6th International Symposium
MINING AND ENVIRONMENTAL PROTECTION
21 - 24 June 2017, Vrdnik, Serbia

Characterization of the sludge generated during the processing of iron ore in Omarska mine

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Abstract: *In present paper there were characterized sludge samples generated as an overflow during the processing of iron ore from Omarska mine (Bosnia and Herzegovina). With the aim to improve the utilization of minerals, we are carrying out research into the possibility of selective flocculation of limonite from the sludge. The first and very important step in this research is the characterization of sludge. In order to determine the present mineral phases and their chemical compositions, it was performed XRPD, FTIR and SEM-EDS analysis. The XRPD results showed that sludge samples are composed of major goethite and quartz, less clay minerals, and minor magnetite and todorokite. The FTIR and SEM-EDS analysis are in very good agreement and confirms the results obtained by XRPD method.*

Keywords: *Omarska mine, processing, sludge, characterization, goethite*

1. INTRODUCTION

Due that the relatively rich ore world's deposits with simple mineral composition are mostly consumed in the past, the mineral industry is nowadays generally generating more and more waste products. Large amount of useful minerals are continuously discarded in terms of fines and sludges every year. Mineral processing techniques, such as flotation and flocculation could be very useful for concentration and exploration of desired minerals that remained in such sludge waste. Furthermore, removal of some toxic or pollution minerals from the waste could contribute to the improvement and remediation of the geo-ecological environment, as well. These techniques often include interfacial processes that depend on mineralogical heterogeneity of fine particles surfaces. Therefore, the first step in choosing the best techniques for the evaluation of complex ores with large amount of fine particles is precisely determination of the mineral phases present in the sludge. Characterization studies are very important in mineral processing because they contribute to the understanding of the behavior of ores and impurities during processing. The characteristics of low-grade ores and slimes vary from region to region, and different beneficiation procedures are required to process them. The most promising techniques for the evaluation of complex ores with large amount of fine particles are flotation and selective flocculation [1-6]. The basis for these methods is selective adsorption of reagents on desired mineral in preference to others. It is well known that the degree of separation depends upon the degree of liberation of minerals [7]. Before choosing adequate methods, it is necessary to know the major impurities.

2. MATERIALS AND METHODS

Two characteristic samples of the sludge with different content of Fe (i.e. 29.43%-sludge I and 41.19%-sludge II) were taken as an overflow on hydro cyclone plant with the ratio of S (solid) : L (liquid) = 1 : 7.

The X-ray powder diffraction (XRPD) patterns of sludge I were obtained by a Philips PW-1710 automated diffractometer using a Cu tube (λ=1,54060Å) operated at 40 kV and 30 mA. The instrument was equipped with a curved graphite monochromatic diffraction beam, and Xe-filled proportional counter. The diffraction data were collected in the 2θ a Bragg angle ranges from 4^o to 65^o, counting for 0.25 second at every 0.02^o steps. The divergence and receiving slits were fixed at 1^o and 0.1 mm, respectively. The XRPD measurements were performed ex situ at room temperature in a stationary sample holder. The alignment of the diffractometer was checked by means of a standard Si powder material.

Identification of the present mineral phases was done with comparison of the interplanar spacings (d) and relative intensities (I) with the literature data, which is corresponding card from the International Centre for Diffraction Data, the Powder Diffraction File ICDD-PDF database (www.icdd.com).

Fourier Transform Infrared (FTIR) spectroscopy study was performed using Thermo Nicolet 6700, at spectral area 4000-400 cm^{-1}, with resolution of 2 cm^{-1} and with 32 scans. Samples were powdered in agate mortar. For the spectra recording it was used KBr technique: in 150 mg of powdered KBr it was added 1 mg of the studied sample, then it was homogenized and tablets were made under specific pressure and vacuum. Identification of the present mineral phases was done with comparison of the IR spectra with the literature data for the corresponding mineral phases.

Scanning Electron Microscope-SEM, studies were carried out in a JEOL JSM 6610LV coupled with Energy Dispersive Spectrometry-EDS by EDS detector model X-Max Large Area Analytical Silicon Drift connected with INCA Energy 350 Microanalysis System for sludge I.

