic environment in their vicinity. The averaged waste samples were subject to sieve analysis, dissolved, and chemically analysed for copper, zinc, iron, lead, nickel, manganese, chromium, molybdenum, cadmium and silver content. Analyses were performed by Atomic Absorption Spectroscopy Method (AAS).

TABLE 2

The granulometric and chemical analysis results of the averaged metallurgical wastes sample

TABELA 2

Wyniki analizy sitowej i chemicznej uśrednionej próbki odpadów metalurgicznych

No	1	2	3	4	5	6	7	8	9	10	11
Grain size [mm]	+6,3	6,3–4,0	4,0–2,0	2,0–1,25	1,25–0,8	0,8–0,5	0,5–0,315	0,315–0,2	0,2–0,1	0,1–0,071	–0,071
Recovery [%]	5,91	6,41	20,61	5,32	4,74	2,56	3,51	3,40	6,76	10,68	30,11
Metal	Cu	Zn	Fe	Pb	Mn	Ag	Mo	Cd	Ba	As	Ni
% average content of metal	0,03	2,88	31,85	1,07	0,05	0,05	0,08	0,06	1,25	0,75	0,03

The content of another metals: chromium, nickel, tin, strontium and antimony have been found in studied samples in trace amount

The granulometric and chemical analysis results of the averaged metallurgical wastes are presented in Table 2.

Leaching tests of the components from the studied wastes were performed according to the Polish Standard PN-Z-15009: 1997. The results of the leachates analysis given in Table 3 show the highest concentrations of barium and arsenic ions. The other analysed elements are present in leachates in amounts not exceeding the Polish Standard level. Cadmium, strontium and zinc were present in leachates in trace amounts. Basing on the literature data and own experience the ionits described in Table 4 were used to remove barium and arsenic from solutions (Gala, Sanak-Rydlowska 2010; Sanak-Rydlowska 2008). Some ionits parameters defined by PUROLITE are given in Table 4.

TABLE 3

The chemical analysis results of the averaged samples of leachates from metallurgical wastes dumping sites

TABELA 3

Wyniki analizy chemicznej wyciągów wodnych uśrednionych próbek odpadów metalurgicznych ze składowiska

No.	pH	Concentration of metal [mg/L]									
		As	Ba	Cr	Cu	Mn	Mo	Ni	Pb	Sb	Sn
1	7,2	0,236	853,6	0,003	0,014	0,003	0,015	0,008	trace	0,115	0,047
2	7,6	0,259	328,5	0,015	0,008	0,002	0,018	0,019	trace	0,019	0,001
3	7,7	0,246	212,6	0,011	0,010	0,002	0,018	0,016	0,016	0,049	0,084
Standard level	6,5–8,5	0,1	3,0	0,5	0,5	0,1	1,0	0,5	0,5	0,3	2,0

TABLE 4

Characteristics of the used ion exchangers manufactured by Purolite (Technical instruction of PUROLITE Company)

TABELA 4

Charakterystyka stosowanych jonitów Firmy PUROLITE (Instrukcja technologiczna Firmy PUROLITE)

No.	Name	Type	Ionic form	CPW [Val/L]	Bulk density [g/L]	Water retention [%]
Strongly acidic cation exchanger						
1	C 160	Macroporous polystyrene	Na <sup>+</sup>	2.4	820–860	35–40
Weakly basic anion exchanger						
2	A 100	Macroporous polystyrene	Free Base	1.3	645–675	53–60
Chelating ion exchanger with iminodiacetic groups						
3	S 930	Chelating	Na <sup>+</sup>	1.8	710–745	45–50

The selected metals elimination from the water extracts was performed using ion exchangers. Selected parameters of the ion exchangers, defined by PUROLITE, are given in Table 4. Ion exchange experiments were performed in a 50 mL column with a 10 g of acclimatized and relevant ion exchanger and then allowed to swell for 24 hours. 200 mL of the solution was poured in from the top and collected in the experimentally determined rate equal 2 mL per minute. Then, 0.5 mL of solution was taken from the 25 mL eluate and diluted with 0.1 M HNO<sub>3</sub> to 50 mL. Thus prepared samples were analyzed by the AAS method to determine concentration of barium and arsenic. The paper gives selected data (Table 5–7) on separation of arsenic and barium using the studied ion exchangers. Aqueous solution of nitric acid(V) at a concentration of 2% vol. was used for regeneration of ion exchanger named S 930 and C 160, while the regeneration of anion exchanger was performed using 0.5 M solution of sodium hydroxide.

