U.P.B. Sci. Bull., Series B, Vol. 85, Iss. 3, 2023 ISSN 1454-2331

PHYSICAL – CHEMICAL CHARACTERIZATION OF SOME MINING WASTE FOR CAPITALIZATION

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The sustainability of mining activities can be developed by applying direct methods for mineralogical characterization. Analysis performed on various types of products resulting from the extractive industry may be necessary in the development of reconditioning projects for closed or abandoned mines. The characterization of mine waste is important for predicting the potential for their re-exploitation. This paper presents physical-chemical methods for characterization of mining waste, including spectral methods: FT-IR, XRF, AAS, UV-VIS.

Keywords: mining waste, physical-chemical analysis, acid mine drainage, metals recovery

1. Introduction

Globally, one of the most important issues of pollution is the contamination of the environment with heavy metals [1-3] This is often associated with mining which has led to significant discharges of acidic wastewater with varying metal content [4, 5]. At European level, a series of socio-economic strategies have been launched in order to improve environmental legislation, assessment methods and process management in the mining industry [6 – 8]. The acronym used to highlight this type of pollution is often the acid mines drainage (AMD) [9] being the most important term used to drain leachate from the mining industry [10]. 'Leached', in accordance with the law, means any liquid which leaks through the landfill, and which results from or is contained in a waste facility, including polluted effluents, and which can be harmful to the environment if not treated in accordance with DIRECTIVE 2006/21 /CE [11].

The risk of contamination posed by mining was also highlighted by mining accidents, such as in Baia Mare, Romania in 1999 and in Aznalcollar, Spain, 2002

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[12]. In order to eliminate the risk of contamination from mining activities, it is mandatory to evaluate the source-path-receiver chain with special attention [13].

Discharges into natural receptors of effluents from mining contain metals such as iron, copper, zinc, nickel, chromium, etc. [14], but also rare elements, most of which having recovery potential [15, 16]. The upstream water treatment process involves neutralization with lime, which produces an effluent whose quality must be in accordance with the regulations for the discharge of water into the environment NTPA 001/2005. After lime treatment the particles of the metal hydroxide precipitate must growed, stabilized and separated from the treated wastewater. Neutralization with lime leads to precipitates of Fe hydroxide and other metals, and also of gypsum ($CaSO_4$). The treatment should lead to an increase in pH from 2.5 to 9 allowing the removal of metals from the solution due to the decreased solubility of metal ions. The pH required for minimum solubility varies depending on the metal species; therefore most neutralizing plants operate at a pH between 9 and 12. Several neutralizing agents can be used: lime, in the form of CaO or hydrated lime $Ca(OH)_2$, is the most commonly used due to its availability, low cost, and high efficiency [17]. The applied process can lead to advanced precipitation of metals (Fe, Mn, Zn, Cu,) with yields over 90% [18, 19].

The different typologies of sources containing metals with potential for capitalization represent major challenges in developing an efficient and economical recovery procedure. In the early stages, mine waste needs to be analyzed, mechanically or physical-chemically treated, followed by selective concentration and separation procedures [20 – 22].

The paper presents data on the classification of mine waste types, their physical-chemical characterization and quantification of concentrations of heavy elements over a period of three months to monitor natural sources of acid mining water and sludge produced during lime treatment of effluents. Two fractions of mining waste have been identified and differentiated based on their physical-chemical characteristics: sludge produced after acidic waters and waste-rock as sterile (pre-consumer mine waste resulting from copper extraction) [23].

The presented information can be used as support material in the mapping and identification of the potential resources for capitalization and recovery of some critical elements. For example, the waste rock can be reprocessed to extract metals, and the remaining waste is used as backfill, landscaping material, aggregate in road construction, or feedstock for cement and concrete. On the other hand, sludge resulted from AMD treatment, which is rich in iron, can be recovered as pigments with designed colours (manuscript under review).

2. Materials and methods

2.1. Samples sampling and preparation

Sampling was performed in hermetically sealed polyethylene containers according to SR ISO 5667-7:1998.