XRPD and SEM-EDS studies of sludge II were performed in the laboratory Global Research and Development, Mining and Mineral Processing, Maizières-lès-Metz, France. XRPD data were obtained on BRUKER D2 PHASER by using software DIFFRAC.EVA V4.0, whereas SEM-EDS data were obtained on HITACHI "TM 3000" Tabletop Microscope with High Sensitivity BSE Detector.

3. RESULTS AND DISCUSSION

Iron ore from Omarska mine was previously assigned as limonite ore in association with clay minerals, quartz and some manganese minerals, as well [8]. This limonite ore is porous and often wrapped with fine-grained clay, which is difficult to remove.

Processing of ore is carried out by following methods: washing, sieving, grading and magnetic concentration. Iron ore is abundant in large quantities of small class and further processing increases the amount of fine classes, which are discarded in forms of sludge as mining waste. This is unsuitable for tailings disposal because it is a stable suspension and therefore represents environmental problem. On the other hand, this sludge still contains a significant amount of tiny fraction of limonite. According to the data from [9], the average content of Fe is 36.12%, but it is highly variable and ranges from 18.19% to 54.71%. The particle size in sludge is fine (<15 µm), and because of that, it is very difficult to process such fine particles. It is therefore imperative to develop adequate technique to treat low-grade ores and waste sludge in this plant. The removing of clay and quartz from iron ore was widely investigated [10-13], but knowledge about fine limonite ore processing is relatively poor.

One of the most important criteria for the selection of the most adequate processing method is related to sludge mineralogy. In order to determine the mineral phases present in the sludge generated during the processing of iron ore and, in particular, its major impurity, in this paper it was performed XRPD, FTIR and SEM-EDS analysis.

3.1 XRPD study

The obtained results of the XRPD studies are shown at Figure 1 and Table 1. By comparison of these, it can be clearly seen that there are more-less similar qualitative mineral compositions determined, but with their different semi-quantitative contents. It can be concluded that sludge samples consists mostly of goethite-FeO(OH) and quartz (SiO_2) which prevails over clay minerals. There are also minor contents of magnetite and todorokite determined.

Identification of clay minerals indicate that they are mostly of illite-sericite and kaolinite composition, and with chlorites, which appears only sporadically. Sericite is mainly of the muscovite mica type.