## 2. Discussion of the results

Analysis of the results given in Table 5 shows, that the barium cations are retained in over 50% in the first fraction using strongly acidic cation exchanger called C 160. In the following

TABLE 5

Results of purification of leachate on cation exchanger called C 160

TABELA 5

Wyniki oczyszczania odcieku na kationicie C160

No.	Work phase of ion exchanger	Volume of eluate [mL]	Ion content in the volume of eluate [mg]	
			Ba	As
		200	215.6	0.034
I				
1	Purification	25	136.50	0.0039
2		25	28.50	0.0036
3		25	14.90	0.0030
4		25	11.40	0.0026
5		25	8.90	0.0022
6		25	7.50	0.0020
7		25	6.00	0.0017
8		25	2.20	0.0017
II				
1	Regeneration	25	66.80	0.0019
2		25	11.50	0.0075
3		25	2.90	0.0011
4		25	1.90	0.0009

stages, the ion exchange process is slowed down significantly. At the same time, the pH of the eluate becomes alkaline. In these pH conditions, arsenic ions exist in anionic form and their retention on ion exchanger should not be expected. Their trace concentrations may be associated with the sorption process. The regeneration performed with the solution of nitric acid(V) at a concentration of 2% vol. showed, that the barium ions desorbed in about 30%. Thus, this process requires further research to determine the acid concentration, and to select the proper acid.

During the ion exchange, the pH changed from neutral to slightly alkaline.

Then, the weakly alkaline anion exchanger named A 100 with the basic groups was tested. The results show, that the anion exchanger adsorbs the barium ions in 50% and simultaneously the arsenic ions are exchanged in about 70% (Table 6). The pH value changed from about 7.8 to about 10.0.

Based on the obtained results, it can be deduced, that the ion exchanger with complexing iminodiacetic groups named S 930, has the highest ability to exchange barium ions (almost 100%) and arsenic ions (about 70%) – Table 7. Also, its regeneration has been most effective,

TABLE 6

Results of leachate purification on anion exchanger called A 100

TABELA 6

Wyniki oczyszczania odcieku na anionicie A 100

No.	Work phase of ion exchanger	Volume of eluate [mL]	Ion content in the volume of eluate [mg]	
			Ba	As
		200	215.5	0.034
I				
1	Purification	25	62.30	0.0011
2		25	13.18	0.0023
3		25	13.07	0.0024
4		25	13.01	0.0028
5		25	13.00	0.0034
6		25	13.20	0.0035
7		25	13.02	0.0038
8		25	12.78	0.0037
II				
1	Regeneration	25	28.70	0.0078
2		25	39.10	0.0018
3		25	23.40	0.0061
4		25	9.13	0.0010

TABLE 7

Results of leachate purification on chelating ion exchanger called S 930

TABELA 7

Wyniki oczyszczania odcieku na jonicie chelatowym S 930

No.	Work phase of ion exchanger	Volume of eluate [mL]	Ion content in the volume of eluate [mg]	
			Ba	As
		200	215.5	0.0340
I				
1	Purification	25	146.00	0.0070
2		25	30.00	0.0019
3		25	14.00	0.0012
4		25	9.00	0.0005
5		25	1.10	0.0005
6		25	1.00	0.0005
7		25	1.40	0.0070
8		25	1.80	0.0015
II				
1	Regeneration	25	35.70	0.0026
2		25	54.10	0.0005
3		25	46.14	0.0115
4		25	1.50	0.0072

especially in case of the arsenic ions, while the barium ions are recovered in about 75% (Table 7).

pH value changed from weak basic do high basic (about 10.0) during the exchange.

### Summary

The aim of the study was to determine the use of ion exchange processes to eliminate toxic ions such as arsenic ions and barium ions from metallurgical wastes dumping sites leachates. Ion exchangers with different ion exchange groups were used, i.e. strongly acidic cation exchanger named C 160, weakly basic anion exchanger called A 100 and chelating ion exchanger with iminodiacetic groups named S 930. All of the resins are manufactured by Purolite.

The study showed that the barium ions are most effectively eliminated by the cation exchanger called C 160 (Table 5) and by the chelating ion exchanger named S 930 – almost 90% (Table 7). The arsenic ions are removed by the chelating ion exchanger with the efficiency of about 60% (Table 7).



The regeneration using inorganic reagents ( $\text{HNO}_3$  or  $\text{NaOH}$ ) require further research to increase efficiency of this process.

The study was carried out as part of the AGH research programme number 11.11.100.196