Mine waste samples have been dried by keeping them in oven at 120 °C for 24 h and sieved through a 2 mm mesh prior to analyses.

For the initial quantitative determination of the majority elements, the samples were digested in Teflon cups, hermetically sealed at room temperature for 48 hours at 100 rpm. The mineralization of the mine samples was performed with concentrated mineral acids (HNO_3 65%, HCl 37%) and hydrogen peroxide 30%, using the microwave digestion system (MLS-1200 MEGA). After digestion the samples were successively filtered on a quantitative filter (Whatman no 42 filter), transferred to volumetric flasks, and filled to 50 cm^3 with deionized water.

Additionally, several leaching experiments were performed to select the most effective procedure for bringing metals into solution from both sludge and sterile samples. Variable acidic solutions, in the range of pH = -3 ÷ 5, have been tested.

2.2. Reagents

The reagents used in the mineralogical analysis of the samples were KCl 1M purchased from Fluka, ultrapure water, 67% HNO_3, 37% HCl, H_2O_2 30% provided by Sigma-Aldrich.

2.3. Characterization methods of mine wastes

pH of mine samples was measured after adding KCl (1M, 20 mL) to a dried sample (20 g). After shaking for 2 h at 400 rpm, the pH sample was measured by a multimeter (Cyberscan PC 300).

Humidity of initial sample was determined by drying at 105°C until constant mass, according to the ASTM D1293 – 18 [24], ASTM D1125 – 14 [25], ASTM E2551 – 20 [26]. Elemental composition of mine samples was determined by X-ray fluorescence analysis using a Spectro Xepos spectrometer with matrix adjusted calibration performed on pressed powder according to the requirements of SR EN ISO 17025:2018, provided with a TurboQuant-Powders analytical program. For the IR spectra, a Thermo Scientific spectrometer with a vertical diamond head ATR device was used to record the IR spectra, in the range 4000-600 cm^{-1}.

The UV-VIS spectra were obtained with a Jasco UV-VIS-NIR-V670 spectrometer with diffuse reflectance accessory ILN-725 and that allowed the determination of chromatic characteristics using CIE-Lab software. The concentration of heavy metals from digested samples were determined by Flame Atomic Absorbtion Spectroscopy (FAAS) using an Analytik Jena AAS –

CONTRAA 700 spectrometer in an air-acetylene flame, equipped with a Xenon lamp and Aspect CS Version 1.5.7.0. software for processing of the results.

3. Results and discussion

3.1. pH and humidity of mine wastes

The mineralogical and geochemical composition of the studied samples can explain the possible elements mobilization. Thus, the pH of the waste rock area presents a moderate acidity (5.5) due to the mineralogical composition according to the FT-IR and XRF analyses. In the sludge deposits area, the pH is neutral (6.2 ÷ 7) due to minerals such as goethite (FeOOH) and gypsum $CaSO_4$ x $2H_2O$. The humidity measurements of the two types of mine samples are differentiated by obtaining percentages of over 50% in the sludge sample compared to the waste rock sample (10%).

3.2. FT-IR analysis of mine waste samples

FT-IR spectra contain information on the chemical structure of the solid matrix of the sludge / sterile samples provided by the vibration spectra shown in Table 1. Fourier analysis (FT-IR) allowed the identification of functional groups and structural fingerprints for each sample. Bands specific to minerals such as kaolinite and bentonite have been identified in this characterization.

The FT-IR spectra of the two mining waste samples cannot define exactly the species of a single mineral, but they place them precisely on a compositional range due to the identified covalence bands. A major composition of *o*-silicates was highlighted by the FT-IR spectra for both types of waste samples, by the bands 3714 cm^{-1}, 3735 cm^{-1}, 3756 cm^{-1}, 3782 cm^{-1}, and 3657 cm^{-}1, specific to the Al-OH and Si-OH groups. These elongation bands and others, 3735 cm^{-1} respectively, are specific for kaolinite, as well as other silicates identified at 3509 cm^{-1} and 3519 cm^{-1}. The differentiation of the two samples can be achieved by the presence of the doublet from 1740 cm^{-1} - 1665 cm^{-1} given by the hydration water from sludge (-OH of deformation and elongation). These bands are imperceptible in the sterile.