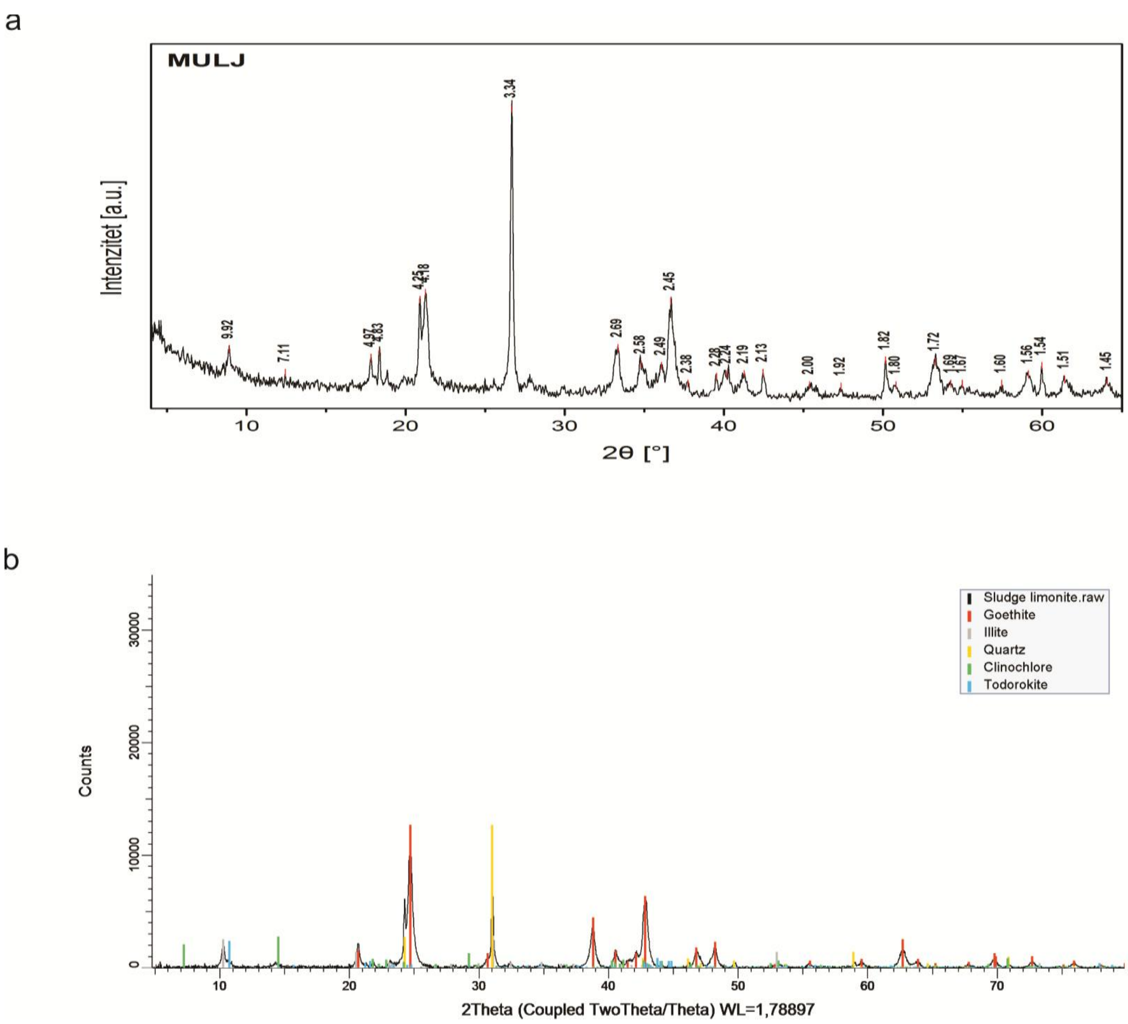

Figure 1. *XRPD patterns of the samples: a). sludge I and b). sludge II*

Table 1*. Identified qualitative and semi-quantitative mineral compositions by XRPD studies*

Sample	Sludge I	Sludge II
Qualitative and semi-quantitative mineral composition	Quartz, goethite, clays (of illite-sericite - kaolinite composition) and magnetite?.	Goethite, quartz, illite-sericite, clinochlore and todorokite.
Comment	Quartz (~63%) which prevails over goethite (~21%) and clay minerals (~10%). In the sample, there is also most probably present magnetite, as well as unidentified phase with small quantity (in total up to ~6%).	Goethite (~72%) which prevails over quartz (~14%) and illite-sericite (~10%). In the sample, there are also most probably present clinochlore (chlorite group) and todorokite with about ~2% of each.

3.2 FTIR study

The obtained results of the FTIR studies were shown at Figure 2 and Table 2. Identification of the present mineral phases were done using the adequate references [14-16]. The obtained results are in very good agreement and mainly confirms XRPD results of the previously determined qualitative and semi-quantitative mineral compositions.

Table 2*. Identified qualitative and semi-quantitative mineral compositions by FTIR studies*

Sample	Sludge I	Sludge II
Identified mineral composition	Quartz (798cm^{-1}), goethite (3130, 908 and 798cm^{-1}) and clay minerals (clays: 3624, 1029 and 908cm^{-1}; illite-sericite: 534cm^{-1}; and kaolinite: 3701 and 473cm^{-1}).	Goethite (3118, 899 and 798cm^{-1}), quartz (798cm^{-1}), and clay minerals (clays: 3622, 1654, 1030, 1008 and 899cm^{-1}; illite-sericite: 534cm^{-1}; and kaolinite: 3696, 470 and 470cm^{-1}).