#### REFERENCES

- Bodzek M., Bohdziewicz J., Konieczny K., 1997 – Techniki membranowe w ochronie środowiska. Wyd. 1. Gliwice, Wydawnictwo Politechniki Śląskiej.
- Florjańczyk Z., Penczak S., 1998 – Chemia polimerów. Wyd. 1. T. 3. Warszawa, Oficyna Wydawnicza Politechniki Warszawskiej.
- Gala A., Sanak-Rydlewska S., 2010 – Sorpcja jonów  $\text{Pb}^{2+}$  z roztworów wodnych na łupinach orzecha włoskiego, *Przemysł Chemiczny*, 89/9, s. 1053–1057.
- Górski J., 1999 – Oddziaływanie składowisk odpadów na środowisko gruntowo-wodne i ich monitoring. IX Międzynarodowa Konferencja „Budowa bezpiecznych składowisk odpadów”. Wisła, 24–26 luty 1999, s. 71–87.
- Instrukcja technologiczna Firmy PUROLITE.
- Jesionek S.K., Sadurski A., 1991 – Nowe federalne kryteria oceny wysypisk odpadów w Stanach Zjednoczonych. *Biul. Kom. Oddział. na Środowisko*. Warszawa.
- Kabata-Pendias A., Pendias H., 1993 – Biogeochemia pierwiastków śladowych. Warszawa, PWN.
- Lema J.M., Mendez R., Blasquez R., 1988 – Characteristics of landfill leachate and alternatives for their treatment. *A review, Water, Air and Soil Pollution*, vol. 40, pp. 223–250.
- Mikołajczak J., 2006 – The assessment of environment at risk on the areas degraded by the landfills. *Gospodarka Surowcami Mineralnymi*, t. 22, z. 4, s. 67–74.
- Motyka J., Adamczyk Z., Czop M., D'Obrzyn K., 2005 – Wpływ składowiska odpadów komunalnych w Ujkwie koło Olkusa na jakość wód podziemnych. *Gospodarka Surowcami Mineralnymi*, t. 21, z. 1, s. 131–152.
- Podniewski A., 1979 – Podstawowe problemy ochrony środowiska w Polsce. Warszawa, PWRiL, s. 149, Polska norma PN-Z-15009: 1997. Odpady stałe – Przygotowanie wyciągu wodnego.
- Sanak-Rydlewska S., 2008 – Wykorzystanie wymiany jonowej do oczyszczania ścieków. *Przemysł Chemiczny*, 87/5, s. 563–565.
- Spinosa L., Brunetti A., Lore F., Antonacci R., 1991 – Combined Treatment of Leachate and Sludge: la experiments. *Proceedings Sardinia 91, Third International Landfill Symposium S. Magherita di Paula, Cagliari, Italy, 14–18 October 1991*, pp. 961–968.
- Tremillon B., 1970 – Jonity w procesach rozdzielczych. Wyd. 1. Warszawa, PWN .

#### ZAGROŻENIE ŚRODOWISKA PRZEZ SKŁADOWISKA ODPADÓW METALURGICZNYCH – ELIMINACJA JONÓW BARU I ARSENU ZA POMOCĄ JONITÓW

#### Słowa kluczowe

Składowiska, odpady metalurgiczne, jonity, wyciągi wodne

#### Streszczenie

W pracy omówiono wpływ składowiska odpadów metalurgicznych na sfery środowiska: powietrze atmosferyczne, glebę i wody powierzchniowe. Przedstawiono niektóre sposoby zapobiegania oddziaływania tych

odpadów. Podano wyniki badań wyciągów wodnych próbek odpadów metalurgicznych, w których stwierdzono obecność jonów metali toksycznych dla środowiska.

Analizy chemiczne wodnych wyciągów wskazują na przekroczenia zawartości metali toksycznych, m.in. takich jak: ołów, arsen, bar i in. Przedstawiono również wstępne wyniki eliminacji zawartości niektórych metali z wyciągów wodnych za pomocą jonitów Firmy PUROLITE. Zastosowany silnie kwaśny kationit z grupami  $\text{Na}^+$  wykazuje zdolność wymiany jonów  $\text{Ba}^{2+}$  prawie w 90%, podobnie jak jonit z grupami chelatującymi S 930 (tab. 5 i 7). Natomiast anionit z grupami hydroksylowymi usuwa z roztworów jony arsenu(V) z wydajnością około 60% (tab. 7).

**ENVIRONMENTAL HAZARDS OF THE METALLURGICAL WASTES DUMPING SITES –  
BARIUM AND ARSENIC IONS ELIMINATION WITH IONITS**

Key words

Dumping sites, metallurgical wastes, ion-exchangers, leachate solutions

Abstract

The paper presents an impact of the metallurgical wastes dumping site on the following parts of the environment: air, soil and surface waters. Some of the methods used to prevent wastes interactions were showed. The results of the metallurgical wastes leachate samples research, in which toxic metal ions have been found, are presented results of examinations performed on water extracts derived from two types of metallurgical wastes were given.

The chemical analysis of water extracts indicate exceeded concentration of toxic metals, such as: lead, arsenic, barium and others. Preliminary results of some metals elimination from the water extracts with PUROLITE ion-exchangers were also presented. The utilised acidous cationit with  $\text{Na}^+$  groups exchanges the  $\text{Ba}^{2+}$  ions in almost 90%, similar to S 930 ionit with chelating groups (Table 5 and 7). Whereas the anionit with hydroxyl groups removes the arsenic ions(V) from the solution with the 60% efficacy (Table 7).