Table 1

FT-IR spectra and bands assessment

Sample	Sludge	Sterile	Attribution
Frequency cm^{-1}		3782	Al-O-H Si-O-H kaolinite
		3756	
		3735	
	3714		Al-O-H Si-O-H
	3657		
	3600		Other aluminium silicates
	3509	3519	
	3648		$Ca(OH)_2$
	3618		

3340		Humic acids
3010		
2938		
1740		H_2O hydration
1665		
1186		Si-Al-OH
1035,6	1061	
	778	
	713	
683		Me-O-H
616		
	548	
	486	

3.3. Electronic spectra of solid waste

To establish some quantitative and qualitative parameters for the objective spectral characterization of the two waste samples, sludge and sterile, the electronic spectra in diffuse reflectance have been registered. They show a quite similar shape in visible domain, with a wide area, relatively intense absorption in the range 450-500 nm, specific to reddish-orange hues. Therefore, the trichromatic parameters, presented in Table 2, seem to be a better and objective option to characterize the sludge and sterile samples.

Table 2

Sample	**L***	**a***	**b***	**C***	**h***	**R, %**
Sludge	64,1	13,8	31,7	34,6	66,5	60,9
Sterile	66,0	6,6	18,2	19,3	70,1	59,2

The chromatic behavior is rendered by the ratio of the values of the color parameters a* (red) and b* (yellow), the predominant being the reddish-orange shade given by the iron oxides. This ratio is correlated directly to the shade parameter H, with values between 67 and 70. The brightness parameter L*, shows values in the range 64-66, indicating an intense color of these mining wastes confirmed by the significant amount of minerals present such as kaolin, bentonite, pyrite, according to FT-IR bands.

3.4. XRF analysis

According to Fig. 1, the results of the XRF analysis confirm the presence in high concentrations of Na, Al, S, Ca, Fe and Cu ions mainly in the sludge sample, as precipitates after lime treatment, while the sterile rock contains mainly clay minerals. These XRF data confirm the results of the IR and UV-VIS spectral data referring to major contribution of Ca^{2+} cation in the composition of sludge as compared to sterile sample. Another distinctive feature between the two types of waste is the predominant concentration of silicon in clay minerals of the sterile sample, in accordance with mineralogical composition of this waste rock.

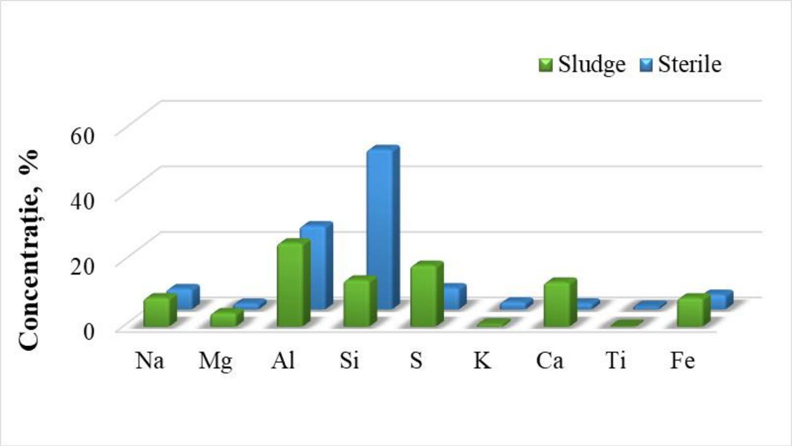

Fig. 1. Percentage concentrations of major elements detected in mine waste by XRF analysis: green - sludge, blue – sterile

3.5. Quantification of concentrations of heavy elements by SAA

The predominant element found in sludge sample is iron (mg/kg). This is due to the rocks pyrite (FeS_2) oxidation in water at neutral pH, generating sulphuric acid and ferric hydroxide, thus promoting the complete oxidation of pyrite in different water contents. The consequence of these reactions is the production of an acidic water with a pH between 1 and 2. Hydroxides metal ions formed are incorporated in very large amounts of sludge resulting from lime treatment.