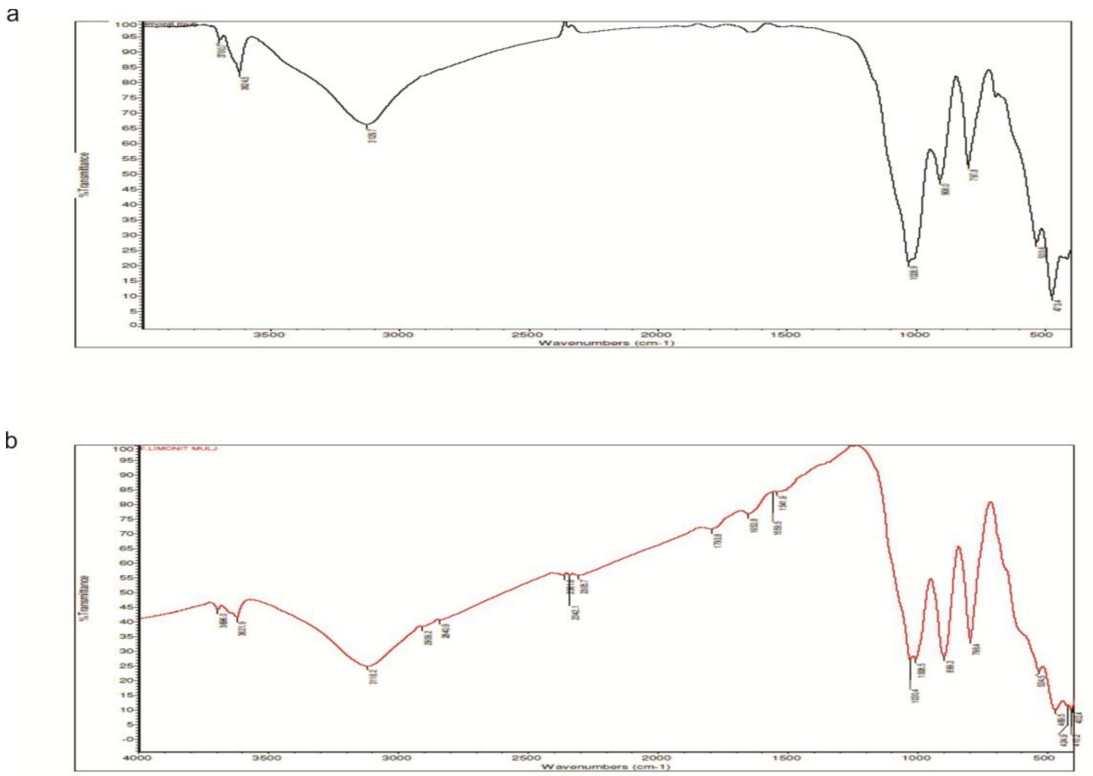

Figure 2. *FTIR patterns of the samples: a). sludge I and b). sludge II*

3.3 SEM-EDS study

SEM-EDS technique was used for the morphological, structural and chemical composition study of sludge samples, and results were shown at Figures 3 and 4 and Tables 3 and 4.
SEM images and EDS chemistry of sludge I samples (Figure 3 and Table 3) show heterogeneity of mineral composition with the predominant oxide (and/or hydroxide?) minerals consisting mainly of iron, silicon and aluminum, and with some Mn, Na and K, as well. Only rarely, there are some Ti and Cu impurities, also. Furthermore, Si/Al ratio indicates also to the presence of free silica with or without Al-silicates. For defining the more precise elemental and mineral composition, it was done analysis of selected points on the surface.

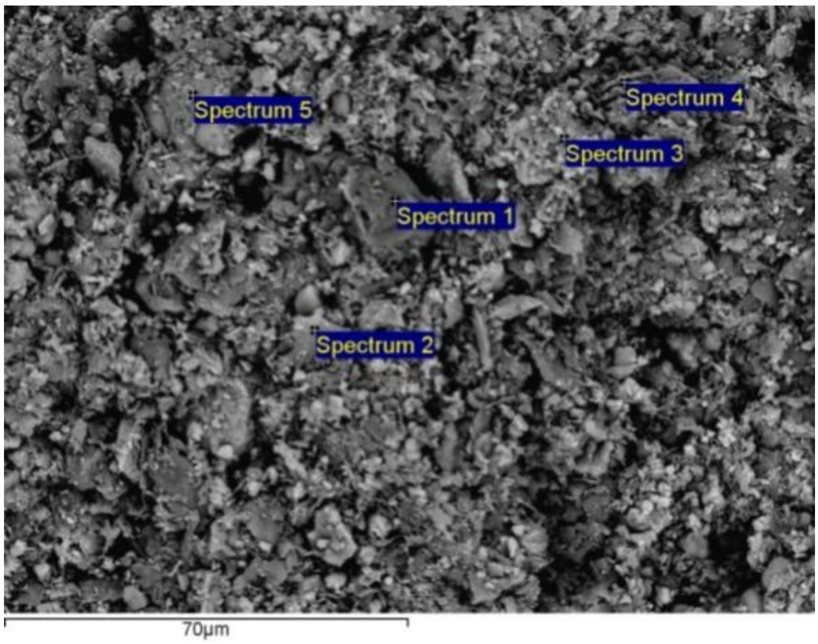

Figure 3. *SEM image of the sludge I sample with analyzed selected points 1-5*

Table 3. *EDS microanalysis data from the selected points 1-5 of the sludge I shown in Figure 3 (in wt. %). Analysis of the whole studied area is also presented*