The presence of the following heavy elements, by their decreasing concentration, iron, copper, zinc and manganese, makes the analysed waste samples a rich source with economic potential (Table 3 and 4). The sludge has much higher heavy metals content than the sterile rock, as it is demonstrated by the average concentrations of heavy elements in Fig. 2. Based on the mass ratios, the content of iron, manganese, nickel and zinc are 28, 14, 13, 9 and 8 times higher in sludge than sterile.

Table 3

Metal concentrations in sludge determined by atomic absorption spectrometry, mg/kg

Element	**sample 1**	**sample 2**	**sample 3**	Average	SD	RSD%
Iron	76684,20	89568,00	82648,60	82966,93	0,002	2,30
Copper	5757,30	5465,80	5168,00	5463,70	0,001	1,00
Zinc	750,80	787,30	717,80	751,97	0,002	4,40
Cobalt	20,40	19,90	20,70	20,33	0,001	1,03
Chromium	12,00	8,60	60,90	27,17	0,000	3,60
Cadmium	1,90	3,20	2,40	2,50	0,001	3,00

Manganese	323,00	184,00	312,00	273,00	0,000	0,90
Nickel	27,53	23,56	17,28	22,79	0,001	2,20
TOTAL	**83583,23**	**96060,36**	**88947,68**	**89534,49**		

Table 4

Metal concentrations in sterile determined by atomic absorption spectrometry, mg/kg

Element	**sample 1**	**sample 2**	**sample 3**	Average	SD	RSD%
Iron	2778,70	3015,00	3001,00	2931,57	0,025	2,96
Copper	730,00	734,00	538,00	667,33	0,000	5,30
Zinc	86,50	102,10	71,90	86,83	0,001	17,20
Lead	84,50	97,90	84,90	89,10	0,005	3,40
Cobalt	3,30	3,20	1,70	2,73	0,001	6,70
Chromium	3,10	35,90	3,10	14,03	0,000	5,30
Manganese	17,36	19,54	20,70	19,20	0,000	0,90
Nickel	2,05	1,78	1,46	1,76	0,001	4,10
TOTAL	**3705,51**	**4009,42**	**3722,76**	**3812,56**		

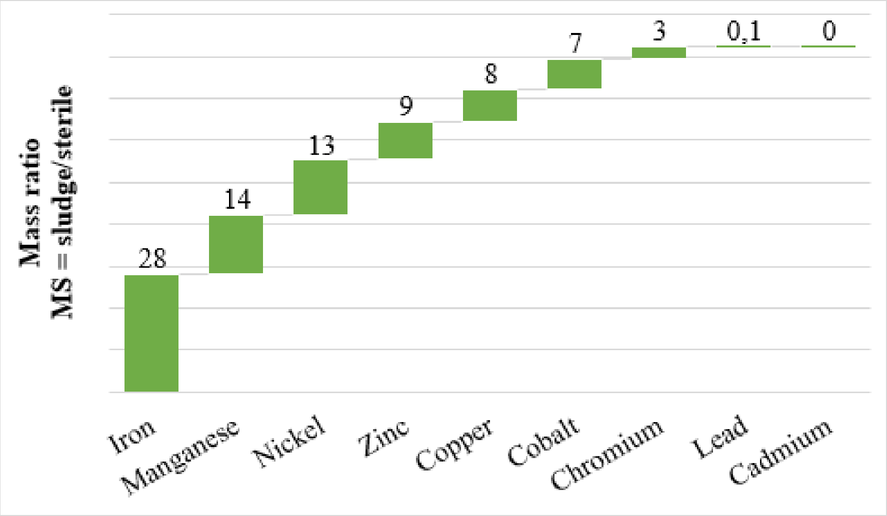

Fig. 2. Mass ratio of heavy metals between sludge and sterile samples

3.6. The potential of mine waste for heavy metals recovery

To evaluate the potential of mine waste as heavy metals recovery resource, the effect of the two matrices, sludge and sterile, on the metals solubilization in aqueous media, at different pH conditions, has been investigated (Fig. 3). The metals availability in the tested acidic solution is expressed by the degree of demineralization. This is a measure of the mass loss of the sample, before and after solubilization, because of the migration of metal ions in the liquid medium. The higher this value is, the easier it is for metal specie to pass from the oxide form to the ionic form in the solution. This is pH dependent. The more acidic its value is, the easier the disaggregation of the solid sample takes place. It also depends on the crystalline form of the samples. Amorphous forms of sludge are disaggregated more easily while tailings samples (sterile) need extreme pH conditions, such as the pH of aqua regia, pH=-3 (which is a calculated pH by using the concentrations of HNO_3 and HCl and the definition formula of pH; it can be used as a semiquantitative information for different interpretation).

The graphical representations from Fig. 3 confirms that the degree of demineralization of the samples decreases as the pH of the acid solution increases; the largest decrease in demineralization from pH = 2 for the sludge sample, while for the sterile sample is for pH = 1. This different behaviour can be a criterion to choose the sludge, rather than sterile, for heavy metals recovery, especially as a significant degree of demineralization can be obtained, in milder pH conditions, compared to aqua regia.

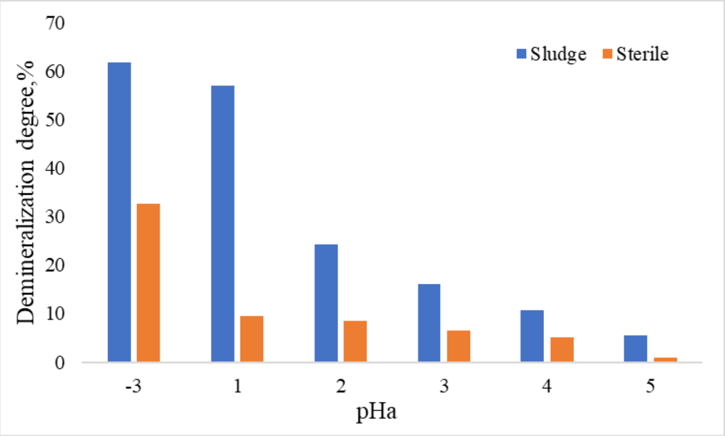

Fig. 3. Demineralization degree for mine samples
blue - sludge, red – sterile

4. Conclusion

This paper presents the main mineralogical and physical-chemical characteristics of the ADM sludge and sterile. The results obtained in the characterization of the waste samples indicate rich resources with capitalization potential, especially for the sludge concentrated in heavy metals. Leaching tests and behaviour at mineralization process are different due to the structural matrices of the two types of samples. Thus, the sludge has mostly calcium sulphate that stores as adsorbent clay elements such as Na, Al, Fe, Cu, etc. compared to the sterile rock poor in these elements. These methods of analysis are crucial in establishing a plan for recovering critical elements, setting the target waste with the greatest potential for exploitation. The sludge is a promising waste in the subsequent perspectives of element recovery, since the main residue obtained from the processing is gypsum.

In the case of sterile rock, a major chemical stability can be observed depending on the pH of the environment and of the organic attack, while the final waste can be included into construction materials.

Aknowledgement

This work has been funded by the European Social Fund from the Sectoral Operational Programme Human Capital 2014-2020, through the Financial Agreement with the title “Training of PhD students and postdoctoral researchers in order to acquire applied fzresearch skills – SMART”, Contract no. 13530/16.06.2022 – SMIS code: 153734;

This work has been funded by the European Union through POC Program, Project ID: P_40_253, Contract 130/23.09.2016, SMIS 105558, Subsidiary Contract 18101/04.10.2019 and Subsidiary Contract 5942/24.04.2020.

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