Element	1	2	3	4	5	Whole area
O	54.08	50.97	46.11	59.02	48.38	45.92
Si	44.11	11.80	4.20	17.20	1.85	14.11
Al	0.47	8.48	2.75	14.60	1.73	6.17
Fe	1.34	23.31	44.21	3.77	47.34	27.88
Na	n.d.	1.00	n.d.	3.87	n.d.	0.55
K	n.d.	1.12	0.34	1.19	n.d.	1.50
Mn	n.d.	2.06	2.39	0.35	0.69	2.80
Ti	n.d.	0.54	n.d.	n.d.	n.d.	0.26
Cu	n.d.	0.73	n.d.	n.d.	n.d.	0.81

n.d. - not detected

X-ray microanalysis (EDS) data for selected points (Figure 3 and Table 3) confirm heterogeneity of sludge I surfaces with detected following possible major phases (calculated from compound % based oxygen by stoichiometry): quartz (point 1), Fe minerals intricately associated with alumo-silicates (point 2), Fe minerals (points 3 and 5), and alumo-silicates (point 4). Small quantities of manganese minerals have been also recorded.

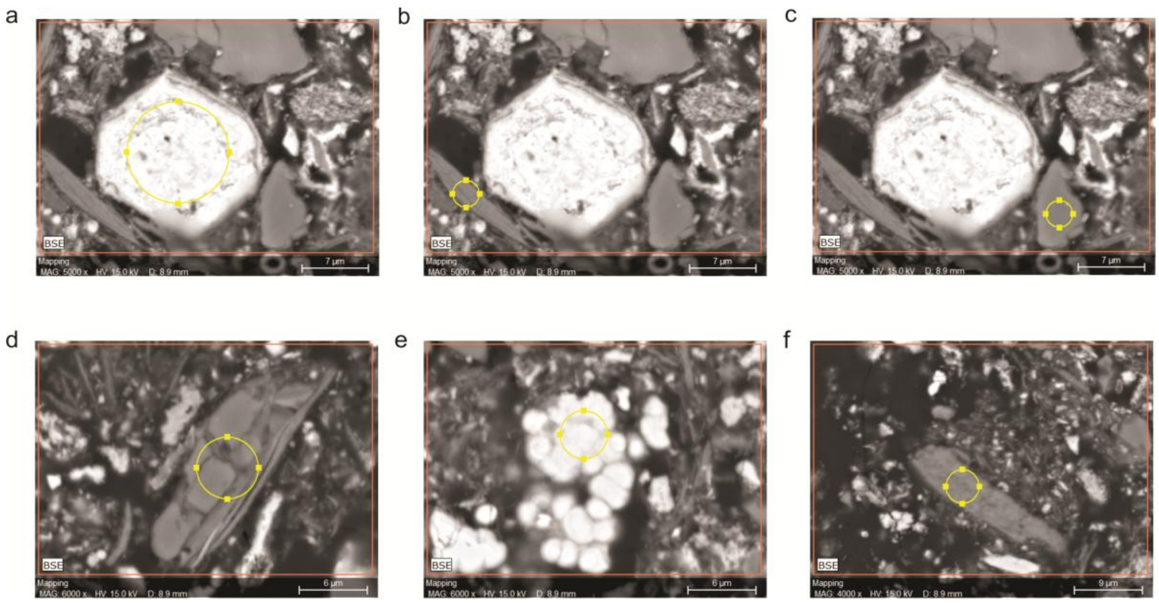

Figure 4. *SEM image of the sludge II sample with analyzed selected points a-f*

Table 4. *EDS microanalysis data from the selected points a-f of the sludge II shown in Figure 4 (in wt. %)*

Element	a	b	c	d	e	f
O	38.12	53.13	43.16	41.90	28.20	36.71
Si	1.17	22.85	56.84	48.06	0.64	29.74
Al	0.27	18.90	n.d.	8.38	0.38	18.11
Fe	58.67	n.d.	n.d.	n.d.	64.55	5.09
Na	n.d.	3.38	n.d.	n.d.	n.d.	n.d.
K	n.d.	1.75	n.d.	1.66	n.d.	8.76
Mn	1.77	n.d.	n.d.	n.d.	6.25	1.61

n.d. - not detected

X-ray microanalysis (EDS) data for selected points of the sludge II sample (Figure 4 and Table 4), compared to sludge I sample, confirm the same heterogeneity of sludge surfaces. In addition, there were mainly detected same of the major possible phases, i.e.: Fe minerals associated with manganese (spectrums a and e); alumo-silicates with K, Na and rarely Fe (spectrums b and f); and quartz (spectrums c and d).

One of the most limiting factors for determination of the mineral phases from EDS data is its inability to measure hydrogen, due that goethite and clay minerals contain appreciable amounts of OH groups and/or H_2O. According to that, we can only speculate about these possible phases. However, we believe that the obtained SEM-EDS results are also in very good agreement and mainly confirms XRPD results of the previously determined qualitative and semi-quantitative mineral compositions presented in this paper.
Beside this, all of the presented results are further in conformity with other ones, which are currently in progress [17, 18].

3.4 Technology of process in GMS "Omarska" mine and possibilities of beneficiations of studied sludge

The present scheme of technological process [9] is shown at Figure 5.

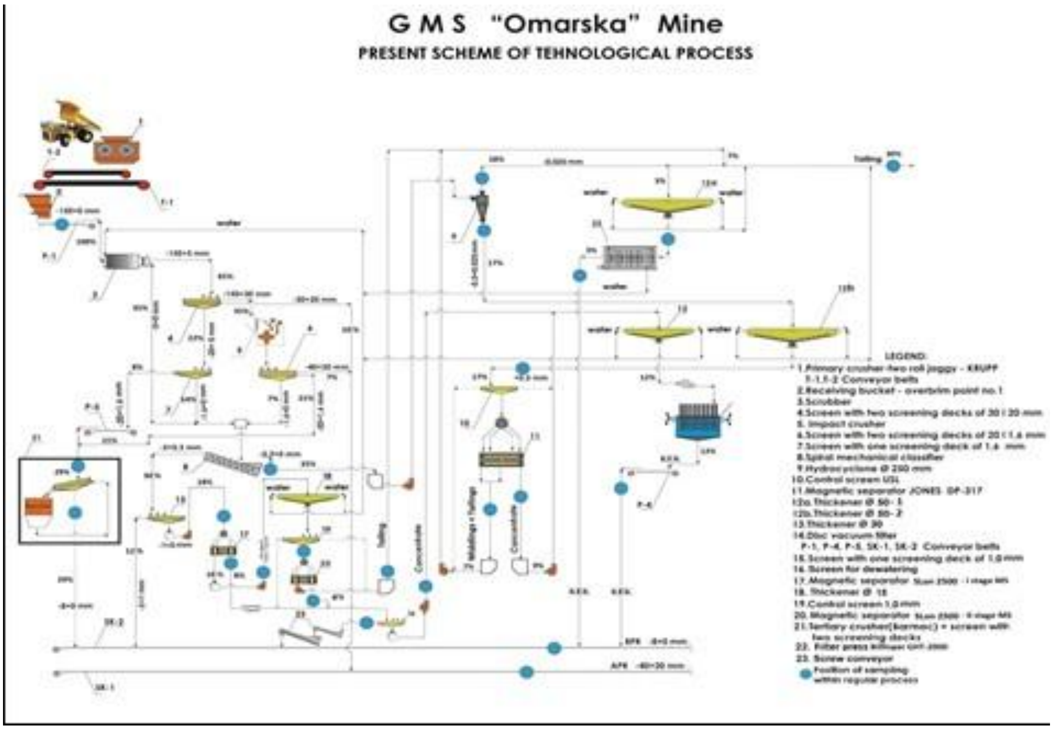

Figure 5. *The scheme of technological process*

Iron ore processing is carried out by washing, sieving, grading and magnetic concentration.
Iron ore is abundant in large quantities of small class and further processing increases the amount of fine classes, which are discarded in forms of sludge as mining waste. This is unsuitable for tailings disposal, because it is a stable suspension and therefore represents environmental problem.
In fact, problem with small classes of ore begins at the open pit, because many parts of the ore deposit containing up to mass 30% of -25 μm size class. Iron content in poorer ore parties ranges from 42 to 48%, and often rich in iron content ore parties is greater than the required content in the concentrate (52-54%). Such an ore with high participation of small classes come to the magnetic concentration plant.
The overflow from spiral mechanical classifier (classes -0.3+0 mm) go to the hydro cyclone. The larger classes, namely "sand" from hydro cyclone (classes -0.5+0,025 mm) go to thickener until the smaller classes, namely overflow from hydro cyclone (classes -25 mm) go to tailing in forms of sludge (Figure 5). Taking into account varying iron content in the incoming ore, sludge disposal as waste is harmful when such incoming ore contains a high iron content.
Studies that have been conducted for a long time, and which are still in progress on Faculty of Mining in Prijedor, are focused on evaluation of goethite. The positive results of this study imply increasing the recovery efficiency of limonite ore up to 30%, thereby increasing the total reserves of goethite. It should be noted that this product has the characteristics of natural ocher pigment, which would mean greater economic benefit on market. On the other hand, allocating more than 50% of the mass of sludge that is disposed of in landfills could be a significant contribution to the environmental protection.

In this paper, we present a part of the above-mentioned research. The reason for the investigation which results are presented in this paper is to examine the possibility of concentration of useful minerals from overflow on hydro cyclone prior to the magnetic concentration plant in the Omarska mine. One of the methods of the concentration of useful minerals from the sludge is the application of selective flocculation as a prior stage, flotation or magnetic ore concentration in order to increase the efficiency of the process. Another important step is choice of the dispersant, which should prevent the nonselective coagulation and provide selectively flocculants effect.
Morphological, structural and chemical composition in this study show a complex system of very fine particles with high heterogeneity of surface. In this case, selectively dispersing the sludge particles can be difficult, because a dispersant does not detect selectively surface. Particles size distribution [17, 18] shows almost 70 mass% of -7 μm size class, which further confirms that it is not possible to use conventional methods without the use of selective flocculation.
Besides, our earlier investigations were focused on examining the selective flocculation of sludge, goethite and clay, while quartz was not involved [19]. The results presented in this paper indicate that the quartz is major impurity. Because of that, in further studies it should be necessarily include quartz and its effect on selectivity.

4. CONCLUSION

The mineral phases present in the sludge generated during the processing of iron ore in Omarska mine, Bosnia and Herzegovina, were studied. According to the obtained results of XRPD, FTIR, SEM and EDS analysis, it can be concluded that sludge samples were composed mostly of goethite-FeO(OH) and quartz (SiO_2), which prevails over clay minerals. Although the phases composition of two analyzed sludge samples are almost the same, their content varies. The results presented indicate quartz as the main impurity. The results obtained from the investigations of area fractions for selected points agree well with the data of mineralogical compositions of these samples and indicate high heterogeneity of surface. These data suggest that it is necessary to examine the individual components and their behavior in a complex system such as the sludge in order to determine the best parameters (conditions, reagents, etc.) for selective flocculation.

Acknowledgment: The authors are grateful to Company ArcelorMittal in Prijedor for technical support and enabling the study visit Lj. Tankosić in the laboratory Global Research and Development, Mining and Mineral Processing, Maizières-lès-Metz, France for the purpose preparation of their PhD. The authors are also grateful to the SEM LAB of Faculty of Mining and Geology, University of Belgrade, for making SEM and EDS measurements.

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6th International Symposium

MINING AND ENVIRONMENTAL PROTECTION

21-24 June 2017., Vrdnik, Serbia

University of Belgrade
Faculty of Mining and Geology
Belgrade, Serbia

Belgrade, 30 June 2017

Subject: Confirmation letter

TO WHOM IT MAY CONCERN

We hereby confirm that Scientific paper entitled *"Characterization of the sludge generated during the processing of iron ore in Omarska mine"*, with authors: Ljiljana Tankosić, Pavle Tančić, **Svjetlana Sredić**, Zoran Nedić, (presented in work session) has been published (after positive reviews) in the Proceedings of the 6th International Symposium Mining and Environmental Protection, ISBN: 978-86-7352-298-2.

Please consider this letter as an official document to facilitate the processing of any procedures related to professional career of authors.

President of the Organising Committee

Prof. dr Ivica Ristović
University of Belgrade
Faculty of Mining and Geology